The Silicification of Eocene Deep-Sea Sediments in the Atlantic Ocean.

John Arthur Klasik

Louisiana State University and Agricultural & Mechanical College

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A Dissertation

Submitted to the Graduate Faculty of the
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requirements for the degree of
Doctor of Philosophy

in

The Department of Geology

by

John Arthur Klasik
B.S., SUNY at Stony Brook, 1970
M.A., Duke University, 1972
December, 1976
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ABSTRACT

The origin of Eocene deep-sea "chert" has been investigated using two approaches. First, a detailed petrographic and mineralogic analysis of a selected set of DSDP "chert" and sediment from the Eocene of the Atlantic was done to evaluate possible sources of silica and the para­genesis of silicification. Second, from Atlantic and Pacific DSDP reports paleoceanographic maps and histograms of "chert" and siliceous sediment occurrences illustrating spatial and temporal distributions of silica for the time interval Jurassic through Pliocene were constructed to investigate possible regional, global, physiographic or tectonic controls on silica distribution and diagenesis.

All silicified samples contain biogenic silica. Enhanced dissolu­tion features were noted as much as 17 cm away from "chert". Intervals undergoing silicification also correspond to areas where mixed-layered smectite/illite or illite were identified as the dominant clay. Samples distant from "chert" units contained smectite. No volcanioclas­tic material was identified.

The paleoceanographic maps of silica occurrences indicate a close correlation between zones of biogenic silica deposition and "chert" formation and little association of volcanioclastics and "chert".

This silica distribution data, coupled with the direct analysis of samples, strongly suggests that biogenic silica is the dominant source of silica for "chert". The concept of a volcanic contribution does not seem to be supported. Mass balance considerations suggest K may be a limiting factor in considering smectite/illite transformation
as an additional source of silica. The transformation may occur during the diagenetic reactions which produce "chert".

Void filling was identified as the initial stage in the silification of sediment. The initial infilling phase is opal-CT spherules. These constitute a boundary between matrices and pore space in weakly silicified samples and mark an in situ reprecipitation of silica derived from dissolution of biogenic silica. In better indurated samples, biogenic silica constitutes the substrate for opal-CT formation. Co-precipitation of opal-CT and clinoptilolite is observed as a second stage of infilling. If opal-CT/clinoptilolite co-precipitation does not complete void filling, then fibrous or GMC quartz is observed to the fill remaining space. This paragenesis could be explained if high silica concentrations favor rapid crystallization, producing more open crystal structures like cristobalite and/or tridymite. Lower silica concentrations during final stages of void filling then permit quartz to form.

Euhedral crystals of the high temperature silica polymorphs, cristobalite and tridymite, were identified in two radiolarian-rich "chert" samples. The lack of opal-CT/clinoptilolite co-precipitation indicates that these polymorphs could have formed from pore waters containing only silica.

The maps illustrate the presence of a marked increase in "chert" in the pre-Oligocene sediment. Histograms of "chert" and siliceous sediment versus depth also show a discontinuous increase in the amount of "chert" at the Oligocene/Eocene faunal boundary at all depths. This sudden increase in "chert" is not consistent with a burial
diagenetic or a time-related silicification theory.

A marked decrease in ocean temperature occurred at this same Oligocene/Eocene boundary. Periodic influxes of cold bottom water would have been likely during the initial stages of this change. Pore fluids which were in equilibrium with respect to opal-A during warm periods would have become greatly supersaturated with respect to opal-CT during periods of cold water incursion. Thus the unusual abundance of Eocene "chert" may not lie in any unusual lithology deposited during that epoch. Rather, diagenesis of biogenic silica may have been enhanced as an indirect result of changes in world ocean temperatures.
INTRODUCTION

Chert is a rock composed predominantly of microcrystalline quartz or fibrous quartz. It is common in sedimentary rocks from Precambrian to Recent. Chert commonly occurs as nodular masses in marine carbonates, such as the Mississippian carbonates of the United States; but bedded cherts of considerable aerial extent, such as the Devonian-Mississippian novaculites of the Ouachita belt, represent a second major variety.

Research into the mode of origin of marine chert is severely hampered because recent chert is lacustrine (Peterson and von der Borsch, 1965; Eugster, 1969; Surdam and Parker, 1972; Sheppard and Gude, 1974); and, thus, there are no modern analogues for marine cherts. Furthermore, the silicification process often alters or obliterates original sediment textures, making an understanding of the silica paragenesis difficult.

With the advent of the JOIDES Deep Sea Drilling Project (DSDP), it became possible to sample sediments buried deeply beneath the sea floor. One of the early discoveries of the DSDP was that middle Eocene strata contained abundant silicified sediments. These "cherts" were found to be different from cherts outcropping on land in being compositionally similar to surrounding sediments except for the presence of interstitial silica cement and in containing thermodynamically unstable silica phases rather than quartz as their predominant minerals (Heath and Moberly, 1971). Thus, for the first time, "chert" in the initial stages of formation could be studied.

It is the purpose of this study to investigate the problems for which the DSDP "chert" seems to provide important evidence - the source of silica and silica paragenesis. Two approaches to these problems have
been used. A general survey of the Atlantic and Pacific DSDP site reports within the first 43 legs of the JOIDES program was made in conjunction with a detailed examination of a selected set of samples from eleven cores from middle Eocene strata of the Atlantic Ocean. These core samples were examined with the scanning electron microscope (SEM), thin sections, x-ray diffraction and qualitative energy dispersive x-ray spectroscopy (EDS). These techniques were employed to determine the mineralogy and textural relationships to a degree which previous studies had not attained.
CHAPTER I

TERMINOLOGY

Definitions

Jones and Segnit (1971) have classified amorphous silica phases, opal-A, opal-C and opal-CT, on the basis of x-ray diffraction patterns, infra-red spectrophotometry and differential thermal analysis. Their classification of amorphous silica will be used in this study.

Opal-A is amorphous opaline material which yields only one broad "diffraction peak" centered about 4.1 Å. Opal-A is isotropic in thin section.

Opal-C is opal-cristobalite. The diffraction pattern of opal-C exhibits weak peaks of cristobalite superimposed over amorphous scattering. This pattern is unchanged upon heating.

Opal-CT is opal-cristobalite-tridymite. Its diffraction pattern contains a weak peak for cristobalite at 4.0+ Å and a weak peak for tridymite at 4.3+ Å superimposed over amorphous scattering.

A cristobalite spherule is a spherically-shaped body consisting of a blade-like mass of crystallites (Weaver and Wise, 1972a). Typically the spheres are 10-40 μm in diameter. Diffraction patterns of insoluble residues of chalk containing these spherules are similar to opal-CT (Wise and others, 1972). Energy dispersive spectroscopy has detected silicon, implying SiO₂ as its composition (Oehler, 1975).

Chert is a hard sedimentary rock composed predominantly of granular microcrystalline (GMC) or fibrous quartz. The Deep Sea Drilling Project initial reports label as chert any sediment with authigenic silica as
the cementing agent. Because the DSDP chert label is inaccurate with respect to the accepted usage of the word, DSDP silicified sediments which do not fit the standard definition of chert will be referred to in quotation marks ("chert").

Porcellanite is a siliceous sedimentary rock that is less hard and less compact than chert. It has a dull luster and usually consists of opal-A, opal-CT and quartz together with impurities such as clays, carbonates, zeolites or iron and manganese minerals (Keene, 1975). It includes what may be termed silicified limestone, shale, siltstone or mudstone (Keene, 1975).

Sample Location Designations

The Deep Sea Drilling Project uses a sequence of numbers to designate a sample location. The sequence strictly begins with a cruise or leg number, a Roman numeral. The specific hole being drilled has a site number. Site numbers are assigned in consecutive order. Each 9-meter core drilled is given a number. The cores are divided into six 1.5-meter sections numbered one through six. Finally a sample is given a location, in centimeters, from the top of the section from which it was taken. For example, I-6-6-3 (73-75) would represent a sample taken from a depth of 73-75 centimeters in section three of core six from Site six of Leg one of the Deep Sea Drilling Project.

Because site numbers are never repeated and are assigned in consecutive order, the leg designation numbers may be dropped. Sample designations with the leg number deleted will be the format followed in this study. If more than one hole is drilled at a single site, a letter is added to the site number. Hole 13A is the second hole drilled at Site 13.
CHAPTER II

BACKGROUND STUDIES IN CHERT AND SILICA

Previous Theories for Chert Formation

Early studies regarding the formation of chert represent two schools of thought. Based on field relationships and/or petrographic evidence in limestones, Van Tuyl (1918) concluded that the cherts he observed had been formed by silica replacement of limestone. Tarr (1926) suggested a primary inorganic origin for cherts. His observations led him to conclude that chert nodules were once inorganic masses of silica gel. The silica was presumed to be derived from the terrestrial weathering of silicates.

Since the initial controversy, more evidence tending to support Van Tuyl's concept of chert as a replacement deposit has been found. From studies of chert nodules in limestone similar in composition and age to those of Van Tuyl and Tarr, Biggs (1957) concluded that the nodules were formed by the mobilization and localization of fine, disseminated silica. Other researchers, working on younger chert, supported Van Tuyl's theory and also speculated on the source of silica for the cherts. Bramlette (1946) interpreted the sequence of interbedded shales, diatomite and tuff in the Miocene Monterey Formation as reflecting the progressive diagenesis of silica and the derivation of silica from diatoms and, possibly, the devitrification of volcanic ash. Audley-Charles (1965) showed that the Cretaceous rocks of Eastern Timor are radiolarian-rich deep-sea deposits. He concluded that the chert was silicified by the mobilization of biogenic silica. Because the Eastern Timor chert contains only small amounts of Ti, Co, Ni, Cr and V, Audley-Charles suggested that the volcanic ash was not an important source of silica.
Many DSDP studies presented evidence for biogenic silica as a source for marine "chert." The coincident downhole disappearance of radiolarians and the appearance of "chert" was noted by Garrison and others (1975). The "chert" from Site 163 preserved the mottling and layering of the unsilicified sediment (Heath, 1973). The sediment adjacent to and as much as a meter away from silicified layers contained less silica than either the "chert" or more distant sediments (Lancelot, 1973). There is a marked lack of silicified material both in sequences with abundant volcanic ash (Lancelot, 1973) and at sites poor in siliceous microfossils (Keene, 1975; Garrison and others, 1975). Calvert (1971) recognized that some North Atlantic "chert" could have formed from biogenic silica and some could have formed as an alteration of volcanic ash. Paleo-reconstruction of the North Pacific by Keene (1975) suggests that the area of "chert" occurrence was once associated with the equatorial zone of high biologic productivity. Dissolution of biogenic silica was thought to occur under alkaline conditions and its precipitation under lowered pH (von Rad and Rosch, 1972). DSDP interstitial water studies have not indicated any anomalously large pH deviations from normal marine waters. It thus seems likely that the chertification process occurs under normal pH values for sea water.

The concept of a major event which triggers chert formation was common in biogenic silica theories. Heath and Moberly (1971) suggested that the ultimate cause for Pacific Eocene "chert" was an event such as a major shift in oceanic circulation. The opening of the Drake Passage and the splitting of Antarctica from Australia (Dietz and Holden, 1970; Kennett and others, 1972) is evidence for such events. Kennett and others (1972) also noted the common presence of unconformities in the
late Eocene to middle Oligocene sediments recovered between 1400 and 4600 meters water depth by the DSDP. These unconformities, they suggest, are probably a result of vigorous bottom current activity caused by the establishment of the Antarctic Circumpolar Current. There was also a general cooling of the world water masses from the middle Eocene to the middle Oligocene (Margolis and Kennett, 1970; Steineck, 1971; Savin and others, 1975).

The origin of most chert through the alteration of biogenic silica is widely accepted, yet other origins, such as clay diagenesis or the alteration of volcanic ash cannot be completely discarded.

Mineral associations are evidence for a volcanic source for some of the silica. Zeolites and smectite, which are primary alteration products of volcanic material, are often associated with chert (Hay, 1966; Heron and others, 1965; Heron, 1969). A mineral assemblage including authigenic zeolite, smectite and opal-CT in deep-sea "chert" is suggestive of devitrification of volcanic ash (Heath and Moberly, 1971; Calvert, 1971; Hay, 1966). However, volcanic ash is not associated with many "chert" occurrences (Calvert, 1971). The coincidence of Eocene volcanism in the Caribbean and the occurrence of a prominent Eocene "chert" in the North Atlantic suggests that the two phenomena may be related (Gibson and Towe, 1971; Mattson and Pessagno, 1971). Hydrothermal solutions emanating from an active fracture zone in the Lau Basin were thought responsible for the occurrence of barite and opal with volcanic detritus (Bertine and Keene, 1975).

Volcanogenic theories have been postulated for the origin of the Tertiary "chert" of the North Atlantic (Mattson and Pessagno, 1971). Pyroclastic detritus delivered to the area by winds or turbidities has
altered to opaline material as well as zeolites and smectite. Gibson and Towe (1971) suggested that Eocene volcanism enhanced the production of biogenic silica for chert by providing nutrients to increase biologic productivity of silica. The coincidence of the opening of the Norwegian Sea and the age of Horizon A prompted Herman (1972) to postulate that the two were related. Deuteric alteration of submarine volcanic material extruded during the opening episode increased bottom water concentrations of silica and preservation of siliceous microfossils. With the completion of rifting, strong temperature zonations were produced vertically, bottom water circulation was increased and the period of formation ended.

The clay transformation smectite to illite liberates silica because smectite contains more silica than illite. Towe (1962) suggested that some sandstone deposits may have been cemented in part by this transformation. Keene and Kastner (1974) suggested that a middle Eocene porcellanite containing illite rosettes formed from silica liberated by the alteration of smectitic clays which were adjacent to the porcellanite unit. Garrison and others (1975) suggested that this clay transformation could account for some of the silica for the deep-sea "chert" which he studied.

**Chert Mineralogy**

To a first approximation, chert is thought of as quartzose in nature, often containing impurities such as calcite, clay or organic matter. However, Cenozoic and some Cretaceous deep-sea "chert" is composed of silica minerals other than quartz (Keene, 1975; Murata and Nakata, 1974, for example).

Levin and Ott (1932) presented x-ray diffraction patterns of
opaline silica samples showing two broad peaks characteristic of cristobalite. An x-ray diffraction pattern of opaline material with a weak peak at 4.1 Å (cristobalite) and at 4.3 Å (tridymite) is classified as opal-CT by Jones and Segnit (1971). Heath and Moberly (1971), in a DSDP "chert" study, termed the mineral identity of similar opaline "chert" as alpha-cristobalite. Alpha-cristobalite or opal-CT is observed in all "chert" of the Cenozoic within non-carbonate rich deep-sea deposits (Greenwood, 1973; Garrison and others, 1975; Keene, 1975).

The diagenesis of opal-CT tends toward a more stable silica phase. Keene (1975), Heath and Moberly (1971) and Heath (1973) demonstrated that the amount of opal-CT with respect to quartz decreases with increasing age. Almost equal amounts of cristobalite (opal-CT) and quartz were identified in Campanian "chert" (Heath, 1973). Murata and Nakata (1974) noted a progressive decrease in the d-spacing of cristobalite with depth in the Monterey Formation, indicative of ordering.

The formation of opal-CT and the rate of inversion of opal-CT to quartz seem to be related to the minerals associated with it. The strong association of opal-CT and clay was emphasized by Lancelot (1973) and Greenwood (1973). Lancelot suggested that the presence of foreign cations and low permeability associated with clays prevented the formation of a more ordered silica phase. The presence of other authigenic minerals, such as phillipsite, in smectitic clays with opal-CT was cited as evidence favoring this conclusion (Lancelot, 1973; Greenwood, 1973). In his DSDP "chert" study, Keene (1975) found that "chert" with no calcite has a high cristobalite-to-quartz ratio; those with carbonate have diverse ratios, dependent upon clay content. He also showed that porcellanite (opal-CT claystone) retained this unstable mineral
assemblage longer than did calcareous "chert." Pre-Albian "chert" with no clay contains no cristobalite. Those with clay are still cristobalitic. Previous work, thus, suggests that opal-CT is apparently preserved best in sediments containing clay and free of carbonates. Quartz apparently forms more rapidly from its precursors in calcareous zones.

**Chert Petrography**

Chert texture and structure have been observed with electron microscopy. Folk and Weaver (1952), using replicas of fracture surfaces of chert for transmission electron microscopy (TEM), found three characteristic textures which have formed the basis for textural analysis of TEM studies of chert. Chalcedony lacked well-defined grains and had a spongy appearance with many pits and holes, which Folk and Weaver (1952) attributed to water. Novaculite type or granular microcrystalline (GMC) quartz yielded a mosaic of well-defined grains of quartz crystallites. A transitional texture contained areas of spongy material and areas of mosaic quartz. Kiabara (1964), Oldershaw (1968) and Monroe (1964) substantiated the textural classification of Folk and Weaver. Madsen (1974), in a TEM study of the Monterey chert, suggested that the spongy morphology was more indicative of porcellanites and represented a transition from cristobalite to quartz.

Use of the scanning electron microscope (SEM) by Wise and his co-workers (Wise and others, 1972; Weaver and Wise, 1972a, 1972b; Wise and Kelts, 1972) has shown that disordered cristobalite, opal-CT, occurs in the form of spherical bodies 10 to 20 μm in diameter. These bodies are aggregates of blade-like crystals several hundred Angstroms in thickness. They occupy pore spaces in nannoplankton oozes and were shown to occupy
molds of diatoms, radiolarians and sponge spicules in chert of the Southeastern U.S. coastal plain (Wise and Weaver, 1973; Weaver and Wise, 1974; Pollard and Weaver, 1973). Cristobalite spherules or lepispheres, as they were termed by Wise and Kelts (1972), have been found in the Monterey chert by Oehler (1975) as well as in DSDP "chert" (Keene, 1975; Garrison and others, 1975, for example). They always form the initial filling of a cavity.

Detailed petrographic studies of DSDP "chert" have been made by Heath and Moberly (1971), Calvert (1971), Heath (1973), Lancelot (1973), Greenwood (1973), Keene (1975) and Garrison and others (1975). These studies have shown that the DSDP "chert," like chert outcropping on land, may be divided into nodular and bedded occurrences. Nodular "chert" is associated exclusively with limestone, while the bedded varieties are associated primarily with pelagic clays or siliceous ooze. However, in some respects the DSDP "chert" is very different from its counterpart on land. Tertiary deep-sea "chert" contains quartz only as void fillings of chalcedony or cryptocrystalline quartz (Garrison and others, 1975; Lancelot, 1973). Also, many occurrences contain much opaline silica (Greenwood, 1973).

"Chert" nodules occur mainly in calcareous sequences containing significant siliceous microfossils (Keene, 1975). They are massive, hard with a vitreous luster and conchoidal fracture, and light in color (Lancelot, 1973). Chalcedony lines form chamber voids. The matrix is usually a mosaic of fine-grained quartz and calcareous remains (Lancelot, 1973), but it can be cristobalitic (Garrison, 1975; Heath and Moberly, 1971). The calcareous tests are replaced by granular microcrystalline (GMC) quartz (Garrison and others, 1975).
Heath and Moberly (1971) postulated the following paragenetic sequence for DSDP "chert" nodules: 1) the filling of foram chambers by chalcedony; 2) the replacement of the groundmass by finely-crystalline cristobalite; 3) the replacement of the remaining carbonate material by chalcedony; and 4) the filling of voids by quartz. This sequence was slightly modified by Garrison and others (1975), who suggested that the silica replacement of carbonate debris takes place in two stages which may overlap somewhat. First, along with chalcedony void filling, QNC quartz replaces forams. Later the replacement proceeds to the matrix, where opal-CT or amorphous silica replaces nannofossils. Keene (1975) added several early stages to Heath and Moberly's sequence. The initial filling of some void spaces are opal-CT plates which grow into spherules. Carbonate replacement takes place before the remaining void spaces are filled by chalcedony.

Bedded DSDP "chert" occurrences are silicified pelagic clay deposits with generally minor amounts of calcareous fossils. They have a poor conchoidal fracture and, more commonly, an irregular or hackly fracture. They are usually dark in color, mostly green and brown. Mottling and/or laminations may be present. In thin section, poorly preserved radiolarians and diatoms are seen, many with no original shell wall present (Garrison and others, 1975). Instead, the fossils are molds, partially or completely filled with cryptocrystalline cristobalite, chalcedony, cryptocrystalline quartz or some combination of these. The matrix is cryptocrystalline cristobalite and clay (Garrison and others, 1975). Clinoptilolite was also noted in x-ray diffractograms of porcellanites (Heath and Moberly, 1971; Heath, 1973).

Heath and Moberly's conception of the paragenesis of bedded "chert" is not as detailed as their nodular "chert" sequence. First, a
cristobalitic claystone develops. Secondly, continued precipitation of cristobalite produces a well-indurated porcellanite. The final step would be the inversion of the cristobalite to quartz.

