

12. CHERT AND SILICA DIAGENESIS IN SEDIMENTS FROM THE CENTRAL PACIFIC¹

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ABSTRACT

Chert recovered during Leg 17 of the Deep Sea Drilling Project in the central Pacific consists of porcelanitic and quartzose nodules and beds. Porcelanitic chert made of disordered cristobalite is found in clay-rich sediments, while quartzose nodules are restricted to carbonate environments. It is suggested that the mineralogical nature of the chert is directly influenced by the composition of the sediments in which it develops, and the roles of foreign cations and permeability are emphasized.

Recrystallization of silica appears to result from differences in solubility between amorphous and crystalline silica. The transfer from amorphous to crystalline forms might be controlled by the nature of the silicates present in the sediments.

INTRODUCTION

Since scientists from the first legs of the Deep Sea Drilling Project recognized that chert was widely spread in ocean basins, in the lowermost Tertiary and older sediments, much interest has been shown in trying to understand the processes involved in its formation. Although progress has been made in determining the nature of the chert, no satisfactory explanation has been given to account for its worldwide distribution as well as for its preferential occurrence in some sections of the stratigraphic column. The purpose of this study is to present some new observations and use the diversity of chert-bearing sediments recovered in the central Pacific to try a new approach to the question.

During Leg 17, chert was encountered in very different sedimentary environments and the mineralogical nature of the chert appears to be strongly influenced by the composition of the host sediments. This observation is used as a guide to investigate the processes involved in the diagenetic recrystallization of silica.

Although the chert studies here is exclusively that recovered from central Pacific sediments, the author believes that the conclusions reported in this paper could apply to the deep-sea cherts from most oceanic basins.

NATURE OF THE CHERT

Occurrence

Chert was found at every Leg 17 site (Figure 1). It lies predominantly in lower Tertiary sediments but is very common also in Mesozoic layers (Table 1). It occurs in biogenic sediments (calcareous and siliceous) as well as in deep-sea brown zeolitic clays.

Stratigraphic Setting

Most of the chert encountered during earlier drilling is reportedly of lowermost Tertiary age and older, with very rare younger occurrences in Oligocene and even more recent sediments. A detailed investigation of the stratigraphic occurrences of chert recovered by drilling in the Atlantic and Pacific shows that there are, in fact, considerable variations in the age of the youngest chert reported, not only in the post-Eocene sediments but also within the middle and lower Eocene stratigraphy. However, on a regional basis the correlation of the chert distribution in the stratigraphic column is usually rather good. For example, such a correlation can be observed at Sites 33 and 34 in the eastern Pacific for some middle Miocene chert (McManus et al., 1970); at Sites 62 and 63 in the western Pacific where the youngest chert is of late Oligocene age (Winterer et al., 1971); and is especially striking at Sites 70, 71, and 72 in the equatorial Pacific (Tracey et al., 1971) where upper Oligocene chert is reported in sediments of exactly the same age (*Theocyrtis annosa* radiolarian zone). This distribution implies that the occurrence of chert is not related to a simple overburden or late diagenesis effect independent of the stratigraphy. If this were the case, the occurrence of the younger chert would be more randomly distributed in the stratigraphic scale.

At all of the Leg 17 sites the youngest occurrence of chert constitutes an abrupt change in the lithology. Generally it occurs in middle Eocene sediments except at Site 164 where chert is present in Oligocene layers. Whether or not such a lithologic change can be correlated on the seismic profiler with the top of the opaque layer is not completely established (see Ewing, this volume). As a rule the entire section cored in the central Pacific can be divided in three units (from bottom to top):

(1) Mesozoic sediments with variable amounts of chert: The variations in the abundance of chert are apparently not correlatable from one site to another although there seems to be a consistently smaller amount of chert occurrence

¹Lamont-Doherty Geological Observatory Contribution No. 1975.

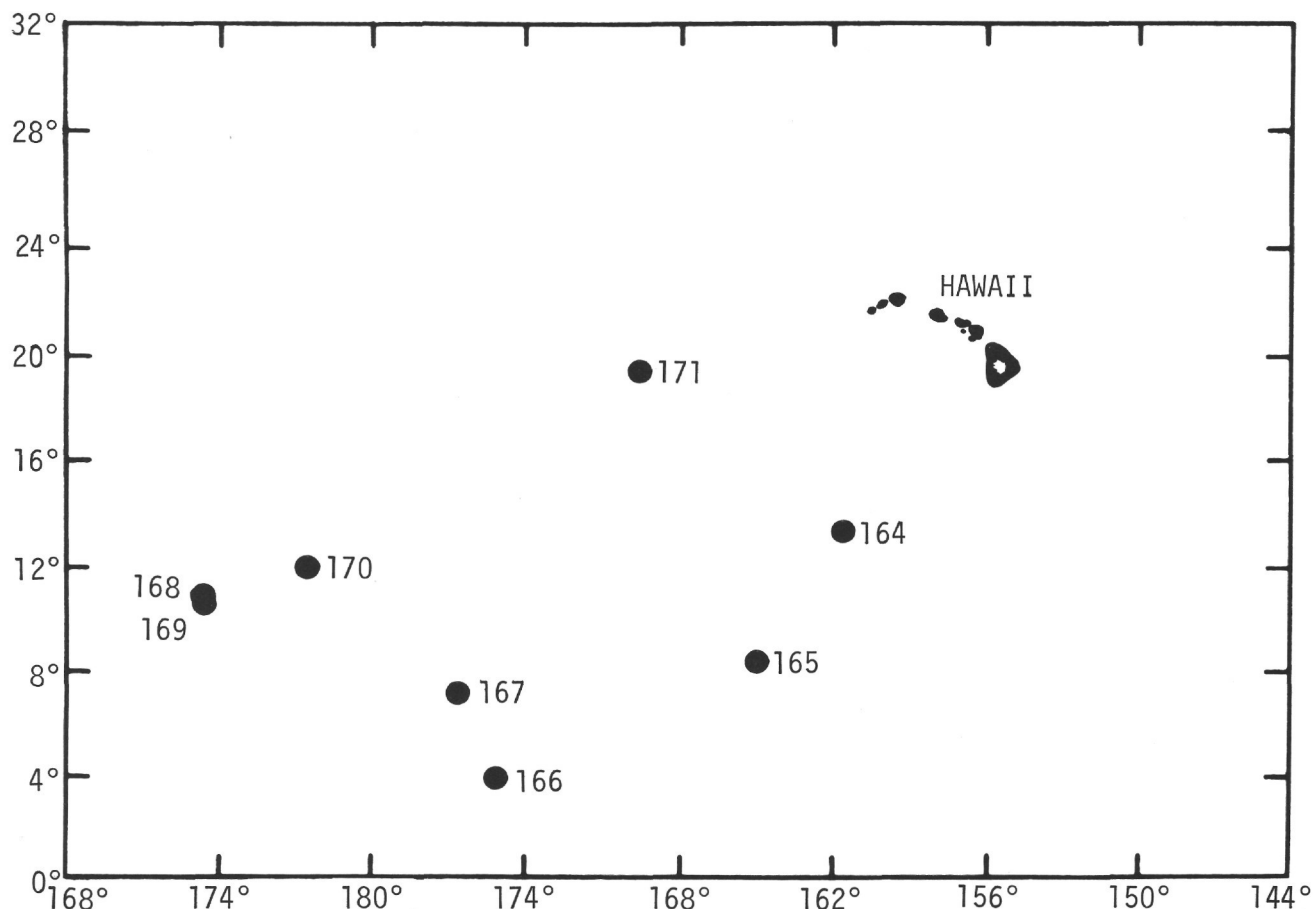


Figure 1. Location of drill sites.

near the base of the Maastrichtian and upper part of the Campanian.

(2) Lowermost Tertiary sediments with abundant chert: Most of the chert is restricted to the middle Eocene, but within this epoch regional correlations are possible. At Sites 164 and 165 in the Line Islands Chain a correlative occurrence can be observed in the lower-middle Eocene sediments (*Thyrsocyrtis triacantha* and *Podocyrtis ampla* radiolarian zones). Another regional correlation can be observed at Sites 166 and 167 where the youngest chert is of middle to late Eocene age (*Podocyrtis chalara* and *Podocyrtis goetheana* radiolarian zones).

(3) Post-Eocene sediments with very rare chert: Except for Site 164, the post-Eocene sediments recovered during Leg 17 do not contain chert. This observation apparently applies to the great majority of the deep-sea sediments in the world oceans.

Lithology of Host Sediments

The fact that chert was found in different kinds of pelagic sediments (biogenic and nonbiogenic) makes the analysis particularly interesting. Table 1 indicates the lithologic facies in which chert was found in Leg 17 cores.

It is especially interesting to note that sediments apparently devoid of any siliceous organisms, such as most of the upper Cretaceous brown clays of Site 164, contain relatively abundant chert.

It should also be noted that the volcanogenic sediments such as tuff and volcanic siltstones, very frequent at Leg 17 sites, are conspicuously devoid of chert. A detailed investigation of the mineralogical composition of the sediments shows that the chert-bearing sediments have some common characteristics. The most significant trends observed in the chert-bearing layers are: high K-feldspar/plagioclase ratio, high palygorskite/montmorillonite ratio, high clinoptilolite/phillipsite ratio. Obviously further detailed analysis is required to establish more firmly these correlations as the X-ray analyses were only performed on a rather random sampling of the sedimentary column at each site (see X-ray mineralogy chapter in this volume). Site 164 provides the most useful data because the relatively small amount of biogenic components leaves a clear picture of the silicate distribution, even in the composition of bulk samples.

A general survey of the mineralogical composition of all the chert-bearing sediments reported in previous Deep Sea Drilling Reports has been attempted; and although correlations are rather imprecise for reasons mentioned above, the same general trends can be observed grossly; and no major contradictions have been found. It is also worth mentioning that the association of chert with silica-rich silicates such as palygorskite, sepiolite, and clinoptilolite on land is abundantly reported in the literature. For example, many of the lower Tertiary silicifications observed in sedimentary basins from the African continent are accompanied by important

TABLE 1
Summary of Chert Occurrence

Core Identification	Nature of Chert	Nature of Sediments	Age of Sediments
164-3-2	Porcelanitic Chert	Radiolarian-rich zeolitic clay	Early Oligocene
164-4-1	Porcelanitic chert	Clayey radiolarian ooze	Middle Eocene
164-6-1	Porcelanitic chert	Clayey radiolarian ooze	Middle to ? early Miocene
164-7-1	Porcelanitic chert	Zeolitic brown clay	? Late Cretaceous
164-7-5	Porcelanitic chert	Zeolitic brown clay	Late Cretaceous
164-8-1	Porcelanitic chert	Zeolitic brown clay	? Santonian to ? Campanian
164-10-1	Porcelanitic chert; fragments and beds or nodules	Zeolitic brown clay	? Santonian to ? Campanian
164-10-4			
164-11-1	Porcelanitic chert	Zeolitic brown clay	? Santonian to ? Campanian
164-11-2			
164-12-1	Porcelanitic chert	Zeolitic brown clay	? Santonian to ? Campanian
164-12-CC			
164-13-1	Porcelanitic chert	Zeolitic brown clay	? Santonian to ? Campanian
164-13-CC			
164-14-1	Porcelanitic chert	Zeolitic brown clay	? Santonian to ? Campanian
164-14-CC			
164-15-1	Porcelanitic chert	Zeolitic brown clay	? Santonian to ? Campanian
164-15-CC			
164-17-1	Porcelanitic chert	Zeolitic brown clay	Late Cretaceous
164-17-CC			
164-19-1	Porcelanitic chert	Zeolitic brown clay and claystone	Late Cretaceous
164-19-2			
164-19-3			
164-19-CC			
164-22-CC	Porcelanitic mudstone	Mudstone	Late Cretaceous
164-23-CC	Sand-size chert fragments (mainly recrystallized radiolarians)	No recovery	? Cenomanian-? Turonian
164-14-1	Small quartzose to chalcedonic chert fragments	Some coarsely crystalline calcite	?
164-25-1	Small quartzose to chalcedonic chert fragments	Mud containing common coccolites and some coarsely crystalline calcite	Albian
164-26-CC	Small quartzose to chalcedonic chert fragments	Mud containing rare coccolites	Albian
164-27-1	Quartzose chert nodules	No recovery	?
165A-14-CC	Small porcelanitic chert fragments	Radiolarian ooze	Middle Eocene
165A-15-CC	Small quartzose chert fragments	No recovery	Early-middle Eocene