**Silica Geochemistry**

The geochemistry of silica is complex and not completely understood. The isolated system, silica-water, has received a great deal of attention. The solubility of silica is greatest in alkaline solutions of pH 9 or greater (Krauskoph, 1956; Okamoto and others, 1957; Alexander and others, 1954). Silica solubility increases with temperature (Krauskopf, 1956; Fournier and Rowe, 1962; Morey and others, 1962) (Figure 1). The solubility is also a function of the mineralogy of the silica phase being dissolved (Figure 1). The more disordered the structure, the greater is the degree of dissolution (Krauskopf, 1956; Fournier and Rowe, 1962; Siever, 1962; Stober, 1967). Krauskopf (1956) has given the solubility of quartz at 25°C as 6 ppm. However, Morey and others (1962), extrapolating from high temperature experiments, have given 12 ppm as the solubility of quartz at 25°C. Opal solubility at 25°C was estimated to be greater than 100 ppm by Krauskopf (1956) and approximately 115 ppm by Morey and others (1964). Working from extrapolation of high temperature experiments, Fournier and Rowe (1962) published a value of 27 ppm for the solubility of cristobalite at 25°C. Stober (1967) pointed out that estimations of silica solubilities at room temperature may be divergent due to surficial absorption of silica acid of dissolving grains. Pressure effects on the solubility of opaline material seem to be negligible. Jones and Pytkowicz (1973) noted approximately a 10 percent increase in the solubility of amorphous silica kept at 2°C over
Figure 1. The solubility of silica phases and the dissolved silica levels in selected DSDP cores. The estimated solubility of amorphous silica, cristobalite and quartz are plotted based on the data of Krauskopf (1956), Fournier and Rowe (1962) and Morey and others (1962) for 25°C and 2°C. The solubilities of deep-sea cristobalite (opal-CT) and Eocene radiolarians are also indicated for 2°C (Jones and Pytkowicz, 1973). Levels of dissolved silica in ocean bottom water and in selected DSDP cores are plotted against estimated in situ temperature not corrected for pressure (geothermal gradient 0.06°C/m, Cook, 1973). Numbered data points indicate the site numbers from which samples were taken for this study. Table 3 (p. 67) lists complete chemical analyses of these selected sites. (Figure modified from Heath, 1974).
SOLUBILITY OF SILICA PHASES & DISSOLVED SILICA LEVELS IN SOME DSDP CORES

\[ \text{Solubility (ppm)} \]

\[ \text{Temp. } ^\circ \text{C} \]
the pressure range 1 to 500 atmospheres (56-62 ppm).

Where other ions are present, the silica equilibrium becomes complex; but it seems to be governed by the precipitation and equilibria of other minerals rather than by an SiO₂ phase. Okamoto and others (1957) found that in the presence of aluminum, the solubility of silica is greatly reduced. Siever (1962) expanded this to include alkalies and alkaline earths. These cations may decrease the solubility of silica and may cause equilibrium with respect to aluminosilicates. However, Greenwood (1967) formed spherules of cristobalite from a solution of KOH and silica, suggesting that the presence of K did not alter the equilibria to an aluminosilicate but merely formed a silica phase. The data of Evans (1965) suggests that the presence of organic matter, such as sugars and nucleic and amino acids, enhances silica precipitation.

Silica geochemistry in natural waters is more complicated than in laboratory experiments because of complex interrelationships between biologic utilization and geologic processes. Rivers are nearly saturated with respect to quartz; however, oceans are very much undersaturated. This fact cannot be explained by simple mixing (Bien and others, 1958). The silica supplies to the oceans by river influx must be either utilized by clay formation (Bien and others, 1958; Mackenzie and Garrels, 1965; Mackenzie and others, 1967; Fanning and Schink, 1969) and/or removed by biologic activity and deposited as oozes (Harriss, 1966; Calvert, 1968; Burton and Liss, 1968).

A considerable amount of silica in the oceans is bound up in the form of opal by organisms, chiefly diatoms and radiolarians. Much of this silica is returned to the ocean before the tests reach the seafloor. Hurd (1973) estimated that only 0.05% to 0.15% of the opal
produced in the water column is actually incorporated into the bottom sediment. Berger (1968) suspended radiolarians at various depths on a wire at a site in the Central Pacific to study dissolution rates. He found recent radiolarian sediment dissolved faster at depths shallower than 2000 meters. Solution was greatest at the surface and decreased with depth. Fresh siliceous plankton dissolved faster than recent sediments. Lewin (1961) found that the removal of organic matter greatly increased the rate of solution of diatom frustules. The presence of other cations, such as Al, Fe and Be, decreased the rate of solution and the degree of solubility of the frustules (Lewin, 1961). However, she concluded that cation concentrations in sea water were too low to have any significant effects on diatom dissolution. The diatoms which reach the sea floor and become part of the sediment are generally the more robust forms (Calvert, 1966).

Upon incorporation into the sedimentary column, biogenic silica continues to dissolve in the interstitial waters. Once silica is confined, the pore water concentrations climb rapidly to values (15-30 ppm) well above those of ocean water (1-3 ppm). This rise in silica concentration in the pore water occurs in the topmost 50 to 100 cm (Bischoff and Ku, 1971). Below this depth the values level off to an average of 10 to 20 ppm, though values as high as 31 to 80 ppm may be found (Bischoff and Ku, 1971). In the uppermost 50 cm, then, there is continued diffusion of silica into the water column (Fanning and Pilson, 1974).

The kinetics of silica inversion from unstable mineral phases to quartz is little understood. Ernst and Calvert (1969) attempted to transform porcellanite of the Monterey Formation into quartz. They
concluded that the inversion of cristobalite to quartz has a direct linear relationship with time. A solid-solid inversion was theorized as a front moving through each grain at fixed velocity. The complete inversion of porcellanite to quartz at 20°C was estimated to take 180 m.y. Heath and Moberly (1971) favored a particle-by-particle inversion of cristobalite to quartz, the rate of which is dependent upon temperature. Heath and Moberly noted that the transformation was a very slow process due to its high activation energy of 23 kcal/mole.
CHAPTER III

RESEARCH METHODS

Problem Discussion

To understand the origin of deep-sea chert, several questions must be answered. What was the source of silica? What was the sequence of events which produced the chert? What was the cause of silicification? What was the nature of the chemical system under which silicification occurred? The answers to these questions are important because they will describe the framework in which silica mobilization, localization and precipitation occur, as well as define, in an orderly fashion, the sequence of events which silicifying sediment undergoes to become a chert.

Answering these questions by studying chert is difficult because chert often loses much of its original textural features through recrystallization. The chemical conditions and reactions which led to the chert may no longer be present. It would be more advantageous to examine chert in a more transitional or early state of silicification. The abundant middle Eocene DSDP "chert" is apparently in this state of early silicification. Detailed examination of this silicified material may provide answers to the questions concerning chert formation.

The present study of silicified Eocene strata involved two approaches - a detailed analysis of a selected group of samples and a broader analysis of Atlantic and Pacific chert as described in the Initial Reports of the Deep Sea Drilling Project of the first 43 legs. These two approaches enabled study of both detailed chert diagenesis and
possible regional or global influences.

Sample Selection

Samples were chosen for study on the basis of the core descriptions and site discussions found in the Initial Reports of the Deep Sea Drilling Project, Legs 1, 2, 3, 11, 12, and 14. The DSDP sample sites selected for study are indicated in Figure 2. The sites cover the entire Atlantic with most coming from the northwestern Atlantic. Atlantic "chert" was chosen for study because there have been few previous studies of the Atlantic "chert" and because the termination of "chert" formation was particularly abrupt in comparison to the Pacific. Appendix 1 lists the location, water depth, recovery interval and general lithology of each sample.

In all but two instances the samples have good biostratigraphic control and are from a relatively undisturbed section of core. All Atlantic middle Eocene "chert" occurrences reported before 1972 which met these criteria were sampled. The middle Eocene silicified material was selected because it is more widely developed than that of other ages. Silicification of these sediments has not progressed to the extent where it has seriously altered original textures. Figure 3 shows the ages of the samples studied. Most are of middle Eocene age. Paleontologic control was not sufficient in the remainder of the samples to classify them better than "Eocene" or "early to middle Eocene."

The stratigraphic relationships of the samples to the surrounding sediments are indicated in Figure 4. In cores containing silicified sediment, the surrounding sediment, as well as the "chert" was sampled.
Figure 2. The location of sites sampled. The location of DSDP sites from which Eocene core material was sampled for this study is shown. Most of the samples were collected from the NW Atlantic because most of the cherts were recovered in that basin; however, samples did cover the entire Atlantic Ocean.
LOCATION OF SITES SAMPLED
Figure 3. The ages of core materials sampled. The ages of the core material from which samples were selected are shown with reference to the foraminiferal biostratigraphic zones of the lower and middle Eocene. The x-axis separates the cores into the D/V GLOMAR CHALLENGER cruise legs to which they belong. In those cores which are indicated by short solid lines the biostratigraphic ages were well-defined. In those cores indicated by dashed lines, the ages were less well defined and were labeled "middle Eocene" (9A, 13, 140) or "Eocene" (8A).
Figure 4. The stratigraphy of sampled cores. The stratigraphy of the cores from which material was sampled is indicated. The number at the upper right of each section is the core identification number. The numbers coupled with arrows indicate the location and centimeter interval sampled in the sections. The numbers on the left of each section indicate the sub-bottom depth interval from which the core was recovered. Generalized lithologic descriptions accompany each sediment section.
Samples of sediment were selected either on the basis of lithologic changes or, if disturbed, at some convenient interval, generally less than a meter away from a "chert." Some samples were taken from unsilicified middle Eocene sediments.

This sampling plan allowed comparison of silicified and unsilicified beds in each core and comparison of sites where silicification has occurred to sites that have not undergone silicification.

Eocene cores from Sites 9A and 98 were disturbed by drilling. "Chert" and unsilicified sediment were collected from these sites in spite of this disturbance due to the unique lithologies of these sites. Therefore, the sub-bottom position and stratigraphic relationships of sediment, "chert" and samples are not exact.

Analytical Techniques

X-ray Diffraction

All x-ray diffraction analyses were run on a Philips Model 3500 APD x-ray diffractometer using monochromated copper K-alpha radiation at a power setting of 40 kv and 21 ma. Random power mounts of the bulk sediment were prepared by hand grinding air-dried portions of the samples in an agate mortar. Silicified samples were ground in a sapphire mortar. The grinding was continued until the sample could pass through a 63 um sieve. Randomly oriented power mounts were prepared from the ground material and x-rayed from 4°20 to 60°20 at one half°20 per minute. The results of the bulk sediment analysis are tabulated in Appendix 2.

Oriented mounts were made from the same powdered bulk samples used for random powder mounts. These were prepared by smearing a small bit of moist powder on a Micarta substrate. These bulk-oriented slides were examined from 4°20 to 30°20 at a scan speed of 1°20 per minute.
This procedure enhanced basal reflections of clays in both the sediment and silicified material, which aided in identifying them within the context of the bulk sample. The results of the bulk-oriented analysis are tabulated in Appendix 3.

Slides were prepared to examine the less-than-2 μm fraction of the sediment. Small portions of the core sample were dispersed in a solution of calgon (2.54 mg/l). The less-than-2 μm fraction was separated from the bulk sample by centrifugation at 1000 rpm for two minutes. Ten ml of 1 N magnesium acetate was added to the supernatent liquid/clay suspension. The solution was then heated in a boiling water bath for 20 minutes, allowing for complete flocculation and magnesium saturation of the clay within a reasonable length of time. After cooling of the flocculated clay, a series of washes and centrifugations were done to remove excess soluble salts. After two such cycles, a portion of the concentrated slurry was pipetted onto a Micarta slide and allowed to air dry. Pipetting was chosen over smearing due to the paucity of the clay material available. These oriented clay fraction samples were x-rayed using the same parameters as those used for the bulk-oriented samples. A second x-ray trace from 4° to 13° was done after ethylene glycol treatment to fully expand any swelling clays. The results of the clay fraction study are tabulated in Appendix 4.

Grain Mounts

A few milligrams of air-dried bulk sample were ground to a powder (less than 100 μm), using an agate mortar or a sapphire mortar for silicified sediments. These were sprinkled into heated liquid canada balsam. A cover slip was pressed onto the mount, and the slide was allowed to cool, making a permanent grain mount. A grain mount was
prepared for each of the 34 samples.

Thin Sections

All silicified sediments were sectioned where there was sufficient material to be spared or where thin sections could not be obtained from the curator of the DSDP. Unsilicified sediments were sectioned if the samples were from a core containing "chert" or if it were the only sample in a core containing siliceous material. Where spatial orientation of the specimen was clear, an oriented thin section was prepared. A total of 21 thin sections were made.

The thin sections were cut by the Roudolf Von Huene firm of Pasadena, California. All unsilicified samples were impregnated prior to thin sectioning. The plastic impregnation of silicified samples was left to the discretion of the firm.

Thin sections of the "chert" layers 6-6-1 (130-132) and 9A-1-4 were obtained from the DSDP collection and are on loan for this study. No thin section of sample 98-7-4 was prepared due to insufficient material.

The samples were examined petrographically for primary sedimentary minerals, authigenic minerals, preservation of siliceous microfossils and paragenetic relationships of mineral species.

Scanning Electron Microscopy and Microprobe Analysis

All samples were viewed with a JOEL Model JSM-2 scanning electron microscope using 25 kv accelerating voltage. Fracture surfaces, either broken surfaces of air-dried sediment or fracture surfaces of "chert," were prepared for SEM study. The treatments and coating materials are summarized in Appendix 5.
Energy Dispersive x-ray Spectroscopy (EDS) of the SEM specimens was done using an Ortec Model 7000 Si(Li) detector and an Ortec Model 6200 Multi-channel Analyzer. Because only fracture surfaces were analyzed and no standards were used, results are solely qualitative or semi-quantitative.

Fracture surfaces of all samples were coated with a carbon thin film and a layer of gold. On some of the more clay-rich samples, an additional layer of carbon was laid down over the gold. This decreased charging and enhanced secondary emission, making high resolution photography easier. The samples were mounted on carbon planchets cemented to the top of aluminum 1-inch diameter stubs. The samples were cemented to the surface of the planchets using a "Collodion-Tube Coat" solution. In a few instances where x-ray analysis was more critical, specimens were mounted on brass stubs or on a carbon planchet cemented to an aluminum stub using "Collodion-Tube Coat" solution as adhesive for both the sample and the planchet. These were then coated with carbon. These samples were examined under the same criteria as those used for the thin section study.

Another group of fracture surfaces was treated with acids prior to mounting and coating. "Chert" chips were etched in 5 percent HF by volume, and other chips of the same sample were etched in 5 percent HCl by volume. A 30-second to one-minute etch time provided the best results. These samples were mounted and coated as the previous samples. This treatment better delineated the silicification process and helped identify the location or occurrence of some mineral species.

For specific mineral analyses, the system was used in the spot mode, which allows an area of about one micron in diameter to be
examined. To determine mineral localizations, either the line profile or map area modes of x-ray data display could be utilized. Counting time for all mineral identifications was 200 seconds at approximately 1500 cps. Line profiles and area maps were done at a 100-second scan speed.

**Comprehensive Site Surveys**

In addition to the techniques designed for direct observation of DSDP samples, a survey of all Atlantic and Pacific site reports of the DSDP (legs 1-43) was conducted. All "chert" occurrences, their depth, age and lithology of the host sediment was recorded. The terms "chert," "porcellanite," "radiolarite," "diatomite" or sediment which had been labeled "silicified" were included as sites where silicification had occurred. All oozes and sediments rich in biogenic siliceous material were also noted using the same parameters from which the "chert" occurrences were tallied. These data should not be regarded as exact values because the methods of data interpretation and display are not unique.

A second area of survey investigation dealt with pore water data. Only two sites of the 34 samples used in this study had interstitial water analyses done on material in the proximity of the sample by the DSDP researchers. To gain more information into the chemistry of the system, data were extracted from the published reports from other DSDP sites of similar lithology to the sediments sampled for this study.
CHAPTER IV

RESULTS FROM ANALYSES AND OBSERVATIONS
OF DSDP SAMPLES

Summaries of the results of the detailed examination of the DSDP samples are included in Tables 1 and 2 (p. 57, 60). This section will cover the results in more detail.

Site 6

Stratigraphy

Site 6 is located on the southwest flank of the Bermuda Rise (Figure 2). This site provides the most complete, least disturbed sequence of "chert" and un lithified sediment of the cores sampled. In this section three lithologic units were cored by the shipboard scientific party (Ewing and others, 1969): 1) a Pliocene to Pleistocene cover of brown clay; 2) a middle to upper Eocene sequence of olive silty clay; 3) a middle Eocene sequence of graded foraminiferal sands and diatomaceous silt and clay. Portions of this lowermost unit were silicified. One of these silicified layers is the prominent seismic reflecting layer, Horizon A, located about 250 m sub-bottom. Drilling terminated at 257 m sub-bottom.

The shipboard scientific party concluded that this site was an abyssal plain below the calcite compensation depth (CCD) during Eocene time. Turbidite influence was mainly from the North American continental margin. In the upper Eocene, turbidite deposition ceased, either because of uplift of the Bermuda Rise or subsidence of the Hatteras and Sohm abyssal plains. The area received pelagic sedimentation from
that time to the present.

Sampling

Silicified and unsilicified samples were taken from the lowermost unit cored at this site (Figure 4). A silicified sand at 6-5-1 (0-4) was unavailable.

X-ray Diffraction - Unsilicified Samples

X-ray diffraction patterns of all unsilicified samples are quite similar; indicating calcite, quartz, smectite and opaline material (Appendix 2). Glaucoponite and chlorite were noted in some samples.

Calcite, opaline material, quartz, glauconite and chlorite were more prevalent in the sands. Smectite was more abundant in the clay-rich units. Distinct mixed layering is present 10 cm above and 17 cm below the "chert" at 6-6-1 (130-132) and 2 cm above the poorly silicified sample at 6-6-3 (73-75) and also, possibly, 20 cm above it.

Mixed layering was identified as areas of more intense scattering at 11 Å after treatment with ethylene glycol (Appendix 4). Minerals detected by x-ray diffraction are common minerals which would be likely to occur in sands and pelagic intervals on a portion of the sea floor subject to turbidite sedimentation. Samples adjacent to the "chert" layers exhibit the early stages of clay transformation from smectite to illite. This mixed layering is not found in samples away from "chert" layers where the clay is composed predominantly of smectite.

Thin Section and SEM Data - Unsilicified Samples

Both SEM photomicrographs and thin sections indicate the presence of abundant sponge spicules, diatoms and radiolarians in the unsilicified samples. Figure 5 contains measurements and ratios of spicule
Figure 5. Sponge spicule diameter ratios. The ratios of the external to internal diameters of sponge spicules from core 6 of Site 6 are plotted against distance from "chert" layers (solid triangles). The ratio tends to decrease in the vicinity of silicified units. Most measurements were made from scanning electron micrographs. Where measurements were obtained from light microscope study of thin sections as well as SEM, both are plotted and designated lm and sem respectively.
SPONGE SPICULE DIAMETER RATIOS

ext

int

Ratio

0 10 20 30 40 50 120 130 40 50 60 70

6-5-1

6-6-1

Core Section & Cm. Interval

sem

lm

sem

lm

sem
external and internal diameters versus distance from silicified layers. The unsilicified sands, 6-4-3 (20-22), 6-4-3 (60-62), 6-5-1 (18-20), 6-5-1 (48-50) and 6-6-3 (52-54), are generally distant from "chert" and usually have larger external and smaller internal spicule diameters, yielding a high external to internal diameter ratio. The clay units are generally nearer to silicified layers and usually have a smaller external diameter, yielding a lower external to internal spicule diameter ratio in comparison to the sands. SEM photomicrographs indicate solution pitting on the surface of the spicules in samples 6-6-1 (120-122), 6-6-1 (147-149), 6-6-3 (46-48) and 6-6-3 (69-71) (Plate Ia, b, f). Diatoms and radiolarians are highly fragmented in samples near "chert" layers (Plate Ic-e).

**X-ray Diffraction - Silicified Samples**

In the silicified layers, 6-6-1 (130-132) and 6-6-3 (73-75), x-ray results show a mineral composition of quartz, calcite, opaline material, opal-CT and illite. A feldspar is present in sample 6-6-3 (130-132), a silicified sandy portion of a turbidite. Sample 6-6-3 (73-75), a silicified coccolith clay, is composed of calcite, opal-CT and a mixed-layer clay, smectite/illite. Thus, the "chert" is compositionally similar to the surrounding sediment; however, the presence of opal-CT indicates that these layers have undergone some silica diagenesis.

**Thin Section and SEM Data - Silicified Samples**

In thin section, the silicified sand contains angular quartz grains, sponge spicules, foraminifera and echinoderm fragments (Plate IIa, b). Fibrous quartz and opal-CT spherules are the authigenic phases seen in various stages of infilling of the cavities of sponge
spicules and foraminifera (Plate IIc, d). SEM photomicrographs show bladed opal-CT as a crust or lining of all the cavities and opal-CT spherules growing from this substrate (Plate IIe, f). This initial overgrowth of spicule cavities by opal-CT makes the spicule appear weakly birefringent in thin section. Silicon was detected from microprobe data on these spherules, implying that they are composed primarily of SiO₂. Aluminum may be present in small amounts but may be below minimum detectable limits. HCl dissolved away much of the carbonate foram tests on the etched SEM samples of the sand, producing internal casts of foraminifera chambers (Plate IIIa). The punctae are filled with silica, indicating that silica filling the chambers had contact with the exterior pore fluids.

Without HCl-etching, the "chert" at 6-6-3 (73-75) is a rather featureless shale as in Plate IIIb. HCl-etched samples illustrate the presence of coccoliths as impressions (Plate IIIc-e). Silica-infilled foram chambers were sometimes noted, confirming that silicification has taken place to some degree (Plate IIIe).

In the thin section of 6-6-3 (73-75), little evidence for silicification is found. A great abundance of coccoliths was noted in the clay. Spicules and radiolarians are rare. One radiolarian test was found to be partially filled by a rind of opal-CT spherules and, as an outgrowth from the spherules, fibrous quartz (Plate IIIf).

Site 8

Stratigraphy

Site 8 (8A) is located on the northwest flank of the Bermuda Rise between the Sohm and Hatteras abyssal plains (Figure 2). Two
lithologic units were cored by the shipboard scientific party (Peterson and others, 1970): 1) a Miocene green clay with minor radiolarians, diatoms and spicules; 2) an Eocene section of clayey and silty radiolarian ooze, occasionally interbedded with graded units. Drilling terminated in Eocene "cherty" radiolarian mudstone at 314.2 m subbottom.

The sedimentary column is essentially devoid of calcareous biogenic and volcanic debris. The shipboard scientific party concluded that the site has experienced pelagic sedimentation almost continuously since the Eocene. Occasionally, a turbidite may have interrupted this pattern. Because these graded units are distinctly different from those at Site 6, a different source (presumed northerly) was suggested by Peterson and others (1970).

**Sampling**

This site is the most extensively silicified of the sites sampled. Although only two meters of the silicified unit were recovered, drilling rates indicate that the unit is at least 16.7 meters thick. The areas sampled, 8A-2-1 and 8A-3-1, are both within this unit (Figure 4).