TABLE 1 – Continued

Core Identification	Nature of Chert	Nature of Sediments	Age of Sediments
165A-16-CC	Quartzose chert	Limestone containing shallow-water carbonates (turbidite)	Late Maastrichtian
165A-17-1	Quartzose chert	Limestone	Late Cam
165A-17-CC			Campanian-early Maastrichtian
165A-23-CC	Recrystallized radiolarians	Volcanic siltstone	? Campanian-? Santonian
166-12-1	Porcelanitic chert nodule	Radiolarian ooze	Late Eocene
166-16-5	Porcelanitic chert	Brown clay and radiolarian ooze	Middle-late
166-17-CC	Porcelanitic chert	Ashy radiolarian ooze	Middle Eocene
166-18-2	Porcelanitic chert	Brown clay	?
166-18-CC			
166-19-3	Porcelanitic chert	Zeolitic siltstone	?
166-19-CC			
166-22-CC	Porcelanitic chert	Zeolitic brown clay	Early Cretaceous
166-23-2	Porcelanitic chert	Zeolitic ashy mudstone	Early Creta Cretaceous
166-27-2	Quartzose chert breccia with drusy quartz veinlet	Zeolitic nanno-fossil marl	Hauterivian
166-28-1	Quartzose chert brecciated	Zeolitic nanno-fossil marl	Hauterivian
166-28-2			
167-33-1	Quartzose chert	Nannofossil chalk	Middle Eocene
167-33-CC			
167-34-CC	Quartzose chert	Nannofossil chalk	Middle Eocene
167-35-CC	Quartzose chert	Nannofossil chalk	Middle Eocene
167-36-CC	Quartzose chert	Partly silicified nannofossil limestone	Middle Eocene
167-37-CC	Quartzose chert	Partly silicified nannofossil lime limestone	Middle Eocene
167-38-CC	Quartzose chert	Partly silicified nannofossil limestone	Paleocene
167-39-1	Quartzose chert	Partly silicified nannofossil limestone	Paleocene
167-39-CC			
167-40-CC	Quartzose chert	Partly silicified nannofossil limestone	Paleocene (Danian)
167-41-CC	Quartzose chert	Partly silicified nannofossil limestone and nannofossil chalk	Paleocene (Danian)
167-42-1	Quartzose chert	Chalky limestone	Middle
to 167-42-5			Maastrichtian

TABLE 1 – *Continued*

Core Identification	Nature of Chert	Nature of Sediments	Age of Sediments
167-43-2 167-43-CC	Quartzose chert fragments (drill cuttings)	No recovery	Middle Maastrichtian
167-44-1	Quartzose chert	Nannofossil chalk and limestone	Middle Maastrichtian
167-48-CC	Quartzose chert	Nannofossil chalk	? Maastrichtian ? Campanian
167-49-CC	Quartzose chert	Nannofossil chalk	? Campanian
167-50-CC	Quartzose chert	Nannofossil chalk	? Campanian
167-51-CC	Quartzose chert	Foraminiferal-nannofossil chalk	Campanian
167-52-1 167-52-CC	Quartzose chert	Nannofossil chalk	Campanian
167-53-1 167-53-CC	Quartzose chert	Nannofossil chalk	Campanian
167-54-CC	Quartzose chert	Nannofossil chalk	Campanian
167-55-CC	Quartzose chert	Nannofossil chalk	Campanian
167-56-CC	Quartzose chert	Nannofossil chalk	? Campanian- ? Santonian
167-59-3	Quartzose chert slightly porcelanitic	Marly limestone	? Turonian
167-60-2	Quartzose to porcelanitic chert	Marly limestone and tuffaceous limestone	Cenomanian
167-61-1	Quartzose to porcelanitic chert	Marly limestone	Cenomanian
167-62-2 167-62-3 167-62-4	Quartzose to porcelanitic chert	Marly limestone	Cenomanian
167-63-1 167-63-2 167-63-3	Quartzose chert, sometimes brecciated, and porcelanitic chert	Limestone, brecciated limestone, pebbly marly mudstone, and marly limestone	Cenomanian
167-64-1 to 167-64-5	Quartzose to porcelanitic chert	Limestone and marly limestone	Cenomanian
167-65-1 to 167-65-3	Quartzose chert	Limestone and tuffaceous limestone	Cenomanian
167-67-1 to 167-67-3	Quartzose chert	Limestone and tuff	Cenomanian
167-68-2 167-68-3	Quartzose and porcelanitic chert	Limestone and shale	Early Cretaceous
167-69-1 to 167-69-3	Quartzose and porcelanitic chert	Limestone and shale	Early Cretaceous
167-70-1 to 167-70-4	Quartzose chert	Limestone and shale	Early Cretaceous
167-71-1 167-71-2	Quartzose chert	Limestone and shale	Early Cretaceous
167-72-1	Quartzose chert	Limestone	Early Cretaceous
167-73-1 167-73-2	Quartzose chert	Limestone	Early Cretaceous (?Hauterivian)