**X-ray Diffraction - Silicified Samples**

X-ray analysis of the "chert" layers show that opal-CT, quartz, illite and clinoptilolite are the chief constituents (Appendix 2). Diffractograms of the bulk material indicate that the clays are illite with possible indications of mixed layering (Appendix 3).

**Thin Section - Silicified Samples**

Preserved radiolarian tests were observed in thin sections of the silicified samples. Some tests from 8A-2-1 (11-14), 8A-2-1 (37-39) and 8A-3-1 (5-7) are completely filled with opal-CT spherules and some
fibrous or GMC quartz. The interior of the other test walls are lined by cristobalite spherules (Plate IVa, b). The quartz phase emanates from that surface. A blocky, rectangular, non-isotropic crystal, 20-40 um in length, was sometimes noted on the surface of the cristobalite spherules in cavities which were not completely filled (Plate IVb). These crystals were identified as zeolites with the SEM/microprobe system, corresponding to the clinoptilolite identified via x-ray diffraction. Microprobe data from the zeolites indicate they are composed of Na, K, Ca, Al and Si.

**SEM Data - Silicified Samples**

In SEM photomicrographs, zeolites are seen growing along the free surface of the spherules (Plate IVe). High magnification photographs show blades of opal-CT growing from a zeolite face and a zeolite interrupting the spherical shape of the cristobalite (Plate IVf, Plate Va). This intimate intergrowth of opal-CT spherules and clinoptilolite indicates that the infilling of these radiolarian tests involved the co-precipitation of silica and a zeolite (clinoptilolite). Because no zeolites were observed with cristobalite spherules adjacent to the radiolarian test walls, this co-precipitation may take place toward the end of the cristobalite formation stage.

HF-etching removed much of the blade-like habit of the lining in the partially filled chambers and revealed rounded areas the same size as spherules in the infilled portion of the cavity (Plate VId). In completely filled chambers, HF-etching revealed spherule-like areas, some with tri-radiate fracture patterns (Plate VId, f). These observations, suggesting that spherules fill voids, differ from thin section observations indicating that infillings could be cristobalite and a
variety of quartz. Either the quartz varieties are pseudomorphs after
cristobalite spherules or no radiolarians examined by SEM with HF-etched
samples contained quartz. HF-etching also revealed the co-precipitation
of zeolites with the spherules in completely filled tests (Plate VIIa).

The clay particles of the matrix of these samples retain a flakey
appearance (Plate IVe). The degree of induration (based on topographic
relief and visibility of clays) is variable in an irregular fashion.
Possibly the porosity and permeability of the matrix material has some
control on the degree of lithification of a porcellanite in a clayey
sequence.

8A-2-1 (20-22) and 8A-3-1 (31-33)

Thin sections of the "chert" of 8A-2-1 (20-22) and 8A-3-1 (31-33)
contain more radiolarian tests than the other 8A silicified samples.
These tests are more extensively filled with either GMC or fibrous
quartz (Plate IVc, d). Cristobalite spherules are seen as the initial
lining of these test walls (Plate IVd). SEM photomicrographs also
show completely filled tests (Plate Vb, c). The difference between the
silicification in these samples and the other 8A silicified samples is
most apparent in the radiolarians which are not completely filled. In
the partially filled vugs of 8A-2-1 (20-22), octahedral crystals were
seen (Plate Vd), sometimes in association with hexagonal plate-like
crystals (Plate Ve). The octahedra and hexagonal plates extend from a
substrate of smaller void-lining crystals of similar octahedral nature
(Plate Vf) on the interior walls of the radiolarian tests (Plate VIb, c).
These initial void-lining crystals are markedly coarser than and
distinct from the typical cristobalite spherule ultramorphology (Plate
VIa).
Energy dispersive analysis of the crystals yielded the characteristic x-ray energy indicative of K-radiation from silicon (1.74 kev). A slight asymmetry occurred in a few EDS spectra on the low energy side of these peaks, suggesting the possible presence of very minor amounts of aluminum. When the EDS system was switched to the line profile mode of operation, increased silicon K-radiation was obtained from the crystals above that of the silicon background, an indication that the x-rays were emanating from the crystals and do not represent stray radiation from the surrounding "chert." This indicates that the crystals were composed of silica.

Most isometric or hexagonal minerals are not silicates (Mason and Berry, 1968). Cristobalite may belong to either the isometric (high cristobalite) or the tetragonal (low cristobalite) crystal systems (Dana, 1962). It may occur as spherical aggregates of blade-like crystals or as octahedral crystals, generally less than 1 mm in size (Mason and Berry, 1968; Dana, 1962; Deer and others, 1966). High tridymite is hexagonal; low tridymite is orthorhombic (Dana, 1962). Tridymite occurs as thin, fragile, or thick, tabular hexagonal plates, flattened on (0001) (Mason and Berry, 1968; Dana, 1972; Deer and others, 1966).

A comparison of the photomicrographs of Grieg and others (1933) and Dutton (1937) with the SEM micrographs shown in Plate Vd, e indicates that the octahedral crystals do resemble crystals identified as cristobalite grown earlier. Oehler (1973) synthesized tridymite-like crystals similar to the hexagonal plates in question, except that his were of the thin fragile variety. Frondel (personal communication) pointed out that the tridymite plates shown in Plate Ve are oriented
parallel to the (111) face of cristobalite, which is the expected epitaxial orientation.

The morphological and chemical data suggest that the crystals in this deep-sea "chert" are high cristobalite and high tridymite. Unlike previously reported occurrences of cristobalite-tridymite in deep-sea "chert," these are discrete crystal growths of the high temperature silica phases. However, because of the small amount of these minerals present in this sample, it is not possible to definitely ascertain whether these crystals are the high-temperature silica polymorphs by x-ray diffraction. 8A-3-1 (31-33) within the same core also exhibits the high cristobalite crystals.

The clay matrix is also different in appearance from the other "chert" samples in this site. It consists of more uniformly and highly indurated tightly packed clay, rather than flakes (Plate Vb, c). The greater amount of radiolarians relative to clay apparently has supplied more silica, allowing for the more extensive lithification.

HF-etching revealed the presence of clinoptilolite in the indurated clay matrix of 8A-3-1 (31-33) (Plate VIIb), indicating that zeolite precipitation in the samples containing high cristobalite and high tridymite was confined to the clay matrix.

**X-ray Diffraction - Unsilicified Samples**

The unsilicified zeolite clay samples had mineralogies similar to the "chert" samples (Appendix 2).

**Thin Section and SEM Data - Unsilicified Samples**

Thin sections of the unsilicified samples, 8A-2-1 (28-30) and 8A-3-1 (27-29) are similar; both are zeolitic and show much dissolution and
fragmentation of radiolarian tests (Plate VIIc). No cristobalite spherules were found in 8A-2-1 (28-30); and very small, poorly developed ones were common in association with zeolites in 8A-3-1 (27-29) (Plate VIIc). However, these spherules appear to be growing on the surface of the zeolites, suggesting a reversal of the order of precipitation found in the silicified samples. The zeolites were found both in the clay matrix and in the interiors of radiolarian vugs.

The SEM photomicrographs clearly show degraded and pitted radiolarian tests in both unsilicified samples (Plate VIIId-f). SEM micrographs also better illustrate the growth of cristobalite spherules on clinoptilolite crystals (Plate VIIa-c). The clay is clearly visible and seems more abundant than in silicified sections of these cores.

**Site 9**

**Stratigraphy**

Site 9 (9A) is located on the northeastern flank of the Bermuda Rise in a region of low, linear ridges and scattered sea mounts (Figure 2). Two basic lithologic units were cored by the shipboard scientific party (Peterson and others, 1970): 1) a Miocene-Pliocene to Recent nannofossil foram ooze; 2) a clayey unit, mostly devoid of fossils except for weakly silicified Eocene and Cretaceous radiolarian "chert" at 680 m and 766 m respectively. Drilling terminated in basalt basement at 834.5 m sub-bottom.

The Eocene "chert" of Site 9A is mineralogically and chronologically similar to that of Site 8A (Peterson and others, 1970). However, the shipboard scientific party did not note any terrigenous components in the 9A samples. Clays and zeolites may have formed from sea mounts.
The transition from clay to calcareous oozes may have been caused by tectonism or by sediment penetration of the calcite compensation depth (CCD).

**Sampling**

A sample of the "chert," 9A-1-4 (64-66), and a sample of the clays with "chert" chips, 9A-1-4 (120-122), were taken (Figure 4). Because of the association of this site with volcanogenic material, a possible silica source, samples were taken in spite of severe drilling disturbance.

**X-ray Diffraction**

X-ray diffraction patterns for the samples are quite similar. The patterns define the presence of mixed-layer illite/smectite, clinoptilolite and opal-CT (Appendix 2). The bulk-oriented samples show distinct peaks of illite and smectite in the sample from 120 cm (Appendix 3). Upon glycolation of the sample 9A-1-4 (64-66), peaks at about 18 Å, 13.5 Å and 11 Å were found, indicating smectite and mixed layer smectite/illite (Appendix 4).

**Thin Section and SEM Data**

The thin section from 9A-1-4 (64-66) shows the interval to be a radiolarian clay with no original test material present. Instead, generally, a rind of opal-CT spherules makes a cast of the cavity (Plate VIIId). Zeolites were commonly observed along the interior wall of the spherules (Plate VIIIe). SEM photomicrographs better illustrate that the frustules consist of a rind of opal-CT spherules and zeolites (Plate VIIIlf). The cristobalite spherules are small, generally less than 10 um in diameter. The zeolites are the typical 20-40 um in
length. A few generally poorly developed zeolites, not associated with any obvious radiolarian test, were found in the clay matrix (Plate IXa, b).

The thin section from the 120 cm location is a siliceous clay. The siliceous component is represented by sponge spicules and radiolarians. Opal-CT with associated zeolites was found as void fillings of the radiolarian tests. Tests completely filled by this assemblage are rare.

Site 10

Stratigraphy

Site 10 is located in the lower western flank of the Mid-Atlantic Ridge, an area typified by abyssal hills (Figure 2). Two lithologic units were cored by the shipboard scientific party (Peterson and others, 1970): a Pleistocene-Cretaceous nannofossil foraminifera chalk ooze, interrupted at one interval, 40.5 m to 48.1 m, by a Miocene clay. Tuff layers were noted and increased in frequency from 305 m down to basement. Lower Eocene radiolarians occurred between 176 m and 185 m. This section contained phillipsite and at least one thin "chert" layer.

Sampling

The middle Eocene section sampled occurs 78 m above the lower Eocene sediments. Sample 10-7-4 (128-130), a nannofossil marl ooze to chalk (Figure 4), was taken to look for early signs of silicification in a non-siliceous core. If silicification were independent of lithology but related to some oceanographic parameter, such as silica concentration, then this site would have been likely to show signs of silicification.
X-ray Diffraction

X-ray diffraction patterns of the sample indicate predominantly calcite, with some clinoptilolite and a clay mineral (Appendix 2). The bulk-oriented diffractogram has a small peak at about 15 Å, suggesting smectite (Appendix 3).

SEM Data

SEM photomicrographs show poorly preserved coccoliths and discoasters with a very small amount of clayey material (Plate IXc).

Site 13

Stratigraphy

Site 13 and 13A are located on the lower continental rise off Sierra Leone, West Africa (Figure 2). Six lithologic units were cored by the shipboard scientific party (Maxwell and others, 1970): 1) Pliocene unconsolidated nannofossil and foraminifer ooze; 2) Upper to Mid Tertiary brown zeolitic clay; 3) Eocene radiolarian-diatom ooze with "chert"; 4) slightly indurated nannofossil ooze and clay intercalated with partly silicified dolomitic claystone (Campanian); 5) Senonian vitreous "chert" to laminated dolomitic "chert" and limestones associated with gray radiolarian sediments; 6) grayish-red shale and "chert" of Senonian (?) age. Drilling terminated at 463 m sub-bottom. The shipboard scientific party concluded that the siliceous Eocene section lies unconformably under the Miocene clays. This Eocene section is very homogenous, porous and generally poorly consolidated. Intercalated are a few hard "chert" stringers. These "cherty" units occur at two intervals, 177 m to 196 m (analogue of Horizon A) and at
Sampling

Samples were taken in order to examine the analogue of Horizon A (as at Site 6) and to study the characteristics of silicification in a predominantly calcareous environment. 13-3-1 (110-112) is a radiolarian ooze. The Horizon A samples are 13A-1-1 (87-89), a silicified coccolith ooze, and 13A-1-1 (128-130), a coccolith ooze with authigenic zeolites (Figure 4).

X-ray Diffraction

X-ray patterns indicate that opaline material, clay minerals and phillipsite are present in the radiolarian ooze (Appendix 2). Calcite, clinoptilolite and clay minerals are common to both 13A samples. Opal-CT is present in the 13A silicified ooze, and opaline material is present in the sample at 128 cm. Bulk-oriented and oriented clay fraction patterns indicate that smectite and possibly some mixed-layer clay are present in sample 13-3-1 (110-112) (Appendices 3-4). Illite, smectite and mixed-layer clay were identified from the unsilicified 13A sample. The 13A silicified sample is illite.

Thin Section and SEM Data - Unsilicified Sample

The thin section of the radiolarian ooze shows some dissolution of the radiolarian tests, manifest as a general lack of morphologic detail (Plate IXd). Diatoms and sponge spicules are also evident. Scanning electron microscopy shows abundant radiolarians, sponge spicules and diatoms associated with a small amount of clay (Plate Xa). Some fragmentation of tests has occurred. Severe dissolution features are uncommon.
Thin Section and SEM Data - Silicified Samples

The thin section of the sample at 128 cm is much more calcareous, with abundant coccoliths and some radiolarians (Plate IXf). The frustules are sometimes fragmented. A few clinoptilolite euhedra were observed in association with radiolarian tests. SEM shows radiolarians and possibly sponge spicules in minor amounts. Partially dissolved pore walls of the radiolarians are often thin and breached, allowing two pores to merge (Plate Xb). Plate Xc shows euhedral clinoptilolite crystals associated with siliceous frustule fragments. The two zeolites to the right in the plate are attached to or have incorporated a siliceous fragment.

In thin section, the 13A silicified sample shows vague, rounded areas where QMC quartz has been concentrated (Plate IXe). Much calcareous material is incorporated into these radiolarian-like areas. Plate Xd, an SEM micrograph, shows many rounded areas which have a smoother texture than the nannoplankton matrix. HF-etched surfaces produce negative relief in these rounded areas and illustrate the presence of carbonate material in a silica matrix. These rounded areas bear much resemblance to radiolarian tests (Plate Xe). Under higher magnification, these HF-etched samples show incorporation of coccoliths into the silicified area (Plate Xf). Tri-radiate cracks near the margin of the more silicified area resemble fracture patterns of HF-etched cristobalite spherules. HCl-etching indicates that the silicification is not restricted to the rounded areas. Coccolith impressions and possibly foram chambers are present (Plate XIa). The wall of a vug consists of a rim of cristobalite spherules and a few zeolites on the interior (Plate XIb). A zeolite found in the carbonate matrix has
small cristobalite spherules growing from the crystal faces (Plate XIc). The spherules are 4-7 μm in diameter, compared to the 10-15 μm spherules found on the vug wall. Line profiles for Ca and Si were made across a silicified area in an HF-etched sample. Plate XId shows Ca remaining relatively constant across the region. The silicon trace, Plate XIe, shows sharp increases over areas where the relief is less, the silicified areas.

Site 19

Stratigraphy

Site 19 is located in the southwest Atlantic on a north-south trending ridge on the west flank of the Mid-Atlantic Ridge (Figure 2). Six lithologic units were cored by the shipboard scientific party (Maxwell and others, 1970): 1) a Pleistocene brown nannofossil clay; 2) a Pliocene or Miocene red zeolitic clay; 3) an upper Oligocene nannofossil sequence with clayey zeolitic interbeds; 4) an Oligocene brownish chalk or ooze; 5) an upper to middle Eocene zeolitic nannofossil chalk to marl-ooze; 6) a middle Eocene brownish nannofossil chalk-ooze. Drilling terminated in a basalt basement at 145 m sub-bottom. This stratigraphy suggests that the site has experienced pelagic sedimentation since its inception in the Eocene. For the most part, it has been above the CCD.

Sampling

Two samples were taken from the middle Eocene section immediately overlying the basalt flow (Figure 4). Samples 19-9-5 (101-103) and 19-11-14 (75-77) are similar in lithology - coccolith oozes with a
minor amount of foraminifera. As at Site 10, samples were taken to look for early signs of silicification in an unsilicified core.

**X-ray Diffraction**

X-ray patterns indicate that both samples are calcite with some clay (Appendix 2). A few peaks for clinoptilolite were noted on the bulk-oriented diffraction pattern in 19-11-14 (75-77) (Appendix 3). The clay in 19-9-5 (101-103) was identified as smectite.

**SEM Data**

SEM micrographs of these calcareous samples show chiefly coccoliths with a small amount of recrystallized foraminifera (Plate XII, Plate XIII). Some carbonate diagenesis is indicated by some overgrowths on the coccolith shields similar to those shown in Matter (1974).

**Site 98**

**Stratigraphy**

Site 98 is located in the Northeast Providence Channel, Bahamas (Figure 2). Drilling penetrated 357 meters and terminated in Campanian sediments. The shipboard scientific party delineated no significant lithologic units (Hollister, Ewing and others, 1972). The site has experienced basically nannofossil deposition since the Campanian. The Holocene sediments are clay-rich, the late Cretaceous is detrital limestone, and the Eocene is radiolarian-rich with some volcanic glass and chert. The shipboard scientific party concluded that deposition has been in deep water since the Campanian. The site has always been above the CCD.
Sampling

Even though the core was disturbed by drilling, sample 98-7-4 (110-114) (Figure 4) was taken for this study from the Eocene section because a sharp linear contact is preserved in the sample, dividing it into a buff chert with a conchoidal fracture and a piece of white, indurated, partially silicified nannofossil foraminifera chalk with an irregular fracture.

X-ray Diffraction

The x-ray pattern from the chert indicated predominantly quartz and opal-CT with some calcite (Appendix 2). The chalk was composed predominantly of calcite with some opal-CT (Appendix 2). The bulk-oriented diffractogram contains broad, low peaks centered around 8.4 Å and 6.7 Å, which may be zeolite reflections (Appendix 3).

SEM Data

HF-etched samples of the chert and chalk indicate that originally both were composed of coccoliths, foraminifera and discoasters (Plate XIIb, c). The chert is homogenous in texture with only an occasional coccolith or foraminifera which has not been silicified (Plate XIIId). HCl-etching of the chalk reveals cristobalite spherules, 10-20 μm in diameter, occupying the pore spaces between carbonate grains (Plate XIIe). Zeolites, 20-30 μm in length, are associated with cristobalite spherules inside foraminifera chambers (Plate XIIIf).

The transition zone from the white, partially silicified chalk to the chert occurs over a distance of a few millimeters (Plate XIIIa). This transition zone is characterized by a change in void filling morphology. Near the silicified chalk, the filling is cristobalite
spherules. Toward the chert the filling becomes massive quartz (?); and the calcareous fossils tend to meld into the void-filling matrix, becoming less recognizable.

Microprobe data for the chert show silica with a small amount of calcium. The chalky area shows calcium with a small amount of silica. A line profile across the transition zone shows a gradual increase in silicon radiation toward the chert (Plate XIIIa).

Site 108

Stratigraphy

Site 108 is located on the continental slope off the coast of New Jersey (Figure 2). The drilling program penetrated 209 meters with sediment recovery only in the interval of 39 to 75 m. The lithologic unit cored by the shipboard scientific party is a middle Eocene firm radiolarian nannofossil foraminiferal ooze to chalk (Hollister, Ewing and others, 1972). The shipboard scientific party concluded that the location experienced continuous sedimentation during the middle Eocene under deep marine conditions.

Sampling

Two samples were selected, 108-1-3 (70-72) and 108-2-1 (98-100) (Figure 4), so that an unsilicified but siliceous biogenic ooze could be analyzed. Both samples contained abundant fragments of diatoms, radiolarians and coccoliths. The deeper sample is more calcareous with small amounts of clay.

X-ray Diffraction

X-ray diffraction patterns of both samples show calcite and
opaline material (Appendix 2). The oriented clay fraction patterns indicate that smectite, kaolinite and possibly illite are present in both samples (Appendix 4).

**Thin Section and SEM Data**

Radiolarians, diatoms, sponge spicules, coccoliths and foraminifera were identified in thin sections. Much of the biogenic material is fragmented and poorly preserved (Plate XIIIb). Silt-size quartz was noted in the thin section of 108-2-1 (98-100).

SEM micrographs also indicate an abundance of poorly preserved siliceous remains (Plate XIIIc, d). Clay seems to be more abundant in the deeper sample.

**Site 118**

**Stratigraphy**

Site 118 is located in the eastern North Atlantic off the coast of France on the Western Biscaye Abyssal Plain (Figure 2). The drilling penetrated 761 meters of sediments into basalt. Two lithologic units were cored by the shipboard scientific party (Laughton, Berggren and others, 1972): 1) gray silty clay interbedded with coccolith clay and graded sand; 2) Paleocene to Eocene brown clay above altered hematitic and zeolitic red clay. Both of the lower clay units are intensively burrowed.

The shipboard scientific party concluded that the clay sequence was a deep-sea deposit of pelagic sediments accumulated below the CCD. Tectonic uplift, occurring perhaps in the middle Eocene, raised the area into a ridge which became buried by turbidities in the Miocene.
Turbidite deposition has continued to Recent.

**Sampling**

Two samples were collected in the middle Eocene section of brown clay to explore any indications of why these sediments had not been silicified. Samples 118-13-1 (42-44) and 118-14-1 (38-40) are compact clays with coccoliths (Figure 4).

**X-ray Diffraction**

X-ray diffraction of both samples indicates the presence of calcite, quartz and the clay minerals illite and kaolinite, identified on the basis of bulk-oriented and clay fraction x-ray patterns (Appendices 2-4). Clinoptilolite was present in 118-14-1 (38-40).

**SEM Data**

Highly degraded, dissolved coccoliths in a clay matrix are evident in SEM photomicrographs (Plate XIIIe, f).

**Site 140**

**Stratigraphy**

Site 140 is located at the base of the continental rise about 450 km west of Cape Blanc, Central Africa (Figure 2). Four lithologic units were cored by the shipboard scientific party (Hayes, Pimm and others, 1972): 1) a Holocene to late Pliocene calcareous sequence of nannofossil chalk, marl and ooze; 2) middle to early Miocene diatomaceous ooze, clay with diatoms and silty units; 3) Eocene to Paleocene clay to silty dolomitic clay with siliceous fossils; 4) a Maestrichtian rhythmic deposition of silty zeolitic clay and arkosic sand beds.
Drilling terminated at 651 m sub-bottom in the Maestrichtian unit.

Evidence of volcanic activity in the Cretaceous and possibly through the Eocene is manifested by the presence of zeolites, palygorskite, smectite and dolomite (Hayes, Pimm and others, 1972). These minerals were detected in the rhythmically bedded clay and silty clay which, probably represent sudden changes in the type of detritus deposited. Deposition below the CCD probably prevailed at this site until possibly the Miocene. Calcareous material in the older sediments was probably resedimented from further up the rise.

Sampling

Sample 140-3-2 (100-102) is a very compact, dense, dark brown clay with radiolaria and diatoms present (Figure 4). It is situated near the top of the Eocene sequence. Unlike Site 118, this unsilicified clay contained a good possible source of silica - volcanic ash.

X-ray Diffraction

X-ray diffraction of the sample indicates quartz, illite, kaolinite, smectite, gypsum and some opaline material (Appendix 2).

Thin Section

The thin section of the sediment shows a laminated clay with preserved sponge spicules, diatoms and radiolarians (Plate XIVa). Many opaque blebs of irregular form are present. In reflected light, some of these blebs are gold in color, indicative of pyrite concentrations (Plate XIVb). The blebs not reflecting this gold color may be organic matter. Some silt-size quartz and several gypsum crystals, which displace the surrounding sediment, are also present.
SEM Data

Electron micrographs of the sample show the laminated clay as in Plate XIVc. The radiolarians and diatoms appear somewhat more degraded than those examined in thin section. The pyrite concretions are common and clearly displace sediment laminations surrounding the concretions (Plate XIVd). Both framboidal and octahedral pyrite occur in these concretions, but these types were never found together in the same concretion (Plate XIVd, e). Two varieties of gypsum, rosettes and a tabular form analogous to selenite, were found on the fractured surfaces of the sample (Plate XIVf, XVa). The rosettes are about 50-60 um in diameter. Based on morphologic data, pyrite framboids occur between the blades of the rosettes. The selenite gypsum is much larger, about 600 um in length. Its crystal form is quite well developed, though much surface irregularity was noted (Plate XVa). This is probably due to growth in the clay, preventing complete displacement of material as the crystal grew. The large size of the selenite gypsum is suggestive of post-recovery growth.

Euhedral native sulfur crystals are associated with the framboidal pyrite concretions (Plate XVb). These crystals were also sometimes noted in the laminated clay (Plate XVc). It is not clear whether the crystals found in the clay are associated with a hidden pyrite concretion beneath the surface or form independently in the clay. The edges of the sulfur crystals seem somewhat rounded, suggesting some post-precipitation degradation.

Clinoptilolite euhedra, 30-40 um in length, were found in one disk-shaped void (Plate XVd). Their presence indicates that there was some silica mobility.
Site 144

Stratigraphy

Site 144 is located on the Demerara Rise, a prominent topographic terrace which extends to the north as part of the continental margin of the Guiana coast (Figure 2). Five lithologic units were cored by the shipboard scientific party (Hayes, Pimm and others, 1972): 1) an Oligocene to Paleocene chalk to nanno ooze with abundant radiolaria in the Eocene portion; 2) a Paleocene to Campanian zeolitic green marl; 3) Senonian to Cenomanian black and olive zeolitic marl and shale; 4) early Turonian to late Aptian green marl, laminated in some portions; 5) late Albian to early Aptian marl, limestone and carbonaceous clay, all of which are quartzose. Drilling was terminated at 325 m sub-bottom.

The shipboard scientific party concluded that during the Cretaceous, deposition took place in a marginally oxygenated environment which favored the preservation of organic matter. The sediments are reworked and redeposited material from further up the Cretaceous slope. The sediment influx was progressively derived from deeper, possibly sinking, sources. A more pelagic influence dominated in the Tertiary with the introduction of siliceous organisms.

Sampling

Sample 144-1-4 (75-77) is a moderately indurated, radiolarian, foraminiferal nannofossil chalk (Figure 4). This lithology is similar to that of the silicified sample of 13A, yet no silicification was reported at this site.
X-ray Diffraction

The x-ray diffraction pattern indicates calcite with opaline material and a minor amount of kaolinite (Appendix 2). One small peak at 9.0 Å and 8.1 Å in the bulk-oriented diffractogram may indicate the presence of a zeolite (Appendix 3).

Thin Section and SEM Data

Abundant coccoliths and forams were observed in thin section (Plate XVe). Fragmented radiolarians and some diatoms are also present.

SEM micrographs show calcareous microfossils with a noticeable admixture of siliceous biogenic detritus, primarily diatoms, with a small amount of radiolarians (Plate XVf, Plate XVIa). Some of the fine micro-structure of the diatoms and radiolarians is preserved, although many of these frustules, like the calcareous tests, are fragmented. This implies that the grains have undergone mechanical abrasion rather than chemical dissolution.
TABLE 1
Summary of Results from Analyses and Observations of DSDP Samples

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<th>SAMPLE</th>
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<th>Illite</th>
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<tr>
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<td>BIOGENIC SILICA</td>
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<td>Presence Signs of Dissolution</td>
<td>Mixed Layer</td>
<td>Illite</td>
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<td>X X</td>
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</tr>
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<td>Illite</td>
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<td>OPAL-CT/ZEOLITE</td>
<td>QUARTZ</td>
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<td>---------</td>
<td>----------------</td>
<td>--------</td>
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<td>6-6-3 (73-75)</td>
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<tr>
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<tr>
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<tr>
<td>9A-1-4 (120-122)***</td>
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<td>13A-1-1 (87-89)</td>
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<tr>
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<tr>
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</table>

* high cristobalite and high tridymite  
** high cristobalite  
*** disturbed by drilling
CHAPTER V

THE SOURCE OF SILICA

Study of the core samples and the general survey uncovered evidence pertaining to three different sources for the silica in the DSDP "chert" examined in this study - biogenic silica, the clay transformation smectite/illite and volcanic ash.

Volcanic Ash

Gibson and Towe (1971), Mattson and Pessagno (1971) and others suggest that volcanic ash has supplied much of the silica for deep-sea "chert." Calvert (1971) suggests that certain Atlantic "chert" occurrences, such as 9A, formed from volcanic sources because the "chert" lacked biogenic opal and contained abundant zeolite and smectite, commonly associated products of volcanic glass alteration. The 9A samples for the present study, however, contain radiolarians and radiolarian tests lined with opal-CT (Plate VIIId-f, Plate IXa, b). No volcanic shards were recognized. The zeolites from other samples are euhedral and co-precipitated with cristobalite spherules in radiolarian tests as in Plate IVb, e, f. Zeolites were also found in clay matrices, as in Plate VIIb. The type of zeolite found is clinoptilolite, a high-silica variety. Microprobe data from the zeolites in the 9A samples indicate they are composed of Na, Ca, K, Al and Si. The cations needed to produce zeolites, Na, K and Ca are available in the pore fluid and clay. In a microprobe study, Lipps (197) estimated that radiolarian tests contain 0.05 - 1.00 percent Al. A possible mechanism for
zeolite formation from clay and opal-A, rather than volcanic ash, is discussed in Chapter IX.

Lancelot (1973) noted that ash layers recovered by DSDP cores are devoid of "chert." In the survey of Atlantic and Pacific DSDP cores for the present study, only four "chert" occurrences or 2.8 percent were associated with volcanic ash. None of this evidence supports the theory that volcanic ash is a source of silica for DSDP "chert."

Smectite/Illite Transformation

Towe (1962) and Keene and Kastner (1974) suggest that the transformation of smectite to illite can liberate enough silica to produce porcellanite. The clay mineralogies of Sites 6, 8A, 9A and 13A may reflect this transformation. The clay mineralogy near the Site 6 "chert" samples is different from the mineralogy in the rest of the core. Diffractograms of these samples have indistinct peaks in the 11Å to 12Å range suggestive of mixed-layer smectite/illite. The "chert," 6-6-1 (130-132), contains illite. Diffractograms of all 8A silicified samples contain low, weak peaks of illite. Glycolation of the intervening zeolitic clay resulted in the resolution of some illite and smectite as well as a distinct peak at 11Å, indicative of mixed-layer clay. The 9A samples also exhibit mixed layering. The diffraction pattern of the more silicified sample at 64 cm has more intensive scattering between 10Å and 14Å, possibly reflecting more pronounced mixed layering. Illite is present in the 13A "chert." Mixed layering and minor illite were found in the biogenic ooze of Site 13A.

The cause or causes of this transformation are not clear, but it may not be related to simple burial. No noticeable change in clay with
depth occurs in a consistent manner in the samples analyzed. Significant changes in clay minerals as reported by others seem to occur at much greater depths than any of the depths from which the samples used in this study were recovered (63 to 680 m). In the Gulf Coast, Burst (1969), Perry and Hower (1970), Weaver and Beck (1971) and Hower and others (1976) did not detect diagenetic clay mineral changes until depths of 3000 to 6000 feet (900 to 1800 meters) had been reached. Hayes (1973) did not find any clay alterations in Gulf of Alaska DSDP cores which had been buried to depths similar to the DSDP sample depths of this study. Matter (1974), using DSDP samples from Site 222 from the Indus Cone in the Arabian Sea, found that clay mineral reorganization may have occurred as shallow as 700 m. The deeper depth range, 1200 to 2500 m, is comparable to the results from the Gulf Coast clay diagenetic studies. Hower and others (1976) point out that this transformation may not be solely a product of burial but also a result of other chemical changes which occur as a function of temperature. In the Gulf Coast, potassium for the clay transformation is supplied by the breakdown of feldspar, which takes place under temperature and pressure conditions found deeper than 900 m. If other sources can supply the needed cations, then the transformation may occur at much shallower depths.

In the samples from Sites 6, 8A, 9A and 13A, the change in clay takes place strictly in and immediately adjacent to silicified layers. Because it is not likely that material buried between 150 and 700 m has experienced burial diagenetic effects of any significance, the relationship of this transformation to chert diagenesis must be explored.

Smectite differs from illite in that it lacks interlayer cations
and that there is more aluminum substitution for silicon in illite than in smectite (Carroll, 1970). As much as one sixth of the tetrahedral silicon site may be occupied by aluminum in illite, while the aluminum from silicon substitution in smectite is minimal (Grim, 1968). Furthermore, illite interlayer sites may be occupied by Ca, Mg and H as well as K, unlike the micas, where K is the chief interlayer cation.

Because of the diversity of the type of interlayer cation which can define an illite, the transformation of smectite to illite may have taken place during silicification rather than before silicification. The presence of authigenic zeolites in the "chert" attests to the reactivity and the availability of cations such as Ca, K, Na and Al, which could also locate in the exchange sites of the clay minerals. "Chert" layers have been shown to be sites of active sediment diagenesis. It seems likely that an adequate supply of cations could accommodate the clay transformation as well as the formation of zeolites (see Chapter IX). Therefore, the "secondary source of silica" may not be a source of silica at all; rather, clay transformation may be prompted by the same processes which cause silicification.

**Biogenic Silica**

**Association with DSDP "chert"**

It has been noted in DSDP studies by Lancelot (1973), Keene (1975) and Garrison and others (1975) that a strong correlation exists between the occurrence of siliceous material and "chert". A strong association between areas of high biologic productivity and "chert" occurrences is indicated from data gathered in the comprehensive survey of DSDP reports done for this study. Such areas as the equatorial
Pacific Zone of high biologic productivity and polar zones of diatom growth are also locations of "chert" recovery. "Chert" seems to be more pervasive in the pre-Oligocene sediment, but generally even then conform to zones of presumed biologic productivity. This global aspect will be discussed more fully in Chapter VII.

Middle Eocene sediments examined which contained no biogenic opaline remains, Sites 10, 19 and 118, did not contain "chert." However, in the lower Eocene cored material from Site 10, similar in lithology to the middle Eocene sample except that biogenic silica was present, "chert" was recovered.

Several sites, 108, 140 and 144, contain biogenic silica; but no "chert" was recovered. Drilling resistance was encountered in the operations at Site 108, suggesting varying degrees of sediment induration (silicification?) were being penetrated. The dense, compact sample from Site 140 may have had such low permeability that opaline frustules were essentially isolated so that no build-up of silica could occur; and, therefore no silicification took place. In the lower Eocene of Site 140, "chert" was recovered in sediments of the same lithologic unit as the middle Eocene section sampled (Hayes, Pimm and others, 1972). Perhaps the paucity of clay or the type of clay mineral (see Significance of Impurities) in the samples from Sites 144 and 108 hindered silicification. Or possibly the shallow depth of the Eocene at Site 144 meant an unusually prolonged diffusion of dissolved silica to the sea floor, which did not allow the build-up of silica to reach levels sufficient for opal-CT precipitation.

Significance of Impurities

If biogenic silica is the source for DSDP "chert," then it should
be expected that pure radiolarian or diatom oozes would be the most extensively silicified. In fact, the pure oozes seem to be very unreactive. Often they have high silica pore water concentrations (80 ppm) (Bischoff and Ku, 1970) (Table 3 and Figure 1). Yet no precipitation of silica occurs. In this system, equilibrium is governed solely by opaline silica. The system must become supersaturated with respect to opal-A before precipitation can occur. The complex geochemistry of silica in the presence of other cations has often been noted (e.g. Okamoto and others, 1957; Siever, 1962). Lancelot (1973) suggested that the role of other minerals may govern the type of silica phase precipitated. If impurities are present, equilibrium with respect to other silica minerals, clays or zeolites, becomes possible and may govern precipitation of opal-CT. Aluminum, as Walton (1973) suggested, might be the critical impurity necessary to achieve the precipitation of silicates other than SiO$_2$. Supersaturation with respect to opal-CT or opal-CT and clinoptilolite is required to have precipitation of the authigenic phases identified. Because Al is required in the structure of silicates other than pure SiO$_2$ phases, it may be the critical cation necessary to favor precipitation of opal-CT or opal-CT and clinoptilolite. The presence of Al and/or other impurities may be a critical part of the disordered structure of opal-CT. This may explain how silification can occur when measured pore fluid concentrations are undersaturated with respect to opal-A.

The chemical composition of the minerals present may possibly be an influence on the availability of cations. Sites 108 and 144 are biogenic oozes which contain kaolinite, whereas the "chert"-bearing sediments at Sites 6, 8A, 9A and 13A contain the compositionally more variable smectite.
### TABLE 3
DSDP Pore Water Data of Sites Lithologically Similar to Study Samples

<table>
<thead>
<tr>
<th>SITE</th>
<th>AGE</th>
<th>DEPTH (m)</th>
<th>LITHOLOGY</th>
<th>Si</th>
<th>K</th>
<th>Ca</th>
<th>SO₄⁻</th>
<th>Mg</th>
<th>pH</th>
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<td>380</td>
<td>2210</td>
<td>1230</td>
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<td>780</td>
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<td>400</td>
<td>2650</td>
<td>1310</td>
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<td>450</td>
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<td>1010</td>
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<td>351</td>
<td>10</td>
<td>40</td>
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</table>

*measured at 110 m
The observed co-precipitation of opal-CT and clinoptilolite at these sites is evidence that cations, including Al, must be present during the formation of opal-CT. The very pure siliceous oozes may not be silicified because in these sediments there are insufficient cations, such as Al, to change the equilibrium from opal-A to opal-CT and clinoptilolite. The significance of the lack of such co-precipitates associated with the presence of high cristobalite and high tridymite will be discussed in Chapter VI.

Silica Dissolution

In the detailed study of DSDP samples, Site 6 provides the best evidence for the correlation between siliceous sediment and "chert." In other silicified sites, 8A, 9A, 13A and 98, the relationships of "chert" and surrounding sediment are not as clearly discernable as at Site 6. However, data from these sites contain supportive evidence for a biogenic silica source.

Sponge spicules compose much of the biogenic fraction of the rhythmically bedded units sampled in Site 6. These sponge spicules are more concentrated in the basal sands of the turbidities. Solution morphologies are manifest as pitted surfaces of the spicules as far away as 17-18 cm from the "chert" layer at 6-6-1 (130-132) and 3 cm from the "chert" layer at 6-6-3 (73-75) (Plate 1a-b, f). The removal of opal-A by dissolution causes a reduction of external diameters and an increase in internal diameters, resulting in a tendency for decreased external to internal ratios toward silicified layers (Figure 5). Data from the unsilicified samples near the silicified sand, 6-6-1 (130-132), indicate external to internal diameter ratios similar to those obtained from the "chert." This pattern is not suggested for the sample 6-5-1.
(18-20), 18 cm below a silicified sand similar to 6-6-1 (130-132). Permeability may be a factor affecting the distance from a "chert" at which dissolution features are manifest. The diatomaceous clay from which 6-5-1 (18-20) was taken would not be as permeable as the chalky units of 6-5-1 (48-50) or near 6-6-1 (130-132), in which dissolution features are more severe. Dissolution of these spicules could have supplied silica for the Site 6 "chert."

The state of preservation of radiolarians and diatoms is also evidence for biogenic silica as a source of silica for DSDP "chert." The diatoms and radiolarians concentrated in the pelagic intervals of Site 6 are degraded (Plate Ia, c-e). The 8A samples are all radiolarian-rich. The friable zeolitic clays, 8A-2-1 (28-30) and 8A-3-1 (27-29), which divide the 8A "chert" into two units, have evidence of silica dissolution and incipient silicification (Plate VIIc-f), Plate VIIla-c). Sample 9A-1-4 (120-122) shows degradation of radiolarians. The radiolarians of 9A-1-4 (64-66) are completely dissolved, leaving only a rind of opal-CT spherules. Siliceous remains have also been completely dissolved in the 13A "chert" (Plate IXe, Plate Xd-f, Plate XIb).

**Diffusion of Biogenic Silica**

The observation that solution features in biogenic silica increase as a "chert" layer is approached (Site 6) suggests that the silica migrated from neighboring sediment into layers presently containing "chert." This process may be viewed as a problem in nucleation and diffusion. Once a sediment is buried to a depth sub-bottom below which interaction with the overlying water is lost, it may be considered a closed system with little pore fluid migration. Bischoff and Ku (1970) present profiles of silica concentration versus depth which may be
interpreted to suggest that below one meter sub-bottom, the system is closed. Thus with depth below the surface, materials should tend to dissolve to achieve chemical equilibrium with respect to the pore waters in which they are immersed. Because sea water is vastly undersaturated with respect to any form of silica, opaline silica in the form of opal-A should tend to dissolve with depth into the sediment until equilibrium is achieved. In the upper meter of sediment, silica concentrations rise precipitously, possibly up to 15-30 ppm (Bischoff and Ku, 1971; Fanning and Schink, 1969; Fanning and Pilson, 1974). Sayles and Manheim (1975) reported a trend of slowly increasing pore fluid concentration with depth and increasing temperature in DSDP core samples.

Pore fluid silica concentrations in DSDP cores rarely exceed 30 ppm (Table 3 and Figure 1). High values, above 20 ppm, are associated with the presence of siliceous organic remains. These values greatly exceed the solubility of quartz and probably exceed the solubility of opal-CT. Thus pore fluids are probably supersaturated with respect to the diageneric phases observed to precipitate, but not saturated with respect to opal-A.

In sediment where little water movement is possible, as in the case of the predominantly fine-grained deep-sea material, diffusion must govern the transfer of dissolved species. According to Berner (1971), the rate of diffusion in a fine-grained sediment is a function of the tortuosity and length of the path, the porosity, the temperature and the concentration gradient. Considering that "chert" usually occurs in pelagic deposits, the tortuosity would increase and the porosity decrease with burial; and, unless the sediment is deeply buried, the temperature would be less than 20°C. Assuming a maximum diffusion coefficient for fine-grained sediment of $2 \times 10^{-5}$ cm$^2$/sec and a change in dissolved silica
concentration from 60 ppm to total depletion in a silicified unit over a distance of one meter, then a maximum diffusion rate of $2 \times 10^{-9}$ moles-cm$^2$/sec would be predicted using Fick's first law. For lesser concentration gradients, the rate of diffusion would be somewhat slower; but probably still geologically quite rapid.

If the concentration of silica is approximately constant over distances of meters, little diffusion would occur. However, if at some location in the sedimentary column (probably where the dissolved silica concentration is highest), crystallization of opal-CT begins, then concentration gradients would be set up. Because the phase that is precipitated has a lower solubility than the phase supplying the silica, additional material in adjacent sediments could be dissolved as crystallization progresses. By diffision of dissolved silica toward the site of precipitation, the lithification process can be maintained and then degraded state of siliceous tests observed in the sediments neighboring "chert" layers would be produced.

The permeability of the sediment affects the mobility of biogenic silica. Greater silica infilling of voids in the samples indicated greater silicification. Sediments with an admixture of clay became indurated while clay-rich sequences remained friable because dissolved silica mobility in clays is restricted due to lower permeability. Well-indurated "chert" occurred in more porous layers because diffusion from larger volumes of silica source material was possible. Higher levels of dissolved silica can be maintained with lesser amounts of dissolution from each individual test. This could account for the observation of opaline test material being well preserved in the more
porous and more siliceous "chert" layers, 6-6-1 (130-132), 8A-2-1 (20-22) and 8A-3-1 (31-33).