TABLE 1 – *Continued*

Core Identification	Nature of Chert	Nature of Sediments	Age of Sediments
167-74-1 167-74-2	Quartzose chert	Limestone	Early Cretaceous Cretaceous
167-75-1	Quartzose chert	Limestone	Early Cretaceous Cretaceous
167-76-1 167-76-2	Quartzose chert	Limestone	Early Cretaceous
167-77-1	Quartzose chert	Limestone	Early Cretaceous
167-78-1	Quartzose chert	Limestone	Early Cretaceous
167-81-CC	Quartzose chert	Limestone	Early Cretaceous
167-82-CC	Quartzose chert	Silicified limestone	Early Cretaceous
167-84-CC	Quartzose chert	Limestone	Early Cretaceous
167-85-CC	Quartzose chert	No recovery	? Early Cretaceous to ? Late Jurassic
167-86-CC	Quartzose chert	No recovery	? Early Cretaceous to ? Late Jurassic
167-88-1	Quartzose chert	Limestone	? Early Cretaceous to ? Late Jurassic
167-92-1	Quartzose chert	Limestone	Berriasian-Late Tithonian
167-93-1 167-93-2	Quartzose chert	Limestone	Berriasian-Late Tithonian
167-94-1	Quartzose chert	Limestone	Tithonian
168-4-1 to 168-4-5	Small porcelanitic chert fragments	Zeolitic radiolarian bearing brown clay	Late Eocene
169-1-1	Porcelanitic chert	Zeolitic claystone	Late Maastrichtian
169-2-CC	Porcelanitic chert	Zeolitic mudstone	Late Maastrichtian
169-3-CC	Porcelanitic chert	Zeolitic clay with rare nannofossils	Campanian
169-8-CC	Quartzose chert	Nannofossil chalk	Cenomanian
169-9-CC	Quartzose chert	Nannofossil chalk	Early Cenomanian
169-10-CC	Quartzose to porcelanitic chert	Nannofossil-bearing zeolitic claystone	Late Albian
170-3-CC	Quartzose chert	Nannofossil chalk	Early Maastrichtian
170-4-CC	Quartzose chert	Limestone	Early Maastrichtian-Late Campanian

TABLE 1 – Continued

Core Identification	Nature of Chert	Nature of Sediments	Age of Sediments
170-5-CC	Quartzose chert	Limestone	Late Campanian
170-12-CC	Pieces of ?quartzose chert (cavings)	Zeolitic brown clay and nannofossil chalk	Late Turonian
170-13-CC	Quartzose chert	Foraminiferal-nannofossil chalk	Early Cenomanian
170-14-CC	Quartzose chert	Nannofossil chalk	Early Cenomanian
171-9-1 to 171-9-6 171-9-CC	Small fragments of quartzose chert	Nannofossil-foraminiferal ooze	Middle Eocene to Maastrichtian
171-10-4 171-10-5 171-10-CC	Quartzose chert	Nannofossil-foraminiferal ooze	Maastrichtian
171-11-4 171-11-5 171-11-CC	Quartzose chert	Foraminiferal-nannofossil ooze	Maastrichtian
171-12-CC	Quartzose chert	Foraminiferal-nannofossil ooze	Maastrichtian
171-13-4 171-13-5 171-13-CC	Quartzose chert	Foraminiferal-nannofossil ooze	Maastrichtian
171-14-CC	Quartzose chert	Foraminiferal-nannofossil ooze	Maastrichtian
171-15-1 to 171-15-6 171-15-CC	Quartzose chert	Foraminiferal-nannofossil chalk	Maastrichtian
171-16-3 to 171-16-6 171-16-CC	Quartzose chert	Foraminiferal-nannofossil chalk	Maastrichtian
171-17-2 to 171-17-6 171-17-CC	Quartzose chert	Foraminiferal-nannofossil chalk	Maastrichtian
171-18-CC	Quartzose chert	Foraminiferal-nannofossil chalk	Maastrichtian
171-21-2 171-21-CC	Quartzose chert	Foraminiferal-nannofossil chalk	Campanian

accumulations of palygorskite (Millot, 1964). Similar observations have been mentioned in previous Deep Sea Drilling Reports (Rex, 1970; von Rad and Rösch, 1972).

Composition

The composition of the chert has been studied using three different methods: thin sections examination, X-ray diffraction analysis, and scanning electron microscope observations. In most cases the three methods have been used on the same sample or portion of sample so that they provide complementary observations.

Terminology

Before describing the results, it is necessary to point out some problems of terminology and to define the meaning of the terms used in this paper.

Various terms are used in the literature to designate diagenetic concentrations of silica in sedimentary environments. Chert and flint usually refer to hard nodules, and sometimes beds, that are largely quartz and/or chalcedony and show a conchoidal fracture and a vitreous luster. These terms are often opposed to porcelanite (or porcellanite) which designates low density, more or less porous and dull-lustered varieties of chert made of opaline silica or cristobalite (Bramlette, 1946; Ernst and Calvert, 1969). Although the term porcelanite is confusing, as it is used quite extensively, at least in Europe, to designate contact metamorphosed marls, it is wisely accepted and shall be used in this paper.

The term chert shall be used in a very broad sense to designate any recrystallized form of silica and the adjectives "quartzose" and "porcelanitic" shall precise its mineralogical nature.

Still more important problems arise from the variety of terms used to designate the different polymorphs of silica that enter the composition of chert (see Table 2).

Nonterrigenous silica appears in deep-sea sediments under different states of crystallization, ranging from amorphous to well-crystallized.

Amorphous silica is present in the tests of radiolarian and diatoms and in siliceous sponge spicules it is characteristic of biologically precipitated silica. A typical X-ray diagram of radiolarian ooze shows only a very broad and flat bulge of amorphous scattering, extending from about 2.9 to 4.8 Å, without any identifiable diffraction peak (Figure 2). Very often in the literature such amorphous silica is referred to as opal or opaline silica, although it has been long recognized that opal is a poorly but definitely crystallized form of silica (Levin and Ott, 1932, 1933). Flörke (1955) defined its structure and showed that opal was made of disordered cristobalite in which the stacking of "low" cristobalite layers is periodically interstratified with "low" tridymite layers. This disordered cristobalite is also sometime called opal-cristobalite. Typical X-ray diffraction traces from disordered cristobalite appear in Figure 3.

The term chalcedony is widely used for designating both a fibrous impure variety of quartz and cryptocrystalline quartz. In the latter case it is often used in the adjective form: chalcedonic quartz. This appears logical if one considers the identical X-ray signature of these varieties. However, as there is a clear and easy distinction between these two varieties under the microscope, in this report the name chalcedony shall be restricted to the fibrous variety of quartz, and microcrystalline to cryptocrystalline quartz shall be referred to as quartz.