In the turbidite sequences in core 6 of Site 6, the sands were the main lithologic unit found to be silicified. Sample 6-6-3 (73-75) represents a weakly silicified pelagic interval of a turbidite. This is probably due to its high clay content and lack of pore space to accommodate silica. The 8A "chert" is similar. The "chert" samples which exhibit the greatest infilling with silica are 8A-2-1 (20-22) and 8A-3-1 (31-33). These two samples contain a greater relative abundance of radiolarians to clay in comparison with 8A-2-1 (11-14), 8A-2-1 (37-39) or 8A-3-1 (5-7). The less permeable the material, the more retarded the silicification, even where there is an adequate supply of silica.

If microenvironments only the vicinity of siliceous organisms can have silica concentrations high enough to cause opal-CT precipitation, then these areas will be the best silicified. Plate IVe shows a radiolarian test and surrounding clays which exhibit distinct clay flakes.

Sites 9A and 13A were poorly silicified. As a coccolith ooze, 13A should have good permeability. Probably because the amount of biogenic silica present was marginal to low, complete dissolution of test material resulted during the silicification process. The space formerly occupied by these tests became occupied by opal-CT spherules and clinoptilolite. Both paucity of a supply of silica and reduced permeability may have retarded the induration process at Site 9A.

Conclusions

In this chapter, evidence has been presented which strongly
suggests that biogenic silica was the dominant source of silica for the "chert" analyzed in this study. The concept of a volcanic contribution, which was suggested by research in the early 1970's, does not seem to be a probable major source of silica, even in those samples where volcanogenic sediments were likely to be present. Mixed-layering of clays, rather than being a supplier of silica, may be a result of the same processes which caused silica diagenesis.
CHAPTER VI

SILICA PARAGENESIS

Void Fillings

The history of formation of the deep-sea "chert" sampled is best exemplified at Site 8A, although the general scheme may be constructed based on the "chert" from Sites 6, 9A and 13A. All of these sites contain early stages of silicification. The intersticies of the radiolarian tests provide the best information for the construction of a diagenetic history of the "chert." Generally in the samples, only partially filled void space exists; but in the 8A "chert," often the entire interior cavity of the radiolarian tests is completely filled with silica phases. The transition zone sample from Site 98 is particularly important for investigating the latter stages of silica paragenesis. It was possible to observe the infilling in all stages of development through the use of SEM samples and etching techniques.

In the 8A "chert" layers, the radiolarian tests are more intact and thickened than those found in the unsilicified zone (compare Plate IVb with Plate VIIId or Plate Xb). This thickening may be partially ordered silica because the tests exhibit weak anistropy. This anisotropy does not appear layered, which would be expected if additional silica were deposited on the interior of the test. Instead, it seems that new material was added to the inner and outer walls, "welding" it to the clay matrix. Based on the optical properties of the initial void fillings, this material appears to be composed of opal-CT. The addition of this material makes the boundaries between the tests and
the clays somewhat indistinct, gradational or irregular (Plate IVa-b). Thin sections show the initial chamber filling as the development of globular masses of cristobalite spherules jutting out from the interior test walls (Plate IVa-b). In oriented thin sections, their growth does not seem to bear any relation to the spatial orientation of the tests.

The voids being filled at Site 6 are primarily sponge spicule axial canals and some foraminifera. The initial morphology recognized on the interior walls of the thickened sponge spicules is a bladed crust of opal-CT (Plate IIe,f). Spherulitic opal-CT grew from the surfaces of this bladed crusts (Plate Ile, f). This growth gives a birefringent character to the opal-A spicules.

The 9A and 13A "chert" occurrences exhibit similar diagenetic histories. The 13A "chert" contains somewhat irregular areas of silicified ooze and areas where evidence for silicification is scant. Few radiolarian tests or other recognizable biogenic silica microfossils are present in "chert" samples from either site. Instead, there are rounded areas, approximately 100-120 μm in diameter, which resemble radiolarian tests in size and shape (Plate VIIId-f; Plate IXe). These are areas where silica has been deposited. In the 13A sample, much carbonate material is found incorporated in the silica filling, although its concentration is not as dense as in the unsilicified nannoplankton matrix. HCl and HF etching shows these rounded areas to be radiolarian tests with dissolved walls. The walls are now represented by cristobalite spherules formed by precipitation from solution. The silica was derived from the dissolution of radiolarian tests. In 9A, opal-CT spherules constitute the boundary between the clay matrix and the remaining unfilled voids.
The Site 98 sample contained a transition zone from a silicified chalk to a chert. HCl etching of the chalk revealed pore space completely filled by opal-CT spherules (Plate XIIe, f). Thus, as in the other silicified samples, opal-CT spherule precipitation was observed as the first stage of void filling.

The "chert" samples 8A-2-1 (11-14) and 8A-3-1 (5-7) contained very well-developed clinoptilolite euhedra (Plate IVe, f; Plate Va). High magnification of these crystals indicate that the bladed crystals of the cristobalite spherules grow from or are attached to the faces of the zeolites (Plate Va). Zeolites are commonly found as co-precipitates with cristobalite spherules in Sites 9A (Plate VIIIId-f), 13A (Plate XI b) and 98 (Plate XIIIf). These relationships of zeolites and cristobalite spherules suggest an important aspect of the paragenesis. While it appears that cristobalite spherules are the sole initial void filling stage, co-precipitation with zeolites seem to be common toward the end of this stage.

In thin sections of silicified samples from Sites 6, 8A and 98, fibrous or GMC quartz was found filling the remainder of the chambers not filled by opal-CT. Plate IIc-d shows this phenomenon at Site 6. In 8A-2-1 (20-22) and 8A-3-1 (31-33), the fibrous quartz is usually a bundle of long, continuous fibers radiating from one point on the cristobalite filling (Plate IVd). Rarely, two generations of the fibrous filling were noted. The second filling is founded on a smooth, round terminal surface of the first generation filling. Another form of second-phase chamber infilling seems to be GMC quartz (Plate IIId). The presence of clay may be detected in some of these non-fibrous quartz infillings. This suggests that the nature of the void filling
is controlled to some degree by the freedom encountered in crystal growth. If, after opal-CT formation, the remainder of the void is completely empty, fibrous quartz will grow. If growth is somewhat obstructed by clay particles, only small crystals will be formed, as in GMC quartz. In time the clay particles may be replaced by silica, and the typical optical appearance of GMC quartz may develop.

X-ray diffraction of the Site 98 chert shows quartz as the predominant mineral; opal-CT is minor. Therefore, minerallogically, this sample best fits the definition of a chert. As the chert is approached, the amount of pore space decreases, and massive structureless infilling of void space is common. The resolution of carbonate fragments from cement is more difficult. Within the chert there is no longer a distinction either morphologically or texturally. This may indicate that the gradual replacement of other minerals by quartz and the inversion of all metastable silica phases to quartz is a later stage of the paragenesis.

**General Paragenesis**

Based on the diagenetic mineral phases identified in the detailed examination of the sampled "chert," general trends of a paragenesis of this "chert" may be outlined. The first stage is apparently the dissolution of siliceous biogenic material and diffusion of dissolved silica to sites of silicification as discussed in the previous chapter. The filling of void space was recognized as the initial lithification step. The second stage of the paragenesis observed is the precipitation of opal-CT spherules in the voids. These spherules are often associated with clinoptilolite. This co-precipitation seems prevalent toward
the latter part of the opal-CT precipitation stage. Thus the presence of cations other than Si seems to be common in the fluid stage present during opal-CT precipitation of opal-CT and clinoptilolite. If this does not occur, a third stage of either fibrous or GMC quartz precipitation can occur to fill the remaining void space. A fourth stage, for which Site 98 may be an example, is the gradual replacement by quartz of other minerals, such as clays or calcite, and the inversion of all metastable silica phases to quartz.

High silica concentrations could favor rapid crystallization and, therefore, more open structures like cristobalite and/or tridymite. Silica concentrations may be too high during initial crystallization to permit quartz to form. The presence of impurities would also be more readily accommodated in an open framework structure, limiting quartz formation to a later stage of silica diagenesis. This final stage in the formation of chert was not specifically studied.

**SEM Identification of Fibrous Quartz**

Fibrous quartz was readily identified with the petrographic microscope in the Site 8A void fillings, and x-ray diffraction clearly indicates the presence of quartz along with opal-CT in these samples. An attempt was made to identify this fibrous quartz with the SEM. All stages of radiolarian test infilling were found with the SEM samples. However, fracture surfaces and HCl or HF-etched surfaces did not reveal any of the fibrous quartz fillings which were so common in thin section. No matter how complete the void fillings, bladed crystals of opal-CT spherules were the only morphology observed from untreated fracture surfaces. HF etching of these completely filled voids resolved
areas which were apparently clinoptilolite crystals, as well as spherule-like bodies (Plate VIa-f; Plate VIIa). It is possible, though unlikely, that none of the cavity fillings observed via SEM contained any quartz.

Folk and Weaver (1952) and Monroe (1964), using TEM, also could not resolve chalcedony fibers. Instead, what they described as spongy textures were characteristic of fibrous quartz samples. In a detailed optical study of chalcedony, Pelto (1956) concluded that chalcedony was composed of fibers incorporated with a large amount of water. Adjacent fibers were joined by a translational structure, a set of dislocations or areas of bad fit of elastically strained quartz. This region of poor fit accommodated impurities such as water. Madsen (1974) suggested that spongy chert inherited its morphology from cristobalite spherules. The holes in the spongy surface were believed to be water vesicles.

The identification of the fibrous structure of quartz does not seem possible with electron optical systems. Since the fibrous character is only brought out with crossed nicols, it is apparent that the fibers are related to domains of crystal lattice orientations and not to crystallite entities. However, based on the morphologic character of the void fillings in the 8A "chert," a solid state inversion is suggested as the mechanism of retaining spherulitic form, yet being quartz mineralogically (as Madsen, 1974).

**Modifications of the Paragenesis**

**High Cristobalite and High Tridymite**

The SEM photomicrographs of 8A-2-1 (20-22) and 8A-3-1 (31-33) show these "chert" occurrences to be very different from the other 8A
"chert" occurrences. These samples have a greater abundance of radio-
larians than either 8A-2-1 (11-14) or 8A-3-1 (5-7) (Plate IVc). Almost
all of the tests in the "chert" are completely filled by silica (Plate
Vb). Tests with void space in 8A-2-1 (20-22) do not contain cristo-
balite spherules and zeolites, but instead contain lath or wedge-shaped
crystals, 5 um in thickness and 10-15 um long, of coarser crystalline
opal-CT (?) (Plate Vf). This coarse void lining is often a substrate
for octahedral crystals of cristobalite and hexagonal crystals of
tridymite (Klasik, 1975) (Plate Vd, e). The tridymite can be seen in
an epitaxial growth position with respect to cristobalite (acknowledge-
ment to C. Frondel). Cristobalite octahedra are also present in
those voids of 8A-3-1 (31-33) which are incompletely filled, but no
hexagonal crystals of tridymite were observed.

The presence of octahedra of cristobalite in association with
tridymite in its high temperature crystal state is highly unusual.
This assemblage indicates a great degree of disequilibrium. Octahedral
cristobalite is the stable phase of silica above 1470°C and at pressures
less than 5000 kg/cm² (Mason and Berry, 1968). Tridymite is stable
between 867° and 1470°C and at pressures less than 3000 kg/cm² (Mason
and Berry, 1968). Assuming a geothermal gradient of 0.06°C/m (Cook,
1973), the DSDP samples in which these minerals were found probably
never encountered temperatures much above 20°C. Therefore, these
minerals were far from their respective stability fields and could not
have formed in an environment of elevated temperatures and pressures.

An explanation must be sought which can account for the formation
of these minerals rather than opal-CT as a consequence of sediment
diagenesis. Oehler (1975) synthesized spherical aggregates of blade-
like crystals of opal-CT from silica gel. He concluded that the lepispheres in the Monterey Formation were the result of crystallization from a colloid. Furthermore, Oehler (1975), using a theory developed by Keith and Padden (1963), concluded that impurities favored spherulitic growth because spherules entrapped impurities, inhibiting development of single crystals.

Whether the precipitation of spherulitic cristobalite-tridymite formed from a colloidal solution is not possible to determine from these DSDP samples. Certainly the silica concentration can exceed 27 ppm, the estimated solubility of cristobalite. Zeolite co-precipitation with opal-CT spherules is evidence for the presence of the cations K, Ca, Na and Al in the pore water. Lancelot (1973) suggested that foreign cations have a controlling influence on the type of silica phase precipitated. Keene (1975) reported the strong association of lepisphere development with pelagic clay deposits. It is possible, then, that the formation of spherulitic opal-CT is to some degree dependent on the presence of cations in solution along with silica (see Chapter V).

The EDS system provides a possible way of testing this contention. If cristobalite spherules are formed in the presence of cations other than silica and if cations are in sufficient quantity, then they should be detected by the EDS. Energy dispersive data from zeolites clearly show the presence of Na, Al, Si, and K and possible Ca (Figure 6). Weight percents calculated from pure end members of clinoptilolite given in Hay (1966):

\[(Na, Ca, K) AlSi_5O_{12}\cdot4H_2O\]

indicate aluminum to be present at 5.9 weight percent in a sodium
Figure 6. Energy dispersive spectra of authigenic minerals. Energy dispersive spectra of clinoptilolite, a high tridymite crystal and an opal-CT spherule are shown. The cations, Na, Ca, K, are present in quantities less than 5 wt. percent and are easily identified in clinoptilolite. The high tridymite crystal does not show any noticeable deviation from the continuum other than silicon K-alpha radiation at 1.74 kev. Aluminum may be present in very small amounts in the opal-CT spherule. The aluminum in the spherule is below the minimum detectable level; and, therefore, its presence is not certain. Clearly the shape of the background radiation is different from that of the tridymite crystal. All spectra were accumulated for 200 seconds of counting time in the spot mode of operation at count rates between 1500 and 2000 cps.
EDS SPECTRA OF AUTHIGENIC MINERALS

Clinoptilolite

Tridymite Crystal

Opal-CT Spherule

log intensity

energy (kev)
clinoptilolite and at 5.7 weight percent in a potassium or calcium clinoptilolite. Sodium can be no more than 5.0 weight percent, potassium can be no more than 8.5 weight percent in pure end member clinoptilolites. These calculations represent maximum values for these elements in a zeolite. The peaks shown for clinoptilolite in Figure 6 must, therefore, represent less than these maximum values because, due to the presence of all three cations, this cannot be a pure end member. Thus it is possible to detect elements in the less than 5 weight percent range and perhaps as low as 1 weight percent by means of EDS.

Aluminum K-alpha radiation was detected as a low, though distinct, hump on the low energy side of the silicon K-alpha peak of cristobalite spherules (Figure 6). No other cations were detected, although they could be below the minimum detectable limits of the system. If the proposed impurity ions are present in the spherules, then they exist at the trace levels. However, the probable presence of aluminum tends to support the idea that foreign cations are present.

EDS data from the cristobalite octahedra and the crystalline tridymite did not definitely reveal any cations other than Si; but, as in the spherules, the presence of other cations could not be completely ruled out (Figure 6). Aluminum did not clearly show up as a hump on the low energy side of the silicon peak at 1.74 kev. The amount of contaminants could possibly be less than in the cristobalite spherules. No zeolites were found associated with the crystalline silica phases. Zeolites were detected only on the illitic clay matrix after HF etching. The clay matrix is, presumably, a readily available source of cations; whereas the interior of radiolarian tests is not. This segregation of micro-sites of precipitation suggests that the purity of the silica
solution led to the development of cristobalite and tridymite crystals rather than to spherulitic aggregates. These specific silica phases may have formed due to high pore water concentration of silica and the high rate of nucleation.

The Zeolitic Clays: 8A-2-1 (28-30) and 8A-3-1 (27-29)

The samples 8A-2-1 (28-30) and 8A-3-1 (27-29) are abundant in zeolites and show only slight development of opal-CT spherules (Plate VIIIa-c). Because no radiolarian tests remain intact, only minor void fillings developed. Zeolite euhedra are developed primarily in intimate association with siliceous biogruments (Plate VIIId). Only rarely does zeolite formation seem to be totally independent of opaline fragments (Plate VIIIa). Often small (5 um) cristobalite spherules are in evidence growing from the crystal faces, suggesting that the opal-CT development postdated zeolite formation, in contrast to the order of development observed in other samples (Plate VIIIb, c).

This reversed pattern can be accounted for by the extensive silica deposition in close proximity to this location. Both the zeolitic clays are less than 5 cm away from the location where silica precipitation had been greatest. Also, there is a marked contrast in proportions of biogenic silica and clay in these two pairs of sites. These data tend to suggest that silica diffusion toward the adjacent "chert," coupled with a greater cation abundance in the zeolitic clays, favored zeolite formation in 8A-2-1 (28-30) and 8A-3-1 (27-29). Furthermore, cations may have diffused from the layers which were silicifying to those which were precipitating zeolites.

Therefore, these two pairs of samples, 8A-2-1 (20-22); 8A-2-1 (28-30) and 8A-3-1 (31-33); 8A-3-1 (27-29), represent a system where
the marked contrast in relative proportions of sediment constituents occurring over a very small vertical distance had a profound controlling influence on the minerals precipitated.
CHAPTER VII

THE CAUSE OF SILICIFICATION

Prerequisites for Chert Formation

Evidence from the detailed study of the DSDP silicified material suggests several prerequisites for "chert" formation. The presence of biogenic opal-A in some quantity is the primary requirement. Other constituents (impurities) from an admixture of clays may be needed to cause precipitation at values of silica concentrations in solution which are more commonly attainable at depth sub-bottom (30 ppm). Because the DSDP encountered silicified material in sand, radiolarian mudstone and coccolith ooze, the only necessary textural parameter may be permeability, which would control the mobility of the dissolved species. Geochemical studies by the DSDP seem to indicate that pH, which could affect silica dissolution and precipitation, remains fairly constant with depth (Table 3 contains some examples).

Time and Burial Diagenesis

In Chapter V, the process of silicification was described on the basis of nucleation and diffusion of silica. What is lacking in this working hypothesis is a mechanism to initiate precipitation of silica. It does not appear that there is anything particularly unusual about the Eocene sediments involved in the cores examined in this study. The Eocene could be more abundant in "chert" because these sediments were buried to a depth where silicification is optimal or because it simply takes a given length of time to produce "chert."
If siliceous sediment is transformed into "chert" with time, then a time-related model would imply an inverse relationship between the percent of siliceous sediment and the percent of "chert," with increasing age independent of depth. This relationship for the Atlantic and Pacific DSDP sites may be examined in Figure 7 where the average percent of siliceous sediment and average percent of "chert" are plotted for the interval Pliocene through Jurassic. "Chert" occurrences are rare in the interval Pliocene through Oligocene, although there is slightly more "chert" in the Oligocene. There is a marked increase in the amount of "chert" recovered from Eocene sediment without a decrease in the amount of unsilicified siliceous sediment. This high percentage of "chert" is consistent in material older than Eocene. Only in pre-Eocene sediment is there a dramatic decrease in the amount of siliceous sediment recovered.

Figure 8 is a plot of percentage of DSDP sites with siliceous sediment and/or "chert" in 50-meter depth intervals to a sub-bottom depth of 600 m for the same time interval. Across any row in Figure 8, the effect of time on siliceous sediment conversion to "chert" for any given depth would be shown. At all depths there is a marked increase in the amount of "chert" below the Oligocene/Eocene boundary. There is no corresponding sudden decrease in siliceous sediment at this same boundary. The Mesozoic periods span vastly more time than the Cenozoic Epochs, so a time-related diagenetic model cannot easily be applied across the Cenozoic-Mesozoic boundary in this diagram.

Figure 8 may also be utilized to examine a burial diagenetic model for "chert" formation. If siliceous sediment transformed into "chert" with depth, then an inverse relationship between "chert" and siliceous
Figure 7. Average percentages of siliceous sediment and "chert." The average percentage of siliceous sediment occurrences (vertically lined bars) and "chert" (diagonally lined bars) in the uppermost 600 meters of sediment based on the total number of sites in DSDP Legs 1-43 recovering sediment of the ages indicated for this depth interval is plotted. An inverse relationship between "chert" and siliceous sediment is not observed with increasing time. Instead, a marked increase in "chert" is observed in the Eocene. This suggests that "chert" formation from silification of siliceous sediment is not a simple time-related process.
AVERAGE PERCENTAGES
of
SILICEOUS SEDIMENT & "CHERT"
Figure 8. Siliceous sediment and "chert" in time vs. depth. The percentage of siliceous sediment (horizontally lined bars) and "chert" (diagonally lined bars) occurring in fifty-meter depth intervals is plotted for the Pliocene through Jurassic based on the total number of DSDP sites in Legs 1-43 recovering sediment of each age in each interval. Data from depth intervals where the total number of holes recovering material from that interval was less than five have been omitted. If "chert" formation were related to time factors, then an inverse relationship between "chert" and siliceous sediment would be expected across horizontal rows. Instead, what is seen is an abrupt discontinuous increase in "chert" at the Oligocene/Eocene faunal boundary for all depths. If "chert" formation were related to burial diagenetic effects, then an inverse relationship between the two sediments with depth would be expected regardless of age. This relationship does not seem to be displayed; and, again, there is a marked discontinuity in the amount of "chert" at all depths above and below the Oligocene/Eocene faunal boundary.
SILICEOUS SEDIMENT & "CHERT" IN TIME VS. DEPTH

percentage of occurrences ($x \times \frac{1}{10}$)

depth in meters

0 50 100 150 200 250 300 350 400 450 500 550

Pliocene  Miocene  Oligocene  Eocene  Paleocene  UK  LK & JR
sediment would be expected with increasing depth independent of time. A Pliocene sediment buried to a given depth would be just as likely to be silicified as a Jurassic sediment at the same depth. At all depths there is, again, more "chert" below the Oligocene/Eocene boundary. Some burial diagenetic conversion to "chert" may be suggested by slightly higher amounts of "chert" recovered from deeper depth intervals. However, the Eocene is abundant in "chert" at all depth intervals, suggesting that some other mechanism is being superimposed over a simple burial diagenetic model.

It may be concluded from Figures 7 and 8 that neither a burial diagenetic model nor a time-related model completely explains the data. The marked discontinuity in "chert" occurrences observed at the Oligocene/Eocene boundary does not fit these models.