Mineralogy of the Chert

Previous reports, and particularly the most detailed ones (Heath and Moberly, 1971; von Rad and Rösch, 1972; Berger and von Rad, 1972), have shown that deep-sea chert can be divided into two categories, namely, (1) porcelanitic cherts, predominantly disordered cristobalite, and (2) quartzose cherts composed of quartz and/or chalcedony. The same two types have been observed at Leg 17 sites. Furthermore, there appears to be a consistent relationship between the mineralogical nature of the chert and the composition of the sediments in which it is found. As a rule, chert occurring in clayey layers (zeolitic clays,

TABLE 2
Different Terminologies Used in Chert Mineralogy

Terms Used in This Report	Equivalent Terms Used in the Literature	Mineralogical Structure	Occurrence in Sediments (nonterrigenous)
Amorphous Silica	Opal, opaline silica	SiO ₄ tetrahedrons randomly oriented, high water content ^a	Tests of siliceous organism (radiolarians, diatoms, sponge spicules)
Disordered Cristobalite	Opal (Berger and von Rad, 1972) ^b Lussatite ^c (Berger and von Rad, 1972) Opal-cristobalite (Flörke, 1955) Cristobalite (DSDP X-ray reports)	Disordered stacking of "low"-cristobalite and "low"-tridymite layers ^a	porcelanitic chert; peripheral parts of quartzose chert nodules; partially silicified carbonate siliceous or shaly rocks
Chalcedony	Chalcedony	Optically fibrous quartz (slightly disordered quartz structure giving relatively broad quartz peaks on X-ray diagrams)	void filling and fracture filling in both quartzose and porcelanitic cherts
Quartz	Chalcedony ^d Quartz	Cryptocrystalline, microcrystalline, and coarsely crystalline quartz (broad to sharp quartz peaks on X-ray diagrams, depending on the size of the crystallites)	quartzose cherts, fracture filling in quartzose chert

^aSee X-ray diagrams in Figures 2 and 3.

^bOpal described by these authors appears intermediate between amorphous silica and disordered cristobalite (highly disordered cristobalite).

^cLussatite was described by Mallard (1890) as a fibrous variety of cristobalite.

^dSee text for explanation.

clayey radiolarian oozes, marls, and marly limestones) is predominantly disordered cristobalite, while chert in carbonate sediments is predominantly quartz. Quartzose chert in carbonates shows a tendency to form nodules, while in clays and marls porcelanitic cherts often occur in thin beds or as a mere impregnation of the sediment.

Cherts in Clays

Site 164 provides an exceptional opportunity to study the nature of chert in clay deposits, as the entire section consists of deep-sea brown zeolitic clays with only variable amounts of Radiolarians in the upper part and very rare carbonates near the base.

X-ray analysis shows that, except for the extreme base of the column, chert at Site 164 has a remarkably constant composition in the entire section ranging in age from middle Tertiary to early Cretaceous. It consists of abundant disordered cristobalite and variable amounts of quartz. It is clearly seen in thin sections (Figure 4) that quartz and/or chalcedony are concentrated only inside former voids that are probably radiolarian molds and that the matrix is disordered cristobalite. Whenever the voids appear unfilled or absent or filled with disordered cristobalite in thin sections, no quartz peak is observed on the X-ray diagrams (Figure 5). In fact it has been possible to verify under the microscope that each increase in the quartz/disordered cristobalite ratio observed on the diffractograms corresponds to an increase in the abundance of chalcedony-filled radiolarian molds. At the base of the section two samples show a different composition. They are made exclusively of quartz and chalcedony (164-24-CC and 164-25-CC). Their origin is not clear as the samples come apparently from drill cuttings. It is remarkable however, that their occurrence seems to correspond to a general change in the lithology as carbonate was observed in smear slides made from the same

sample. The carbonate components consist of abundant calcareous nannofossil and some coarsely crystalline calcite (fracture filling?).

The boundary between chert and nonsilicified sediment is rather transitional in nature. In thin sections the transition is marked by the disappearance of chalcedony fillings inside the radiolarian molds and a gradual outward increase in clay minerals and zeolite contents. X-ray diagrams confirm these observations (Figure 5). It is generally in such transitional zones that abundant small silica spherules made of blade-shaped radiating crystals are observed on scanning electron micrographs (Figures 6 and 7). They occur as a lining on the inner parts of voids (radiolarian molds). Similar spherules have been described by Wise and Hsü (1971), Wise et al. (1972), von Rad and Rösch (1972), and Berger and von Rad (1972). Wise et al. (1972) identified these spherules as disordered cristobalite by running X-ray diffraction analyses on insoluble residues from chalks and chalk inclusions in cherty radiolarian oozes. Some very small spherules have a strongly different shape, and it is not known at present if they also consist of reprecipitated silica (Figure 8).

The observations from Site 164 have been confirmed by analysis of samples from clay-rich layers at other Leg 17 sites. There seems to be a consistent correlation between the porcelanitic nature of the chert and the presence of clay minerals in the host sediments. A survey of the nature of the chert described in previous DSDP reports leads to similar conclusions.

Chert in Carbonates

The composition of the chert recovered from carbonate sediments is remarkably different from that described above. Macroscopically, chert nodules have a massive, hard, and dense aspect. They show a vitreous luster and con-

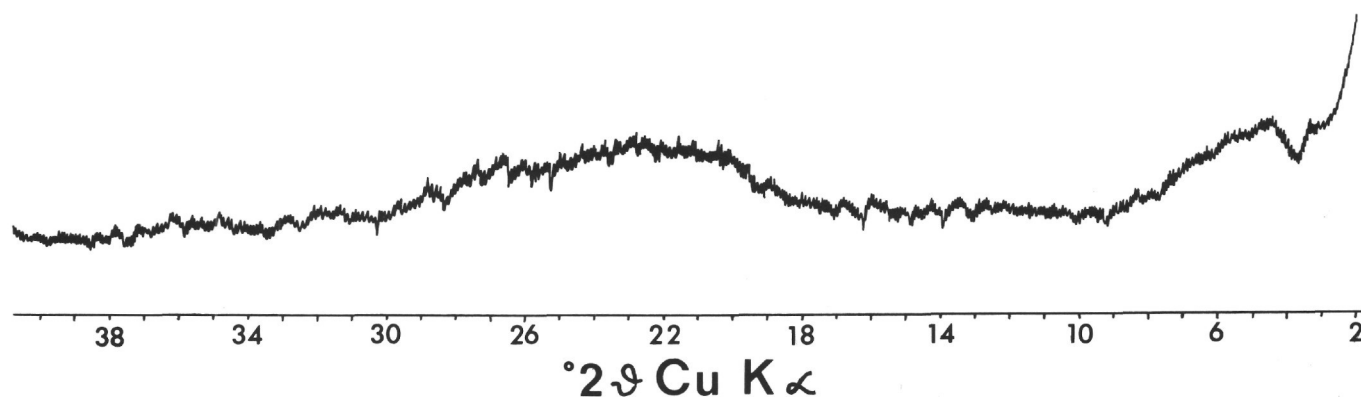


Figure 2. X-ray diffraction pattern of a radiolarian ooze (116-16-2, 150 cm).

choidal fracturing. Although the nodular form appears most common, thin layers and stringers were observed in the lower part of Hole 167.

X-ray analyses and thin section examination show that these cherts are composed almost exclusively of chalcedony and quartz. Disordered cristobalite is regularly observed only at the periphery of chert nodules and seems to be characteristic of the zone of transition from chert to the sedimentary matrix. X-ray diagrams indicate that quartz is predominantly "chalcedonic" in nature (either chalcedony or cryptocrystalline quartz) although very well-crystallized quartz is often found associated with fractures or geodes.

A typical aspect of these cherts in thin sections is that of a fine-grained mosaic of quartz with variable amounts of calcareous organism remains. These remains are usually well-preserved foraminifera that have had their chambers filled with chalcedony. In other cases they show evidence of dissolution and may even be completely replaced by silica (Figures 9 and 10). In one sample, small clusters of dark-brown needles are found associated with these chalcedony-filled foraminifera. Their definite mineralogical nature is unknown, and they are tentatively identified as rutile needles (Figure 11). In the lower part of Hole 167 (from Core 62 down) the carbonate lithification processes reach such an extent that sparry calcite has precipitated in some of the foraminifera chambers while others are filled with silica. Many of the foraminifera show cooccurrence of sparry calcite and silica (Figures 12 and 13). As calcite filling occurs only at subbottom depths (860 meters in this case) where the sediment overburden is sufficient to produce extensive lithification of the limestone, while silica-filled foraminifera are found much higher in the sediment column, sparry calcite can be considered a late diagenesis product. It probably precipitated preferentially in foraminifera chambers that had been left unfilled during previous silica precipitation. In some cases of cooccurrence of silica and calcite, it seems that calcite has been growing from the foraminifera tests and replacing part of the silica (Figure 13), although the order of crystallization cannot be clearly established.

The contact between chert and carbonate sediment is characterized by a transitional zone in which disordered cristobalite is the main component of the matrix, while chalcedony and quartz are restricted to the foraminifera and/or radiolarian chambers. The boundary between quart-

zose chert and disordered cristobalite is generally sharp and outlined by a concentration of impurities visible in thin sections (Figure 14). Carbonate inclusions in chert nodules are very common and show the same transitional zone. In most cases they are relatively small and are completely cemented by disordered cristobalite. The outer limits of the disordered cristobalite zone toward the original carbonate sediment is rather diffuse. Foraminifera chambers are generally void or lined with disordered cristobalite spherules of the same type as those described in porcelanitic cherts. Scanning electron micrographs show that small spherules are also present within the predominantly carbonate matrix in the immediate vicinity of the transitional zone. They seem to be responsible for some cementation of the carbonate ooze around chert nodules (Figure 15).

Chert in other Types of Sediments

During Leg 17 chert has been rarely found in sediments other than clays, radiolarian-rich clay, and calcareous sediments. However, at Site 166 some rare nodules of porcelanitic chert occur in a radiolarian ooze (Core 12). They consist of disordered cristobalite. Although the radiolarian ooze appears devoid of clay minerals in smear slides, X-ray diagrams show that these are present in a noticeable amount. Therefore, these cherts seem to have the same environmental basis as those found in clays.

MECHANISM OF CHERT FORMATION

The observations reported above allow for the consideration of possible mechanisms leading to the formation of concentrations of recrystallized silica in lithologically different sediments. Again the duality observed in the mineralogy of chert shall be emphasized in order to estimate the role of the sedimentary environment in chert formation.

Origin of Silica

The origin of the silica found in chert has been often debated, and no clear answer to the problem has been provided. Generally two different origins are considered: (1) alteration of volcanic material (montmorillonite and volcanic glass) and (2) dissolution of tests of siliceous organisms (radiolarian, diatoms, and sponge spicules). A volcanic origin could be invoked to explain both the absence of radiolarian remains in some silicified claystones