"Chert" Distribution in the Atlantic and Pacific

Perhaps if the spatial and temporal distribution of "chert" and its most frequently proposed sources, volcanic ash and siliceous sediment, are examined, global, regional or physiographic controls on silicification may become apparent. In order to examine this larger aspect of the "chert" problem, data from the DSDP Legs 1-43 for the Atlantic and the Pacific were utilized. Maps plotting the site location of "chert," volcanic ash and siliceous sediment were prepared for the Cenozoic epochs, Pliocene through Paleocene, the Upper Cretaceous and the Lower Cretaceous-Jurassic. These are shown in Figures 9 through 22.

Ramsay (1971) postulates that the Atlantic "chert" occurrences are related to equatorial zones of high productivity. There was flow
The distribution of Pliocene siliceous sediment in the Atlantic Ocean. The distribution of Atlantic Pliocene sediment indurated by authigenic silica ("chert") recovered by the DSDP are shown by the solid triangles; sediment described by the DSDP as siliceous-rich by open triangles and sediment described by the DSDP as bearing volcanic ash by open circles. The small dots indicate the sites where the DSDP recovered Pliocene sediments, which did not include "chert", siliceous sediments or ash in the core descriptions. Superimposed symbols indicate the occurrence of more than one lithology at the site during the time interval. The position of the Mid-Atlantic Ridge (mar) is indicated by the dashed line. The polar belts of diatomaceous sediment are clearly indicated. A "chert" was recovered off the Bahamas. Scattered volcanic sediments were recovered from the Caribbean Sea, Gulf of Mexico and the North Atlantic. This data is based on the site descriptions from the legs conducted in the Atlantic Ocean, Gulf of Mexico and Caribbean Sea during the first 43 Legs of the DSDP. Site 323 in the Southern Ocean contained siliceous sediment but is not shown due to its extreme high latitudinal position.
Figure 10. The distribution of Miocene siliceous sediment in the Atlantic Ocean. The polar belts of diatomaceous sediments are clearly shown. Some "chert" (diatomite) was also recovered from the Miocene of these sites. A zone off west Africa where upwelling occurs also indicates the presence of siliceous material and "chert." Site 323 in the Southern Ocean recovered a Miocene "chert" but is not indicated due to its extreme high latitudinal position. The dashed lines represent the boundary between crust younger than 5 m.y. (inside the lines) and older crust. The symbol designations and data source are explained in Figure 9.
DSDP MIOCENE SEDIMENTS
ATLANTIC
Figure 11. The distribution of Oligocene siliceous sediment in the Atlantic Ocean. The polar belts of siliceous sediment are well developed. "Chert" and siliceous sediment are present in the northern subtropical Atlantic, Caribbean and Gulf of Mexico as well as off western Africa. The Isthmus of Panama was open during the Oligocene, allowing low latitude communication with the Pacific. The dashed lines represent the boundary between crust younger than 23 m.y. (inside the lines) and older crust. The symbol designations and the data source are explained in Figure 9.
Figure 12. The distribution of Eocene siliceous sediment in the Atlantic Ocean. The great abundance and sudden appearance of "chert" in the Atlantic at all latitudes is indicated for the Eocene. There are polar zones as well as a broad northern mid latitude zone of biogenic silica and "chert". The area of upwelling off Africa is also abundant in "chert". The dashed lines represent the boundary between crust younger than 38 m.y. (inside the lines) and older crust. The symbol designations and data source are explained in Figure 9.
Figure 13. The distribution of Paleocene siliceous sediment in the Atlantic Ocean. A northern subtropical zone of "chert" and siliceous sediment is clearly developed in the Paleocene. Fewer sites are penetrating to the Paleocene, but the trend is little changed from the Eocene. The dashed lines represent the boundary between crust younger than 38 m.y. (inside the lines) and older crust. The symbol designations and data source are explained in Figure 9.
Figure 14. The distribution of Upper Cretaceous siliceous sediment in the Atlantic Ocean. A trend similar to the Lower Cenozoic is present in the Upper Cretaceous of the Atlantic. The subtropical zone of siliceous sediment and "chert" is well developed. The dashed lines represent the boundary between crust younger than 65 m.y. (inside the lines) and older crust. The symbol designations and data source are explained in Figure 9.
Figure 15. The distribution of Lower Cretaceous and Jurassic siliceous sediment in the Atlantic Ocean. The scant data points of sediments of Lower Cretaceous and Jurassic age tend to indicate the same trend of a northern subtropical zone of "chert" formation as do the maps for the Lower Cenozoic and Upper Cretaceous. The dashed lines represent the boundary between crust younger than 65 m.y. (inside the lines) and older crust. The symbol designations and data source are explained in Figure 9.
Figure 16. The distribution of Pliocene siliceous sediment in the Pacific Ocean. The distribution of Pacific Pliocene sediment indurated by authigenic silica ("chert") recovered by the DSDP is represented by the solid triangles, sediment described by the DSDP as siliceous by open triangles and sediment described as bearing volcanic ash by open circles. The small dots indicate sites where the DSDP recovered Pliocene sediment which did not include "chert", siliceous sediment or ash in the core descriptions. Superimposed symbols indicate the occurrence of more than one lithology during the time interval. The position of the East Pacific Rise (epr) is indicated by the dashed line. The equatorial zone of high productivity is well delineated by a zone of siliceous sediment extending across the Pacific. The north polar belts of biogenic silica productivity are well developed and contain diatomite. Volcanic ash is associated with spreading centers and subduction zones. This data is based on the site descriptions for the legs conducted in the Pacific Ocean during the first 43 legs of the DSDP. Sites 265, 266, 274 and 278, which recovered Pliocene siliceous sediment, are not indicated due to their extremely high southern latitudinal positions. They would indicate the presence of a south polar belt of high silica productivity.
Figure 17. The distribution of Miocene siliceous sediment in the Pacific Ocean. The equatorial zone of high productivity is well developed as shown by the zone of siliceous sediment extending across the Pacific. The north polar belt of high productivity is clearly indicated. "Chert" occurrences, associated with the areas of biogenic silica production, are centered in tectonically active areas during the Miocene. Sites 266, 267, 268, 269, 272, 274 and 278 were siliceous. Some of these sites also contained "chert"; however, due to their location in high southern latitudes, they are not plotted. These additional sites would indicate the presence of a south polar belt of high silica productivity. The dashed lines represent the boundary between crust younger than 5 m.y. (inside the lines) and older crust. The symbol designations and data source are explained in Figure 16.
Figure 18. The distribution of Oligocene siliceous sediment in the Pacific Ocean. Plate motion has shifted the equatorial zone of Oligocene high productivity westward. "Chert" occurrences are more numerous and associated with this high productivity zone. No north polar zone is present. Sites 274 and 278 are siliceous and Site 268 contains "chert"; however, they are not plotted due to their location in high southern latitudes. They would tend to indicate the existence of some biologic silica production in a south polar belt. The dashed lines represent the boundary between crust younger than 23 m.y. (inside the lines) and older crust. The symbol designations and data source are explained in Figure 16.
Figure 19. The distribution of Eocene siliceous sediment in the Pacific Ocean. Plate motion has shifted the equatorial zone of Eocene high productivity westward and strongly northward, since Pacific plate motion was northwesterly in pre-Oligocene time. "Chert" abundance is markedly greater than in the Oligocene and is clearly associated with siliceous sediments. Sites 274 and 277 recovered Eocene "chert"; however, due to their high southern latitudinal location, they are not plotted. These sites would extend the Tasman Sea "chert" farther southward. The dashed lines represent the boundary between crust younger than 38 m.y. (inside the lines) and older crust. The symbol designations and data source are explained in Figure 16.
Figure 20. The distribution of Paleocene siliceous sediment in the Pacific Ocean. The few sites recovering Paleocene sediment seem to indicate a trend similar to that shown in the Eocene. Plate motion has moved the depositional sites westward and northward. "Chert" is common in the Paleocene and is associated with siliceous sediments. The dashed lines represent the boundary between crust younger than 38 m.y. (inside the lines) and older crust. The symbol designations and data source are explained in Figure 16.
Figure 21. The distribution of Upper Cretaceous siliceous sediment in the Pacific Ocean. Motion of the Pacific plate has moved the Upper Cretaceous sites far to the north and west. Probably during Upper Cretaceous time, these sites were associated with an equatorial zone of high productivity. "Chert" would thus have been associated with zones of high biologic productivity. The dashed lines represent the boundary between crust younger than 65 m.y. (inside the lines) and older crust. The symbol designations and data source are explained in Figure 16.
Figure 22. The distribution of Lower Cretaceous and Jurassic siliceous sediment in the Pacific Ocean. The pattern shown for the Lower Cretaceous and Jurassic is similar to that of the Upper Cretaceous. "Chert" is numerous; and if Pacific plate motion is considered, these sites were probably associated with an equatorial zone of high productivity. The dashed lines represent the boundary between sediment younger than 65 m.y. (inside the lines) and older sediment. The symbol designations and data source are explained in Figure 16.
DSDP LOWER CRETACEOUS & JURASSIC SEDIMENTS

PACIFIC
of equatorial, highly productive waters from the Pacific via the area occupied by the Isthmus of Panama. Ramsay (1971) states that by Miocene this circulation pattern had ceased. Biogenic silica production was then restricted to the areas of upwelling off Africa and the extreme North and South Atlantic.

Ramsay's conception for the Atlantic holds fairly well based on the data from Figures 9 through 15. "Chert" is indeed restricted to zones of high productivity or areas where produced biogenic material could be transported. This transfer factor is likely to account for the large expansion of the equatorial zone of productivity in the northwest Atlantic (Figures 11-15). The maps of the Pliocene through the Oligocene contain few sites of extensive "chert" and/or siliceous sediment (Figures 9-11). The areas of biogenic silica accumulation correspond primarily to areas of upwelling and polar zones of biogenic silica productivity. There is a marked increase in both "chert" and siliceous sediment in the Eocene (Figure 12). This trend continues, with diminishing data points, through the Jurassic (Figures 13-15). Low latitude deposition of siliceous sediment and "chert" formation is prominent. These abrupt changes in biologic productivity in the subtropical northern latitudes may be related to the termination of the pre-Oligocene circulation and the communication between the oceans as Ramsay (1971) postulates.

The history of the distribution of "chert" and siliceous sediment in the Pacific is much clearer and better illustrated than in the Atlantic. Figures 16 through 18 contain the distribution for the Pliocene through the Oligocene. The Pliocene pattern is very similar to the Recent. There is a prominent equatorial zone of biogenic silica
productivity extending from Central America across the Pacific. A northern band of siliceous production is also found extending from the pronounced upwelling zones off California across to the Sea of Japan. Three sites, 76, 178 and 301 recovered Pliocene silicified sediment. Sites 178 and 301 were reported to contain diatomite, which could be very weakly silicified.

Figure 17, the Miocene of the Pacific, is very similar to the Pliocene. "Chert" development along the equatorial zone of high productivity is restricted to tectonically active areas, like the East Pacific Rise, where high heat flow could have accelerated silica diagenesis (as in Heath, 1973). Sites 53 and 59 were reported as "lower Miocene-lower Oligocene," so they may not actually be Miocene in age. High latitudinal development of diatomite and deposition of siliceous material is still prominent.

The Oligocene (Figure 18) is considerably different from the Pliocene or the Miocene. An equatorial zone of high productivity appears to be present. Plate motion, though, has shifted the sites westward. There is an increase in "chert" in the Oligocene within a somewhat broader band of siliceous productivity. This increase in "chert" and siliceous sediment is mirrored, though not as pronounced, in the Atlantic Oligocene (Figure 11). Clearly shown in the Oligocene is the association of "chert" with sites of siliceous sediment. Very few locations tend to correlate volcanic ash with "chert."

The Eocene distribution (Figure 19) is radically different from the post-Eocene patterns. "Chert" is abundant and spread over much of the central western Pacific as well as the waters off eastern Australia. Plate motion has changed to a more northerly direction (Clague and
others, 1975; Jackson and others, 1972). This may have "smeared" the equatorial zone of high productivity into a broader band than that of the original zone. No recovery of Eocene sediment was made in the northern latitudes, so it is not known if there existed any biologic silica productivity in these waters. This marked increase in Eocene "chert" is again reflected in the Atlantic (Figure 12).

The Paleocene through the Jurassic (Figures 20-22) show, with diminishing data points, trends similar to that of the Eocene. Plate motion has moved the sediment far to the north and west of their sites of deposition. These sites would roughly correspond to an equatorial zone of high productivity in Paleocene and Mesozoic time.

Based on the maps of the Atlantic and Pacific, the following observations may be made. The Oligocene/Eocene boundary separates periods of time when "chert" was rare (post-Eocene) from periods of time when "chert" was common (pre-Oligocene). The time boundary does not correspond to an interruption of biogenic silica production, although pre-Oligocene sediment seems to be more abundant in siliceous material. Areas of biologic silica accumulation are located beneath belts of high productivity. Surface zones of high productivity, then, have spatial patterns similar to those of the modern oceans, consisting of equatorial zones and polar belts.

**Paleoceanographic Factors**

Bottom water circulation may have been radically different from today in the pre-Oligocene oceans because of significant changes in ocean-continent relationships after this epoch. Bottom water production today is restricted to two high latitude areas, the area east of
Greenland and the Weddell Sea in Antarctica, and is distributed to all the oceans via the Antarctic Circumpolar Current. Avery and others (1968) state that the Norwegian Sea opened about 60 m.y. ago. The Dietz and Holden (1970) reconstruction indicates some separation between South American and Antarctica in the Cretaceous. The lack of Eocene and Miocene sediment at all DSDP sites in the Drake Passage and Falkland Plateau is assumed by Barker and others (1974) to represent the opening of the Drake Passage. The rifting of Antarctica from Australia was completed in the late Eocene or Oligocene (Kennett and others, 1972; Kennett and others, 1974a; Kennett and others, 1974b; Luyendyk and Davies, 1974). With the Drake Passage open and water capable of flowing between Australia and Antarctica, bottom water distribution would be more efficient. In pre-Oligocene oceans, global bottom water circulation would have been hampered and probably distributed via low latitude inter-ocean connections. Van Andel and others (1975) present data indicating bottom water circulation north of Australia in the pre-Oligocene.

Paleotemperature estimates of the Oligocene and Eocene also indicate a "boundary" at the Oligocene/Eocene interval. Surface water of the world ocean seems to have been warmer and to have exhibited lesser latitudinal temperature zonation in pre-Oligocene time. Steineck (1971) found warmer bottom water foraminifera in the Eocene of California. At the close of the Eocene, a cooling trend occurred. Frakes and Kemp (1972) states that the surface South Atlantic water temperature in the Eocene was warmer; the Pacific was comparable to today. The Oligocene cooling of the oceanic surface waters indicated a change in the climate. Jacobs (1974), in a study based on clay mineralogy
changes, detected a cooling of the Antarctic climate by Miocene.

Savin and others (1975), in an extensive study of Tertiary marine paleotemperatures, provided the first quantitative data for the time interval of the Cenozoic for both the surface and bottom water masses. They found that the pre-upper Eocene of the oceans was marked by warmer bottom waters and warmer surface waters. Oxygen isotope temperatures indicates bottom temperatures of 10°-15°C, while surface paleotemperatures were about 25°C. A dramatic cooling occurred at the Oligocene/Eocene boundary, where a drop in bottom temperatures of 7°C is noted. This decrease continued until the present temperatures were established.

This radical change in oceanic bottom water temperatures must be related to severe cooling at the high latitudes where bottom water is produced. Vigorous bottom water circulation may have been one result of this cooling. Kennett and others (1974a) noted the presence of widespread hiatuses in the Southern Ocean beginning below Australia in Oligocene and extending into the South Indian Ocean by Miocene. Van Andel and others (1975) also noted a change in the pattern of Western Pacific hiatuses during the same time interval. There is a shift in location of hiatuses from north of Australia older than 40 m.y. to south of Australia 35 m.y. ago and younger.

**Silica Precipitation Mechanism**

Given these pronounced differences in paleoceanographic conditions from Eocene to Oligocene, a relationship to silica precipitation may be explored. The fact that silica solubility and temperature are directly related forms the basis for these hypotheses. A ramification of the pronounced cooling of the ocean would be a restructuring of the
thermal profiles of sub-bottom temperatures. Although Knauth and Epstein (1975) report a Cretaceous temperature derived from analysis of a chert of 5°C, indicating the possible presence of cold bottom water as early as Cretaceous, it may be concluded from the data of Savin and others (1975) that the average paleotemperature was quite warm. With the onset of cooling and the establishment of the Southern Ocean at the close of the Eocene, cold bottom water would have been able to circulate throughout the oceans. This change of bottom water temperature probably did not occur instantly, nor is it likely that it occurred as one single infusion of cold bottom water. It seems reasonable to suggest that during the time of establishment of this new oceanic environment pulses of cold water may have entered the oceans, temporarily cooling the bottom. Cooling would begin at the sediment-water interface and gradually move deeper into the sediment. The cold bottom water would act as a heat sink, extracting heat from greater depths. For a decrease of 10°C (13°C down to 3°C), amorphous silica solubility would decrease 20 ppm; and cristobalite solubility would decrease 10 ppm (Figure 1). If silica concentration is controlled by saturation with respect to solid silica phases, then a decrease in temperature would cause supersaturation. This might be sufficient to initiate precipitation. Once opal-CT formation has begun, the model based on nucleation and diffusion (Chapter V) would be established and additional dissolved silica would diffuse to sites of silica precipitation.

This somewhat cyclic change in temperature may account for such large amounts of DSDP "chert" in the Eocene. Each influx of cold bottom water could initiate silicification of siliceous material
deposited during the preceding warm period. Such extensive amounts of "chert" could not have formed with only a single incursion of cold bottom water.

This hypothesis may also account for the paucity of "chert" in the DSDP post-Eocene sites. The mechanism outlined requires a cooling of the ocean floor after some interval of milder temperatures. According to the data of Savin and others (1975), there has been a progressive cooling of the world oceans since the Oligocene. There has never been a re-establishment of the warmer conditions and another cooling cycle, so "chert" would not be an expected common rock type produced in the ocean since the Oligocene.

This mechanism links changes in paleoceanographic circulation patterns and world-wide changes in ocean water temperatures to the widespread occurrence of "chert" in Eocene sediment. It is a tenuous association at best, but no other explanations have been offered to better account for this unusual period of enhanced silica diagenesis.
CHAPTER VIII

THE TIMING OF SILICIFICATION

Whether silicification is an early or late postdepositional event could be estimated by knowing either the geologic time period or the depth of burial at which silicification occurred. Under normal circumstances, depth of burial and increasing age are directly related; if the depth of burial at which silicification occurs can be determined, then the timing can be inferred. This simple pattern can be upset by tectonism, non-deposition or erosion.

Because sea water is very much undersaturated with respect to any form of silica, opaline silica will dissolve readily. Fanning and Pilson (1974) found a continued release of silica from the Atlantic Ocean core material in the laboratory for the entire two-year duration of their experiment. Rapid increase in silica up to one meter sub-bottom may produce silica concentrations ranging up to 15-30 ppm (Fanning and Schink, 1969; Bischoff and Ku, 1971; Fanning and Pilson, 1974). Below about one meter, the silica concentrations level off to the 15-30 ppm range, implying a steady state equilibrium with respect to pore fluids. Thus it appears that the capacity for "chert" formation, defined by high silica concentrations, is present at quite shallow depths.

Pore fluid analyses by the DSDP are not taken on the scale necessary to judge small changes in composition which may be related to lithologic variations. Broad trends indicate a variability in minor or trace elements. Silica concentrations (Table 3 contains some examples)
are in the range of 15-30 ppm, which Fanning and Pilson (1974) found in their study of the upper few meters of sediment.

Isotopic data by Knauth and Epstein (1975) on DSDP chert from the Pacific are concerned with two phases in the silicification process, opal-CT and QM quartz precipitation. They found isotopic values of opal-CT possibly indicative of temperatures of formation within 5°-13°C of ocean bottom water temperatures and isotopic values for QM quartz suggesting deeper burial. This indicates that initial silicification is an early diagenetic event. Because Knauth and Epstein's shallowest chert was located at 86 m sub-bottom, they conclude that opal-CT formation had to take place at burial depths less than 86 meters.

Petrologic studies of DSDP silicified material have produced conflicting evidence pertaining to the timing of silicification. In a study of the "chert" recovered in Leg 32, Keene (1975) found some "chert" formed prior to the lithification of carbonate material; although Keene states that the limestone formation may not have occurred until 40 to 50 m.y. after burial. Lancelot (1973) found evidence for early diagenesis in "chert" that predated sediment lithification; compaction of the sediment fractured "chert"nODULES. However, "chert" postdated dolomite, a late diagenetic stage, in a dolomitic porcellanite from Site 307 and also postdated the recrystallization of carbonate grains in other sites (Keene, 1975). Keene also found silica-rich (greater than 50 percent SiO₂) Eocene sediments which were unaltered, suggesting a late diagenetic phenomenon. Keene (1975) suggests that such variables as the source of the silica and the in situ temperature may strongly influence when silicification occurs. Biogenic silica is more readily soluble than clays or volcanic ash. High in situ temperatures such as
found near a ridge crest, may accelerate "chert" formation (Keene, 1975).

Sedimentation rates for the samples used in the present study were rarely estimated by the shipboard scientific parties. The estimates which are available show a range from a low of 0.21 cm/1000 years (Site 8) to a maximum of 1.5 cm/1000 years (Site 118). Therefore, within 500,000 years by the slowest rate of accumulation, the material would be below the meter depth judged by Fanning and Pilson (1974) to be where equilibrium with the pore fluids is achieved.

Figure 8 in Chapter VII was utilized to examine the validity of a "chert" formation model based on a simple burial diagenetic or time-related model. It was suggested that neither of these simple models adequately explained the data, but a burial diagenetic model may be feasible for deeply buried sediments. If these models do not explain the cause of silicification because of inconsistencies at shallow depth or discontinuities in the abundance of "chert," then estimating the time of silicification by either depth of burial or age would also lead to contradictory results. "Chert" buried to a shallow depth may be an early diagenetic lithification event and "chert" deeply buried may be a late diagenetic event. The data in Figure 8 seem to support both early and late diagenetic events.