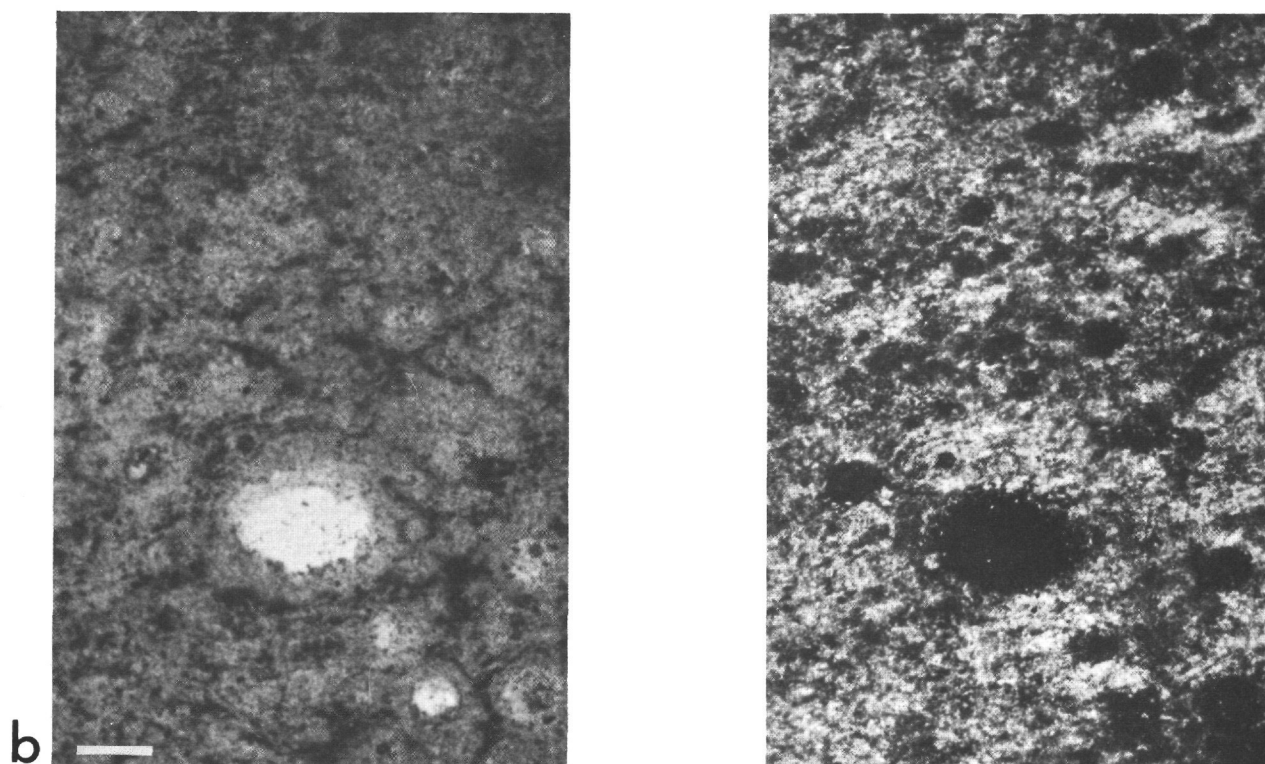
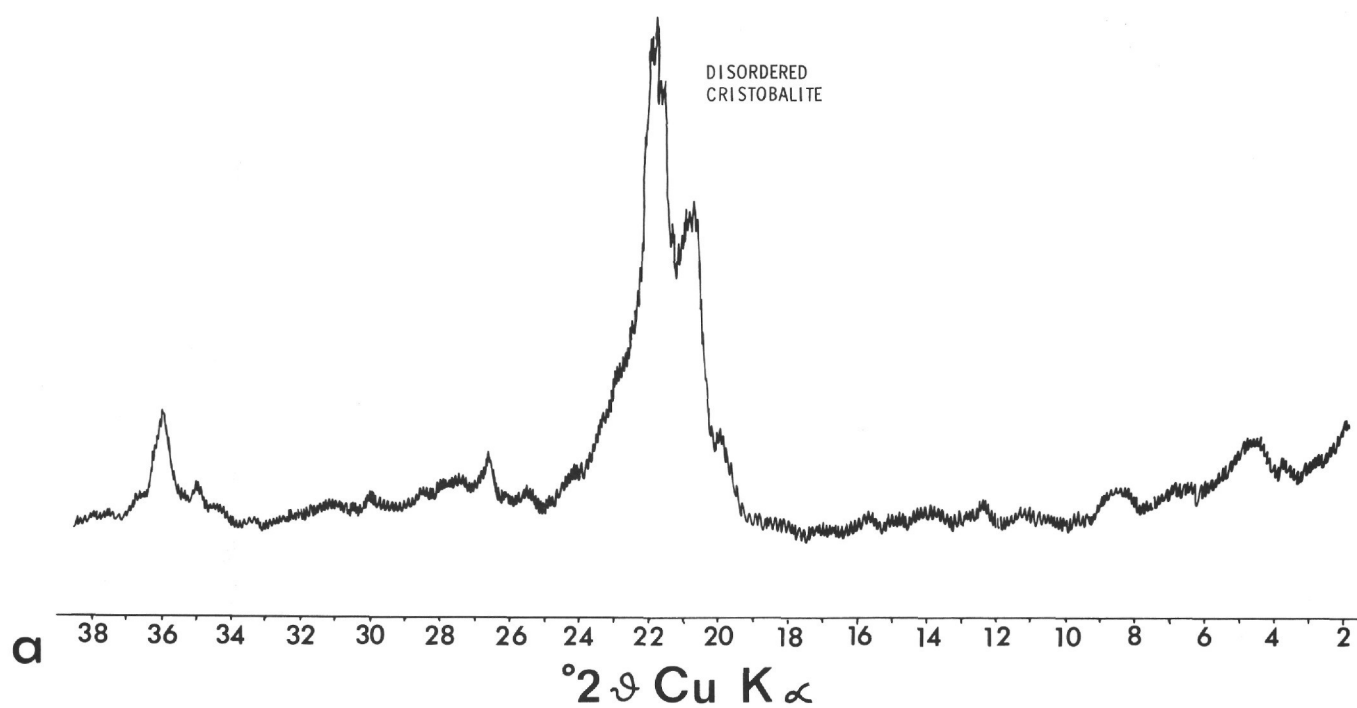


Figure 3. (a) *X-ray diffraction pattern of a porcelainitic chert devoid of quartz (164-14-1-20, 25 cm), (b) Aspect in thin section: most radiolarian molds have been filled with sediments and are replaced by disordered cristobalite. A large one remained unfilled and is devoid of silica. (left: plane polarized light; right: crossed nicols; white bar = 100 μ).*