Only the silicified sand, 6-6-1 (130-132), the silicified nanno chalk, 98-7-4 (110-114), and possibly 8A-2-1 (20-22) and 8A-3-1 (31-33) are grain-supported. The remainder of the "chert" sampled is probably matrix-supported. Pressure solution cannot be a factor in the formation of "chert" because these sediments are matrix-supported. Therefore, "chert" formation seems to be related to chemical phenomena.

It can be seen from Figure 4 that the silicified material studied
covers a wide range of depths. The shallowest chert sample, 98-7-4 (110-114) from about 168 m sub-bottom, is the most silicified of the samples. The deepest sample, 9A-1-4 (64-66) from about 683 m sub-bottom, is the most poorly silicified. If all the DSDP "chert" is considered, then the shallowest chert is a Middle Cretaceous chert in a chalk encountered at 9.5 m in Site 306; the deepest is a Miocene silicified mudstone from 1015 m in Site 106.

If silicification by the cold bottom water mechanism is assumed to be a practical explanation of the data (see Chapter VII), then these seemingly contradictory results become clearer. The relationship between the termination of a cold pulse and the deposition of a specific unit of siliceous sediment can offer a possible way of explaining the results. If a sediment which accumulated under the still predominantly warm episodes were deposited soon after the termination of a cold cycle, then it may have been possible for it to become deeply buried before initiation of another cold cycle. Those sediments deposited under the cold regime would escape shallow lithification. Subsequent lithification of these sediments, perhaps by burial diagenetic means, would imply a late diagenetic event. Siliceous sediment deposited just prior to an influx of cold bottom water, lithified by the decrease in temperature mechanism, would acquire early diagenetic silicification properties.

Proof of this idea might lie in the type of authigenic silica deposited in chert. Knauth and Epstein (1975) suggest that quartz forms at temperatures indicative of deep burial. Perhaps the more quartzose Eocene deep-sea chert was formed deeper than the more opal-CT-rich "chert." However, subsequent depositional or tectonic history of a chert site could confuse the resolution of this problem. Quartzose
chert could be placed at shallow depth and cristobalitic "chert" at deep depths. Subsequent burial of a cristobalitic "chert" may produce some inversion of opal-CT to quartz.

Analyses of the samples used in this study provide little insight into the timing of the silicification. The only valid direct observation pertinent to this problem is the fact that the "chert" from most sites is matrix-supported, which is not consistent with a pressure solution model. What has been suggested is that the potential for silicification, defined by high pore water concentrations of silica, occurs quite early in the postdepositional history of the sediment. With the potential for silicification achieved early in the depositional history of a site, whether chert acquires early or late diagenetic properties may depend upon the means by which the material becomes lithified. This, along with compositional variations, may account for so much conflicting evidence concerning a late or early diagenetic time of silicification.
Mass Balance Considerations

Much was observed in this investigation which suggests that the general chemical system under which silicification occurs does not have significant interaction with normal ocean water. Silicification cannot take place unless there is a source of silica and the dissolved silica concentration is high (saturated with respect to cristobalite). This requirement for high dissolved silica concentrations is the most compelling argument for the need for a chemical system isolated from marine bottom water.

Because sea water is undersaturated with respect to silica, opaline material in contact with moving ocean water will dissolve. The material which does dissolve will eventually be uniformly mixed over the entire ocean. Ultimately it will be reincorporated either into siliceous tests or into some other mineral. Even within the upper meter of sediment below the ocean bottom, burrowing organisms cause interstitial dissolved material to escape into the overlying water column. This cycle will continue until the silica is removed from contact with the sea.

Because the bottom water circulation in the Eocene was, in all probability, very much different than it is today (see Chapter VII), bottom water circulation could have been more sluggish. Oceanic temperatures were warmer as well. Sluggish bottom water circulation could have allowed more silica to be dissolved in the bottom water. However,
bottom water would have to become saturated with respect to amorphous silica before precipitation of opal-CT would begin at the sediment-water interface. Due to mixing processes, it seems unlikely that pronounced vertical and/or horizontal concentration differences could be created in the open ocean. It thus seems unlikely that bottom water with dissolved silica levels approaching the solubility of amorphous silica could have developed.

If more material were precipitated than could possibly be supplied in an isolated system or if elements for silicification could not be adequately supplied by the interstitial waters, then a system in contact with marine waters must be accepted.

This problem of whether the system was in contact with or isolated from marine bottom water is best evaluated by determining what the original composition of the sediment was prior to silicification and comparing that to the composition after silicification. The Site 6 samples neighboring the "chert" may best duplicate the original sediment. The "chert" itself may be considered the product. If reactions can be written which conserve elements, then a closed chemical system is feasible.

Because no chemical analyses of sediment constituents were done, balanced chemical reactions cannot be written. Smectite, opaline silica and sea water, somewhat enriched with respect to silica, would be starting materials. Opal-CT, clinoptilolite and mixed-layer smectite/illite may be considered as major products.

Clay Transformation

A mechanism has been proposed by Towe (1962) and utilized by Keene and Kastner (1974) to make some silica available to be precipitated as
cement by the clay transformation smectite to illite. Keene and Kastner (1974) present a calculation which indicates that enough potassium to support this transformation could be supplied by the pore fluids within a geologically short period of time.

Because potassium is necessary in the clay transformation which Keene and Kastner suggest is a primary source of silica, the volume of sediment necessary to supply the potassium for this transformation is important in determining the practicality of this mechanism for "chert" formation. A hypothetical calculation of this volume can be made based on the following assumptions:

1) 40 percent porosity (consistent with DSDP data)
2) 85 percent smectite and 15 percent radiolaria
3) 2.5 gm/cc as density of smectite
4) 0.38 gm/l as pore fluid concentration of K

Then

4.0 cc pore water
6.0 cc clay and radiolarians
10.0 cc sediment + water

If 85 percent of the 6 cc of sediment is clay, then 5.1 cc are occupied by clay. If the volume of clay is multiplied by the density of smectite (2.5 gm/cc), then the clay in the volume would weigh 12.7 gm. Keene and Kastner (1974) state that 10 gm of smectite will produce 6.4 gm of illite and 3.3 gm of SiO₂. Using their proportions, the 12.7 gm of smectite would produce 8.2 gm of illite and 4.2 gm of SiO₂. Illite contains approximately 10 weight percent potassium. Thus it would require 0.82 gm of potassium to be extracted from the pore water to satisfy the illite structure.

The 0.004 l of sea water in the 10 cc volume would supply $1.52 \times 10^{-3}$ gm of potassium. To satisfy the reaction, 540 times the amount of potassium supplied by 10 cc would be needed. Assuming total depletion of potassium, this would require a volume of 2.16 l of water. If 40
percent of the sediment is pore space, then 2.16 l of water would occupy about 0.55 m$^3$ of sediment.

Thus the transformation smectite to illite requires the interaction of large volumes of sediment. Because total depletion of potassium in a given volume would not occur, the volume of interaction is probably much larger than the 0.55 m$^3$ calculated. The rate of transformation, then, becomes the primary factor in evaluating the validity of this mechanism. Given sufficient time, enough potassium could theoretically be supplied. Due to low temperature (compared to in situ temperatures of Gulf Coast sediments where this transformation has been studied), the rate and quantity of smectite transformed may be somewhat limited compared to the silica supplied by dissolution of biogenic silica.

**Zeolites**

It has generally been accepted that authigenic zeolites in the deep sea are derived from volcanic ash (Bonatti, 1963; Arrhenius, 1963). Because no volcanic shards were observed in thin section or via SEM, this source may not be feasible for the zeolites found in these samples. All constituents necessary to produce zeolites are present in sea water, but Al and Si are at very low levels of concentration. Direct extraction from sea water would require prolonged time at the sediment-water interface. Therefore, the argument for a closed chemical system must include some mechanism to produce zeolites without the alteration of volcanic ash or prolonged contact with the sea floor.

A calculation similar to that for the clay transformation can be made to estimate whether an adequate supply of elements for the zeolites can be extracted from a 10 cc sediment-water volume of the same composition (85 percent clay, 15 percent radiolarians at 40 percent
porosity). Because zeolites were primarily noted in the radiolarian tests, it will be assumed that the amount of zeolites in the clays is small compared to the amount found in the radiolarians. Furthermore, it will be assumed that an average of 5 zeolites are found per radiolarian test (a value consistent with SEM observations) and that radiolarians are hollow spheres 100 μm in diameter and 5 μm thick.

If 15 percent of the 6 cc of sediment is occupied by radiolarians, then the radiolarians will occupy 0.9 cc of sediment. If the tests are 100 μm in diameter, then that 0.9 cc of sediment will contain $1.7 \times 10^6$ radiolarians. This number of radiolarian-size spheres can be converted to a weight by assuming a density of opal-A of 2.0 gm/cc. This translates into a total of $4.76 \times 10^{-1}$ gm of opal-A.

Using a microprobe, Lipps (1970) estimated that silicoflagellates could contain 0.05-1.0 percent Al and about 0.05-0.5 percent Ca, Na and Cl. If it is assumed from this data that a radiolarian contains 0.1 percent Al, then $4.76 \times 10^{-1}$ gm of opal-A would contain $4.76 \times 10^{-4}$ gm of Al, which could be available for zeolite formation.

The zeolites observed to co-precipitate with the cristobalite spherules were about $40 \times 10 \times 10$ μm in size. This represents a volume of $4 \times 10^{-9}$ cc/zeolite; or assuming a density of 2.1 gm/cc, a mass of $8.4 \times 10^{-9}$ gm/zeolite. This would amount to a total mass of zeolites in the sediment volume of $7.4 \times 10^{-2}$ gm. Assuming 6 weight percent Al in a heulandite-type zeolite, $4.4 \times 10^{-3}$ gm of Al would be required to produce all of the zeolites. According to these calculations, a little over 9 times more Al than would be supplied by the complete dissolution of opal-A spheres in the 10 cc volume would be needed to form the zeolites observed. Even with this conservative estimate of the amount
of Al in radiolarians, a volume of only 90 cc of sediment and water would be needed. If a 1% Al composition for radiolarians had been assumed, the 10 cc volume would contain adequate Al with almost complete depletion.

Because K is the least abundant of the cations (Na, K, Ca) needed to produce zeolites, if enough K can be supplied by sea water, then it is assumed that the supply of Na and Ca would be adequate. Assuming that a pure potassium heulandite contains about 8 percent K, $6 \times 10^{-3}$ gm of K would be required for the zeolites in 10 cc of sediment. Pore water contains 0.38 gm/l K and could account for $1.5 \times 10^{-3}$ gm of K within the 10 cc volume. A water volume of only 16 cc could supply enough K to produce the calculated amount of zeolites. This would be a volume of sediment plus water of only 40 cc. So, from a relatively small volume of sediment, enough material could be extracted to yield the amount of zeolites calculated to be present in the "chert" layers. However, this mechanism may not be sufficient if larger amounts of zeolites are present in the clay matrices. Additional K, Ca and Na as well as Si and Al may also be derived from the dissolution of radiolarians and could be another source of cations for the zeolites.

These calculations tend to support a chemical system isolated from bottom water for "chert" formation. Enough elements seem to be present in a small volume of sediment to produce zeolites. However, a large volume of sediment would be required for a complete transformation of small amounts of smectite to illite. Therefore, the clay transformation may not be a reasonable means of producing silica for "chert." The observed mixed layering could be a diagenetic product of silicification and zeolite formation.
Site 140: The Sulfur-bearing Minerals

Sample 140-3-2 (100-102) is anomalous in its authigenic mineral assemblage, considering the fact that is quite siliceous. Authigenic pyrite, gypsum and native sulfur were identified in this single sample (Plate XIVd-f; Plate XVa-c). Based on petrographic analysis of a thin section, the paragenesis of these sulfurous phases was discerned. The pyrite blebs were formed first. Pyrite is seen being displaced by the growth of gypsum. The SEM indicated that native sulfur was present in the sediment as well as on the pyrite nodules. No sulfur-gypsum relationship could be evaluated. Therefore, it is assumed that the sulfur formed after the pyrite but prior to the gypsum. This assumption is based on the oxidation of sulfide, first to native sulfur then to sulfate.

Sample 140-3-2 (100-102) is a dark brown laminated compact siliceous clay. Diatoms are the primary siliceous component. Radiolarians and sponge spicules form a minor proportion. The sample is located on the continental rise off Sierra Leone, Africa. Considering its position, there is a high potential for input of material derived from the African continent. The clay mineralogy, kaolinite, illite and smectite, reflects a detrital influence. Furthermore, according to Ramsay (1971), the site would have been under a zone of upwelling. Therefore, it should have accumulated much siliceous and organic material. This organic material would be derived from the overlying productive water column as well as from land-derived material.

Because the diagenesis of sulfur-bearing minerals is better understood than silica diagenesis, it would be advantageous to link silica diagenesis to the paragenesis of the sulfur-bearing phases. However,
there is a distinct possibility that the gypsum crystals in 140-3-2 (100-102) formed after recovery, sometime during storage. Crystals much larger than the ones found in this sample have been found in other DSDP samples to have a post-recovery origin (Van Andel, personal communication). This mechanism can not be refuted and may be the most likely explanation. The native sulfur may have formed in a similar manner. If desiccation and oxidation of the core occurred as the presence of gypsum suggests, then native sulfur could have formed in proximity to the pyrite concretions. The facts that the gypsum and sulfur may be artifacts and that no lithification was noted in the sample makes further study of the sulfur chemistry of this sample unwarranted.
A detailed analysis of a selected set of 34 Eocene DSDP samples from the Atlantic Ocean was done in conjunction with a comprehensive survey of silica occurrences recovered in the first 43 legs of the JOIDES Deep Sea Drilling Project dealing with the Atlantic, Pacific and Caribbean. This study enabled an in depth analysis of the process of silicification of Eocene "chert". Based on this analysis, the following conclusions may be made concerning the source of silica, the paragenesis of silica, the timing and cause of silicification and the general chemical system in which silicification occurs:

1) The source of silica for the Eocene "chert" examined is biogenic silica. Data from the detailed analysis indicate the presence of severe dissolution of biogenic silica adjacent to "chert" layers. In addition, regional trends show a strong correlation between zones of biologic productivity and sites where "chert" has formed. The transformation of the clay smectite to the clay illite can not provide enough silica to produce the observed "chert". This clay transformation more likely occurs during the diagenetic reactions which produce the "chert".

2) The paragenesis of silica begins with the dissolution of biogenic silica until equilibrium with opal-A is approached. Pore water near saturation with respect to opal-A is supersaturated with respect to opal-CT. As soon as precipitation of opal-CT commences, concentration gradients cause increased dissolution of siliceous biogenic material in beds adjacent to the site of opal-CT precipitation. Toward the end of the stage of opal-CT precipitation, clinoptilolite is a
co-precipitate. The presence of impurities, such as clay, seems to be an important factor for production of opal-CT rather than other silica phases. Void filling may be completed with opal-CT and clinoptilolite. It is also possible to have a third stage, a second precipitation phase, involving the formation of fibrous quartz or GMC quartz, which would fill the void space remaining after termination of opal-CT precipitation. The fourth stage in the formation of a chert would be the inversion of all metastable phases to quartz and the replacement of all other minerals by quartz. This fourth stage was not studied in this research.

3) Silicification does not seem to be caused by any unusual lithology of the Eocene sediments, nor is it strictly a burial diagenetic or time-related problem. The major requirements seem to be the presence of biogenic opal-A and some admixture of clay. A possible silicification mechanism involves a decrease in the temperature of the sediments caused by a cooling of the overlying bottom waters. Much evidence from diverse sources supports a dramatic change of the world climate at the close of the Eocene. This, coupled with the rifting of Australia from Antarctica and the formation of the Antarctic Circumpolar Current, allowed the efficient distribution of cold bottom waters to the oceans. In the early stages of this developing paleoceanographic and paleoclimatic regime, pulses of cold bottom water may have periodically circulated, alternating with the still dominant warmer-water regime. A possible ramification of influxes of cold bottom water would be the periodic cooling of the bottom sediments. Siliceous deposits in a steady state equilibrium with pore water at warmer oceanic temperatures may possibly have become supersaturated with respect to opal-CT as the bottom sediment cooled, initiating silicification. Once this "new" colder regime had been completely
established, fluctuations in bottom water temperature were no longer possible. This scheme accounts for the widespread occurrences of "chert" in the Eocene and the marked lack of "chert" since that time, in spite of the fact that the presumed sources of silica are still accumulating.

4) Two Site 8A silicified samples contain the high temperature crystalline phases of cristobalite. One of these samples also contained high tridymite. Elevated temperatures were not a factor in the formation of these unique mineral occurrences. It is suggested that these minerals were precipitated from pore fluids containing only silica. Adjacent zeolite-rich clays may have acted as a sink for other cations, leaving the radiolarian-rich claystones more pure in silica than other sites.

5) If silicification by influxes of colder bottom water is accepted, the timing of silicification becomes clearer. Data presented do not fully clarify the relationship of silicification to a postdepositional event. The resolution of the timing of silicification by direct means, depth of burial, age of silicified units, or relative relationships of silicification to other lithification events, leads to contradictory conclusions -- an early diagenetic event for some chert and a late diagenetic event for others. "Chert" formation by periodic cooling would cause siliceous sediments deposited just after the termination of a cold cycle to acquire properties indicative of a late stage lithification event, while sediment deposited just prior to cooling would acquire properties indicative of an early diagenetic event.

6) Mass balance considerations seem to support the idea that the "chert" formed in a closed chemical system. There may be an inadequate supply of K available to transform smectite to illite in the quantity necessary to produce "chert". Aluminum for zeolites is not readily
available from the pore fluids or clays. It has been suggested, based on microprobe data of silicoflagellates from Lipps (1970), that aluminum and possibly some other cations can be incorporated in siliceous tests in sufficient amounts to supply aluminum upon dissolution of the tests for the formation of the zeolites observed to co-precipitate with the silica phases.

7) Some data from HF-etched fracture surfaces of SEM samples suggest that microcrystalline quartz may be pseudomorphic after opal-CT. Etching revealed only cristobalite spherule-shaped cavity fillings in samples where quartz was observed in thin section and identified by x-ray diffraction.

8) The permeability of the sediment and the ratio of opal-A to sediment may influence the degree of silicification. Well-indurated "chert" contains abundant siliceous microfossils and little clay. Where the amount of biogenic opal is low or where the clay content is high, samples are poorly silicified.
REFERENCES CITED


Wise, S. W., Jr., and Kelts, K. R., 1972, Inferred diagenetic history of a weakly silicified deep-sea chalk: Gulf Coast Assoc. Geol. Soc. Trans., V. 22, p. 177-203.


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Appendix 2. Tabulation of the results of the diffractograms of the random powder mounts of the bulk samples. Q = quartz; A = opal-A; CT = opal-CT; Ca = calcite; Cl = clinoptilolite; S = smectite; I = illite; K = kaolinite; ML = mixed-layer clay; F = feldspar; Ph = phillipsite; G = gypsum.

An "X" indicates that the mineral is present. A "?" indicates that the mineral may be present but could not be identified with certainty.
### APPENDIX 2
Results of Bulk X-ray Diffraction

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Appendix 3. Tabulation of the results of the diffractograms of the bulk oriented mounts. Q = quartz; A = opal-A; CT = opal-CT; Ca = calcite; Cl = clinoptilolite; S = smectite; I = illite; K = kaolinite; ML = mixed-layer clay; Ph = phillipsite; Ch = chlorite
An "X" indicates that the mineral is present. A "?" indicates that the mineral may be present but could not be identified with certainty.
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Results of Bulk Oriented X-ray Diffraction

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Appendix 4. A tabulation of the results of the diffractograms of the oriented clay fraction mounts. Q = quartz; A = opal-A; Ca = calcite; Cl = clinoptilolite; S = smectite; I = illite; K = kaolinite; ML = mixed-layer clay; Ch = chlorite
An "X" indicates that the mineral is present. A "?" indicates that the mineral may be present but could not be identified with certainty.
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Results of Oriented Clay Fraction X-ray Diffraction

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## APPENDIX 5
Coating and Treatment of Samples for SEM Analysis

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*also coated with C-AuPd*
PLATE I

a) A scanning electron micrograph of the sample at 6-6-1 (120-122). This micrograph shows an example of a sponge spicule which exhibits a highly pitted surface suggestive of dissolution. Other siliceous debris in the sample is found in a similar state of degradation. The sample is located 10 cm above the "chert" at 6-6-1 (130-132).

b) A scanning electron micrograph of the sample at 6-6-1 (147-149). Sponge spicules are shown which exhibit highly corroded surfaces suggestive of dissolution. The surrounding matrix is made up of coccoliths and clay. The sample is located 17 cm below the "chert" at 6-6-1 (130-132).

c) A scanning electron micrograph of the sample at 6-5-1 (18-20). The sample contains evidence for some dissolution of siliceous material. The siliceous frustules in this laminated clay are fragmented and generally lacking fine microstructure. The sponge spicules are pitted. The sample is located 18 cm below a "chert" which was not sampled.

d) A scanning electron micrograph of the sample at 6-5-1 (18-20). A close-up of radiolarian and diatom frustules in this siliceous sample exemplifies the paucity of microstructure found in this sample. This sample is located 18 cm below a "chert" which was not sampled.

e) A scanning electron micrograph of the sample at 6-6-1 (120-122). The diatoms found in this coccolith-rich clay exhibit a poorly preserved microstructure implying that the sample was a site of silica dissolution. The sample is located 10 cm above the "chert" at 6-6-1 (130-132).

f) A scanning electron micrograph of the sample at 6-6-3 (69-71). A pitted sponge spicule is shown in a state of degradation common to the siliceous material found in this coccolith-rich clay. The sample is located 2 cm above the "chert" at 6-6-3 (73-75).
PLATE II

a) A thin section of the "chert" at 6-6-1 (130-132) viewed in plane light. The large circular masses are sponge spicules with greatly enlarged internal diameter. The hemispherical and spherical bodies on the interior of the spicules are cristobalite spherules. Foraminifera and quartz grains are also found in the micrograph. This is a site of silica precipitation.

b) A thin section of the "chert" at 6-6-1 (130-132) viewed in plane light. Foraminifera and quartz grains as well as sponge spicules (some infilled with silica) are seen in a matrix of clay.

c) A thin section of the "chert" at 6-6-1 (130-132) viewed with crossed nicols. Both fibrous quartz (chalcedony) and GMC quartz may be seen filling the interior of sponge spicules. This is a site of silica precipitation.

d) A thin section of the "chert" at 6-6-1 (130-132) viewed with crossed nicols. GMC quartz may be seen filling the intersticies of sponge spicules. Cristobalite spherules are also present as part of the void filling of the spicules.

e) A scanning electron micrograph of a fracture surface of the "chert" at 6-6-1 (130-132). The interior of the sponge spicule (broken obliquely to its long axis) is lined with bladed opal-CT. Spherulitic opal-CT may be noted as a pillar growing from the completely filled portion of the sponge spicule. This is a site of silica precipitation.

f) A scanning electron micrograph of a fracture surface of the "chert" at 6-6-1 (130-132). The interior of the sponge spicule is lined with bladed opal-CT crystallites. The spherical objects in the interior are cristobalite spherules. These are authigenic growths indicative of a site of silica precipitation. Void filling seems to be the initial stage of silica precipitation.
a) A scanning electron micrograph of an HCl-etched fracture surface of the "chert" at 6-6-1 (130-132). An internal cast of a foraminifera is shown. The punctae are also filled with silica, indicating the solution from which the material filling the test chambers were precipitated had communication with the exterior pore fluids.

b) A low magnification scanning electron micrograph of the "chert" at 6-6-3 (73-75). A bedding plane of a silicified shale is shown. Little can be discerned from the micrograph concerning the silification process.

c) A scanning electron micrograph of an HCl-etched fracture surface of the "chert" at 6-6-3 (73-75). Etching has resolved smoother areas where the sediment is better silicified.

d) A scanning electron micrograph of an HCl-etched fracture surface of the "chert" at 6-6-3 (73-75). Etching has created an undulating surface reflecting differential amounts of induration by silification. Impressions of coccoliths and discoasters may also be seen.

e) A scanning electron micrograph of an HCl-etched fracture surface of the "chert" at 6-6-3 (73-75). A silica-infilled foraminifera chamber is seen in the upper left corner. Impressions of coccoliths and discoasters may also be seen. The chamber filling in this weakly silicified "chert" suggests that void filling may be the initial stage of the silification of this "chert".

f) Two thin section photomicrographs, the upper in plane light, the lower under crossed nicols, of the "chert" at 6-6-3 (73-75). In plane light (upper picture) the rounded area is seen to be filled by cristobalite spherules and a second generation infilling. Under crossed nicols (lower picture) the second generation infilling is shown to be fibrous quartz. The spherules are weakly birefringent.
PLATE IV

a) A thin section of the "chert" at 8A-2-1 (11-14) viewed in plane light. A radiolarian test partially filled with cristobalite spherules is seen in the center of the photomicrograph. The light areas in the remainder of the photograph are areas of greater silicification. The sample is siliceous but richer in clay than the other variety of "chert" found at this site (Plate IVc).

b) A thin section of a radiolarian in the "chert" at 8A-2-1 (11-14) viewed in plane light. The chamber contains well developed zeolite crystals (clinoptilolite). Cristobalite spherules may be seen growing from a zeolite crystal (center) and growing from the interior wall (right and top). The clay appears somewhat transparent, suggesting silicification of the clay matrix to some degree.

c) A low magnification thin section photomicrograph of the "chert" at 8A-2-1 (20-22) viewed in plane light. The radiolarians (round clear areas) are more abundant here than in areas not as well silicified at this same site (such as Plate IVa). Most of the radiolarians are completely filled by silica phases.

d) Two thin section photomicrographs, the upper viewed in plane light, and the lower viewed with crossed nicols, of the "chert" at 8A-2-1 (20-22). A radiolarian test displaying a prominent growth of cristobalite spherules is seen. Under crossed nicols the remainder of the chamber is shown to be filled by fibrous quartz.

e) A scanning electron micrograph of a fracture surface of the "chert" at 8A-2-1 (11-14). The radiolarian test is shown to be partially filled by cristobalite spherules. The zeolite, clinoptilolite, is shown to be intergrown with the spherules, suggesting co-precipitation. The zeolites seem to be more numerous toward the center of the cavity, suggesting development in the latter stages of opal-CT precipitation. The clays of the matrix still retain their flakey character, implying slight silicification.

f) A scanning electron micrograph of a fracture surface of the "chert" at 8A-3-1 (5-7). The intimate intergrowth of opal-CT spherules and clinoptilolite in a radiolarian vug is well exemplified here. The co-precipitation of these minerals seems to take place toward the latter stage of opal-CT precipitation.
PLATE V

a) A scanning electron micrograph of a fracture surface of the "chert" at 8A-2-1 (11-14). The incorporation of a zeolite crystal into cristobalite spherules in a radiolarian chamber is indicative of the co-precipitation of clinoptilolite and opal-CT. Blades of opal-CT may be seen growing into the clinoptilolite crystal.

b) A scanning electron micrograph of a fracture surface of the "chert" at 8A-3-1 (31-33). This chert is characterized by very complete infilling of radiolarian test chambers. The circular areas outline the boundaries of radiolarian tests. The clay matrix does not retain its distinct flakey appearance as in Plate IVe, suggesting that this "chert" is better indurated.

c) A scanning electron micrograph of a fracture surface of the "chert" at 8A-2-1 (20-22). Two radiolarian tests are shown. The one on the left is almost completely filled with silica. Remaining void space is being filled by coarse crystals of opal-CT. The indurated clay matrix is well exemplified.

d) A scanning electron micrograph of an HF-etched fracture surface of the "chert" at 8A-2-1 (20-22). Octahedral crystals of high cristobalite are seen growing from a substrate of smaller radiolarian void-lining crystals of similar octahedral nature. The crystals are somewhat elongated along one crystallographic axis, suggesting differential growth rates.

e) A scanning electron micrograph of an HF-etched fracture surface of the "chert" at 8A-2-1 (20-22). The hexagonal plates are high tridymite occupying an incompletely filled radiolarian chamber. They are seen growing with high cristobalite. The hexagonal plates are in the expected epitaxial growth position for intergrowth of high cristobalite and high tridymite.

f) A high magnification scanning electron micrograph of a fracture surface of the "chert" at 8A-2-1 (20-22). These radiolarian void-lining crystals are much coarser and more tabular than the typical opal-CT crystallites shown in Plate VIa.
PLATE V

[Images of micrographs with scale bars indicating measurements in micrometers]
PLATE VI

a) A high magnification scanning electron micrograph of a fracture surface of the "chert" at 8A-2-1 (37-39). The morphology characteristic of the opal-CT crystallites forming cristobalite spherules is shown. The blade-like habit of opal-CT is well exemplified.

b) A scanning electron micrograph of an HF-etched fracture surface of the "chert" at 8A-2-1 (20-22). The relationship between the matrix, the radiolarian test and the void filling of high cristobalite and high tridymite is indicated.

c) A scanning electron micrograph of an HF-etched fracture surface of the "chert" at 8A-2-1 (29-22). A grouping of crystal aggregates of high cristobalite and high tridymite is shown in a partially filled radiolarian chamber. The epitaxial relationships between the two crystals is indicated in several orientations. The coarse crystal substrate from which these unusual crystals are growing is also visible.

d) A scanning electron micrograph of an HF-etched fracture surface of the "chert" at 8A-2-1 (11-14). A partially filled radiolarian test is shown. The HF has removed much of the blade-like habit from the spherules seen in the upper right. Etching also reveals rounded bodies similar in size to these opal-CT spherules filling the remainder of the cavity.

e) A scanning electron micrograph of an HF-etched fracture surface of the "chert" at 8A-2-1 (37-39). A completely filled radiolarian test is shown. The chamber is filled with small round bodies the same size as cristobalite spherules.

f) A scanning electron micrograph of an HF-etched fracture surface of the "chert" at 8A-2-1 (27-39). In this higher magnification of the interior of a filled radiolarian test, a tri-radiate fracture pattern in the round spherule-like bodies is revealed.
PLATE VII

a) A scanning electron micrograph of an HF-etched fracture surface of the "chert" at 8A-3-1 (5-7). In this almost completely silica-infilled radiolarian chamber, the co-precipitation of clinoptilolite and opal-CT spherules is revealed by etching. This demonstrates that the co-precipitation of silicate phases continues to the complete filling of the void space.

b) A scanning electron micrograph of an HF-etched fracture surface of the "chert" at 8A-3-1 (31-33). One (center) and possibly a second (left of center) zeolite is shown to have grown in the clay. This indicates a possible segregation of microenvironments in this "chert". The filling of radiolarian chambers (Plates Vd-f) is high cristobalite and high tridymite, whereas the zeolites are confined to the clay matrix.

c) A thin section of sample 8A-3-1 (27-29) viewed in plane light. Well developed clinoptilolite crystals are seen partially filling a radiolarian test. Smaller opal-CT spherules are also present, best shown on the upper left of the chamber. The test wall does not appear to be intact.

d) A scanning electron micrograph of the sample at 8A-2-1 (28-30). Abundant well developed clinoptilolite crystals characterize this unsilicified silty zeolitic clay. The zeolites are associated with degraded, fragmented radiolarian frustules. The clay is in distinct flakes.

e) A scanning electron micrograph of the sample at 8A-2-1 (28-30). Several fragmented siliceous microfossils are present. The surface of the diatom frustules in the center is pitted, suggesting the sample has undergone some dissolution of silica.

f) A scanning electron micrograph of the sample at 8A-2-1 (28-30). This sample, described as a silty zeolitic clay, contains numerous diatoms. The diatom frustules are fragmented and generally lack fine microstructure, implying dissolution of silica in this sample.
PLATE VII

Image a: 10 μm
Image b: 10 μm
Image c: 50 μm
Image d: 50 μm
Image e: 10 μm
Image f: 20 μm
PLATE VIII

a) A scanning electron micrograph of the sample at 8A-3-1 (27-29). Several euhedral zeolite crystals are shown in the clay. Small spherical objects are seen on a clinoptilolite crystal near the center of the photograph. These spherical bodies appear to be small opal-CT spherules.

b) A scanning electron micrograph of the sample at 8A-3-1 (27-29). A vug in the clay is shown to contain many euhedral clinoptilolite crystals. These clearly show opal-CT spherules growing from the zeolites.

c) A high magnification scanning electron micrograph of the sample at 8A-3-1 (27-29). This micrograph is a close-up of the clinoptilolite crystal in the center of Plate VIIIb. The relationship of the small opal-CT spherules and the zeolite is well illustrated. The spherules are growing from the zeolite, suggesting they formed after the zeolite.

d) A thin section of the sample at 9A-1-4 (120-122) viewed in plane light. The two rounded areas in the clay matrix are approximately the size of radiolarian tests. The test walls have completely dissolved. A zeolite crystal is seen on the left side of the smaller circular void, along with some small round objects which may be opal-CT spherules.

e) A thin section of the 'chert' at 9A-1-4 (64-66) viewed in plane light. A rounded area similar in size to a radiolarian test is shown containing euhedral zeolite crystals and small rounded objects which may be opal-CT spherules. These rounded areas in this clay-rich sample are not numerous.

f) A scanning electron micrograph of an HF-etched sample at 9A-1-4 (120-122). The cavities are lined with small opal-CT spherules. Zeolites may be seen as co-precipitants.
a) A scanning electron micrograph of the "chert" at 9A-1-4 (64-66). Well developed euhedral clinoptilolite crystals are shown associated with abundant small cristobalite spherules in a vug in this sample.

b) A scanning electron micrograph of the "chert" at 9A-1-4 (64-66). Poorly developed zeolite crystal aggregates are found in the clay matrix of this "chert" as shown in this micrograph.

c) A scanning electron micrograph of the sample at 10-7-4 (128-130). This micrograph is characteristic of the sediment sampled at this site. Poorly preserved coccoliths and a minor amount of clay are shown.

d) A thin section of the sample at 13-3-1 (110-112) viewed in plane light. This sediment is described as a radiolarian ooze. The radiolarians are found in varying stages of degradation, suggestive of some dissolution.

e) A thin section of the "chert" at 13A-1-1 (87-89) viewed in plane light. The clear areas are better silicified than the calcareous clay matrix. The shape of these clearer areas is indicative of radiolarians, although no test walls are detectable.

f) A thin section of the sample at 13A-1-1 (128-130) viewed in plane light. Poorly preserved radiolarians in a calcareous clay are seen. These radiolarians seem to have undergone some dissolution.
PLATE X

a) A scanning electron micrograph of the sample at 13-3-1 (110-112). The sediment is siliceous. Radiolarians and diatoms are abundant. The frustules do not exhibit much evidence of excessive dissolution.

b) A scanning electron micrograph of the sample at 13A-1-1 (128-130). The radiolarian seen at the left is an example of the moderate state of preservation of the siliceous biofragments in the sample. Dissolution has removed the walls which separate the pores resulting in the joining of two pores.

c) A scanning electron micrograph of the sample at 13A-1-1 (128-130). Well developed zeolites are found in this sample associated with siliceous biogenic material. The sample contains abundant coccoliths and some clay as well as fragments of siliceous biogenic material.

d) A low magnification scanning electron micrograph of a fracture surface of the "chert" at 13A-1-1 (87-89). Rounded areas, smoother than the matrix, are present. These areas are similar in size and shape to radiolarian frustules.

e) A low magnification scanning electron micrograph of an HF-etched fracture surface of the "chert" at 13A-1-1 (87-89). The etching has more clearly defined the areas of smooth texture as radiolarian frustules. However, the test walls do not seem to be present. Much calcareous material has been incorporated into the chamber filling.

f) A scanning electron micrograph of an HF-etched fracture surface of the "chert" at 13A-1-1 (87-89). A close-up of the boundary between the calcareous matrix and the filling of a radiolarian test is shown. No test wall can be detected. A tri-radiate fracture pattern is revealed (as in Plate VIIf), suggesting infilling by cristobalite spherules. A coccolith (left) has been incorporated into the silica infilling.
PLATE XI

a) A scanning electron micrograph of an HCl-etched fracture surface of the "chert" at 13A-1-1 (87-89). Impressions of coccoliths are revealed, indicating that silicification is not restricted to the interior of radiolarian tests but has affected the calcareous matrix of this sample.

b) A scanning electron micrograph of an HCl-etched fracture surface of the "chert" at 13A-1-1 (87-89). There is no test wall between the cristobalite spherules and zeolites in the cavity on the right and the calcareous matrix on the left.

c) A high magnification scanning electron micrograph of an HCl-etched fracture surface of the "chert" at 13A-1-1 (87-89). The zeolites found in the calcareous matrix exhibit opal-CT spherules growing from them. This suggests that zeolite growth preceded opal-CT formation in this matrix.

d) A scanning electron micrograph of an HF-etched fracture surface of the "chert" at 13A-1-1 (87-89). A line profile for Ca is superimposed over the micrograph. The intensity of Ca K-alpha radiation does not decrease across an area which has been silicified to a greater extent than the more calcareous matrix. The silicification process does not seem to have altered the amount of calcium present.

e) A scanning electron micrograph of an HF-etched fracture surface of the "chert" at 13A-1-1 (87-89). A line profile for Si is superimposed over the micrograph. There is an increase in Si K-alpha radiation over areas of silicification suggesting that these are sites of localization of silica.

f) A scanning electron micrograph of the sample at 19-9-5 (101-103). The micrograph is characteristic of those viewed of this sample. The sediment is calcareous, predominantly coccoliths. Little clay was observed. Some carbonate diagenesis has occurred as may be noted by the calcite overgrowths on the coccoliths.
a) A scanning electron micrograph of the sample at 19-11-4 (75-77). The sediment is calcareous, predominantly coccoliths and other calcareous biogenic debris. Little clay is observed.

b) A scanning electron micrograph of an HF-etched fracture surface of the silicified chalk at 98-7-4 (110-114). The weakly silicified chalk consists predominantly of coccoliths with some foraminiferas and discoasters.

c) A scanning electron micrograph of an HF-etched fracture surface of the chert at 98-7-4 (110-114). The micrograph shows that the chert was originally a coccolith ooze similar to that shown in Plate XIIb.

d) A scanning electron micrograph of an HF-etched fracture surface of the chert at 98-7-4 (110-114). In this micrograph, coccoliths and a foraminifera (?) may be seen. The chert is homogeneous in character except where some calcareous material still remains unsilicified.

e) A scanning electron micrograph of an HCl-etched fracture surface of the silicified chalk at 98-7-4 (110-114). The removal of much of the calcareous material has revealed that the pore spaces are occupied by opal-CT spherules. A cast of foraminifera chambers may be seen in the right side of the micrograph.

f) A scanning electron micrograph of an HCl-etched fracture surface of the silicified chalk at 98-7-4 (110-114). The matrix between two foraminifera chambers is shown to contain cristobalite spherules with zeolites as intergrowths.
PLATE XIII

a) A scanning electron micrograph of a fracture surface of the chert and silicified chalk at 98-7-4 (110-114). A line profile for Si is superimposed over the micrograph. The transition between the silicified chalk (right) and chert (left) is shown. The textural change from a porous calcareous chalk to a dense homogenous non-porous chert occurs over a few millimeters. Silicon K-alpha radiation increases as the chert is approached, indicating that localization of silica is greater in the chert than in the chalk.

b) A thin section of the sample at 108-2-1 (98-100) viewed in plane light. A biogenic ooze is shown, containing both calcareous and siliceous biogenic debris.

c) A scanning electron micrograph of the sample at 108-2-1 (98-100). The biogenic material is fragmented and not well preserved. This sample contains mostly calcareous material; however, some siliceous material is also present.

d) A scanning electron micrograph of the sample at 108-3-1 (70-72). This sample contains abundant diatoms and coccoliths. The diatoms are broken, although much of their microstructure is preserved. The carbonate debris is better preserved than in Plate XIIc.

e) A scanning electron micrograph of the sample at 118-13-1 (42-44). This sample, like 118-14-1 (38-40) in Plate XIIIe, is a compact clay containing highly degraded coccoliths.

f) A scanning electron micrograph of the sample at 118-14-1 (38-40). This sample, as in Plate XIIe, is a compact clay containing highly degraded coccoliths.
PLATE XIII
PLATE XIV

a) A thin section of the sample at 140-3-2 (100-102) viewed in plane light. The laminated nature of this dense compact siliceous clay is well exemplified in this micrograph.

b) A thin section of the sample at 140-3-2 (100-102) viewed with reflected light. Numerous pyrite concretions are shown in the laminated clay. The non-reflective blebs are probably organic material.

c) A scanning electron micrograph of the sample at 140-3-2 (100-102). The laminated nature of the clay is well exemplified. A degraded diatom is also shown, characterizing the state of preservation of the siliceous material present.

d) A low magnification scanning electron micrograph of the sample at 140-3-2 (100-102). A pyrite concretion is shown displacing the laminated sediment surrounding it. The concretion is made up of framboidal pyrite spheres. A native sulfur crystal may be seen in the lower left portion of the concretion.

e) A high magnification scanning electron micrograph of the sample at 140-3-2 (100-102). Some of the pyrite concretions are composed of this octahedral pyrite. Framboidal and octahedral pyrite were not observed together in the same concretion.

f) A scanning electron micrograph of the sample at 140-3-2 (100-102). A cluster of small gypsum rosettes is shown in the clay of this sample. The round objects scattered among the rosettes' blades are probably pyrite frambooids.
PLATE XV

a) A low magnification scanning electron micrograph of the sample at 140-3-2 (100-102). The selenite variety of gypsum found in this sample is shown. The large crystals are euhedral, though some faces are irregular due to growth into a clay matrix.

b) A scanning electron micrograph of the sample at 140-3-2 (100-102). This micrograph is a close-up of the native sulfur crystal observed in Plate XIVd. Its somewhat rounded edges are suggestive of slight post-precipitation degradation.

c) A scanning electron micrograph of the sample at 140-3-2 (100-102). Native sulfur crystals are shown to be growing in the laminated clay. They do not seem to be associated with a pyrite concretion.

d) A scanning electron micrograph of the sample at 140-3-2 (100-102). Euhedral crystals of clinoptilolite are shown growing in a disk-shaped vug in the laminated clay. The presence of authigenic zeolites is evidence for some mobility of silica.

e) A thin section of the sample at 144-1-4 (75-77) viewed in plane light. The sample is rich in foraminifera. Some coccoliths and siliceous biogenic material are also present.

f) A scanning electron micrograph of the sample at 144-1-4 (75-77). Fragments of both calcareous and siliceous biogenic material are seen. Both types of biogenic debris are found in a moderate state of preservation. This may be indicative of mechanical abrasion during resedimentation.
a) A scanning electron micrograph of the sample at 144-1-4 (75-77). Numerous siliceous microfossils may be seen. The microstructure of these tests is moderately preserved. Much calcareous material is also present.
VITA

John Arthur Klasik, son of John Klasik and Ruth E. Klasik, was born in Dobbs Ferry, New York on April 28, 1948. He attended the Dobbs Ferry Public School system and graduated from High School in June 1966. He did his undergraduate studies at the State University of New York at Stony Brook. Upon receiving his Bachelor of Science degree in geology from SUNY at Stony Brook in June 1970, he began his graduate studies at Duke University in September 1970. In August 1972 he was awarded a Master of Arts degree from Duke for completion of graduate studies there. He entered the doctoral program in the Department of Geology at Louisiana State University in September 1972. He received his Doctor of Philosophy degree in geology from Louisiana State University in December 1976. He was a geology instructor at the University of New Orleans for the academic year 1976-1977.

He married the former Jeralyn Sue May on July 15, 1975.
EXAMINATION AND THESIS REPORT

Candidate: John Arthur Klasik

Major Field: Geology


Approved:

[Signatures]

Major Professor and Chairman

Dean of the Graduate School

EXAMINING COMMITTEE:

[Signatures]

Date of Examination:

November 16, 1976