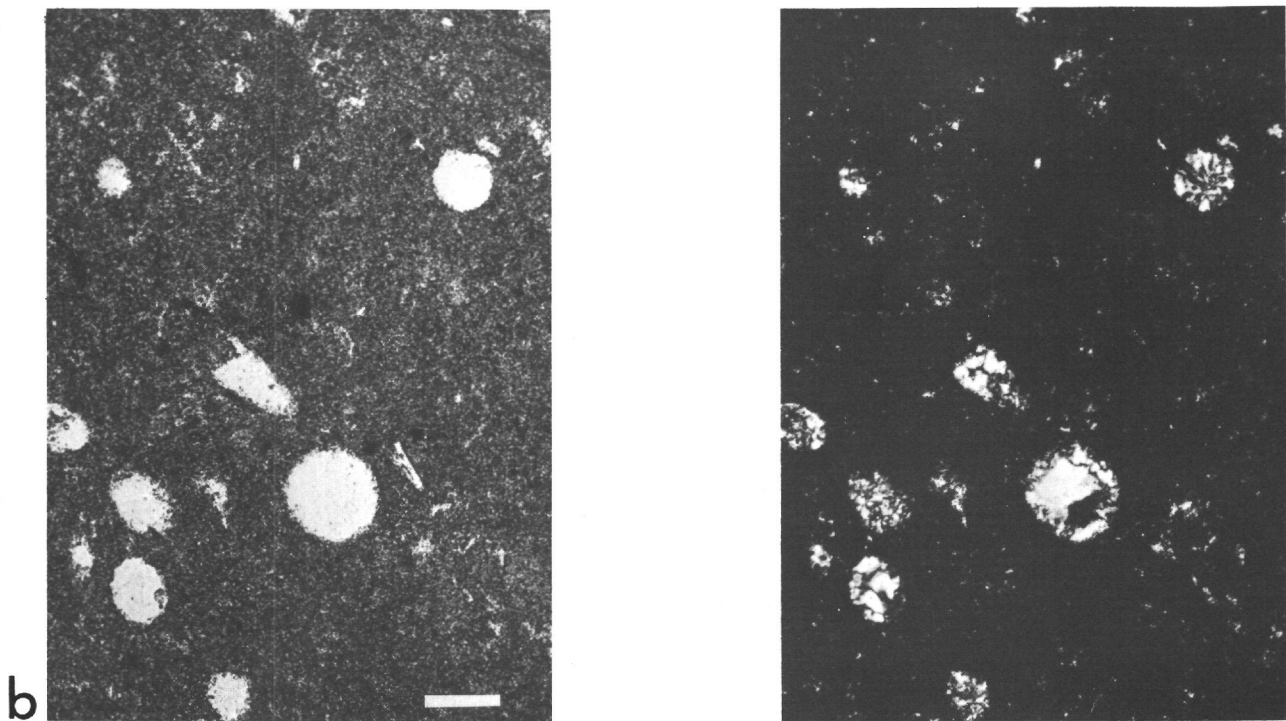
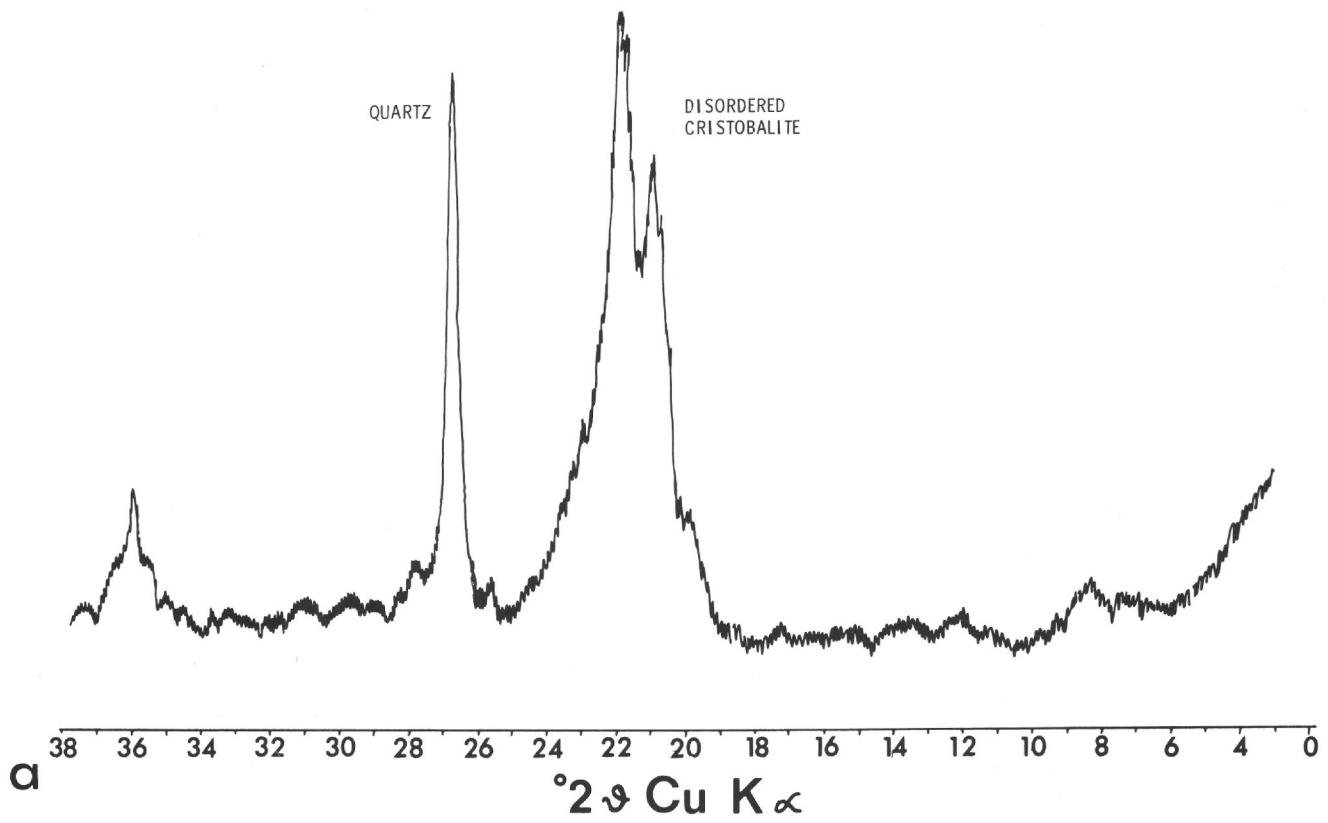


Figure 4. (a) X-ray diffraction pattern of a typical porcelanitic chert. Note the cooccurrence of disordered cristobalite and quartz. (164-13, CC), (b) Aspect in thin section: chalcedony is restricted to radiolarian molds. (left: plane polarized light; right: crossed nicols; white bar = 100 μ).

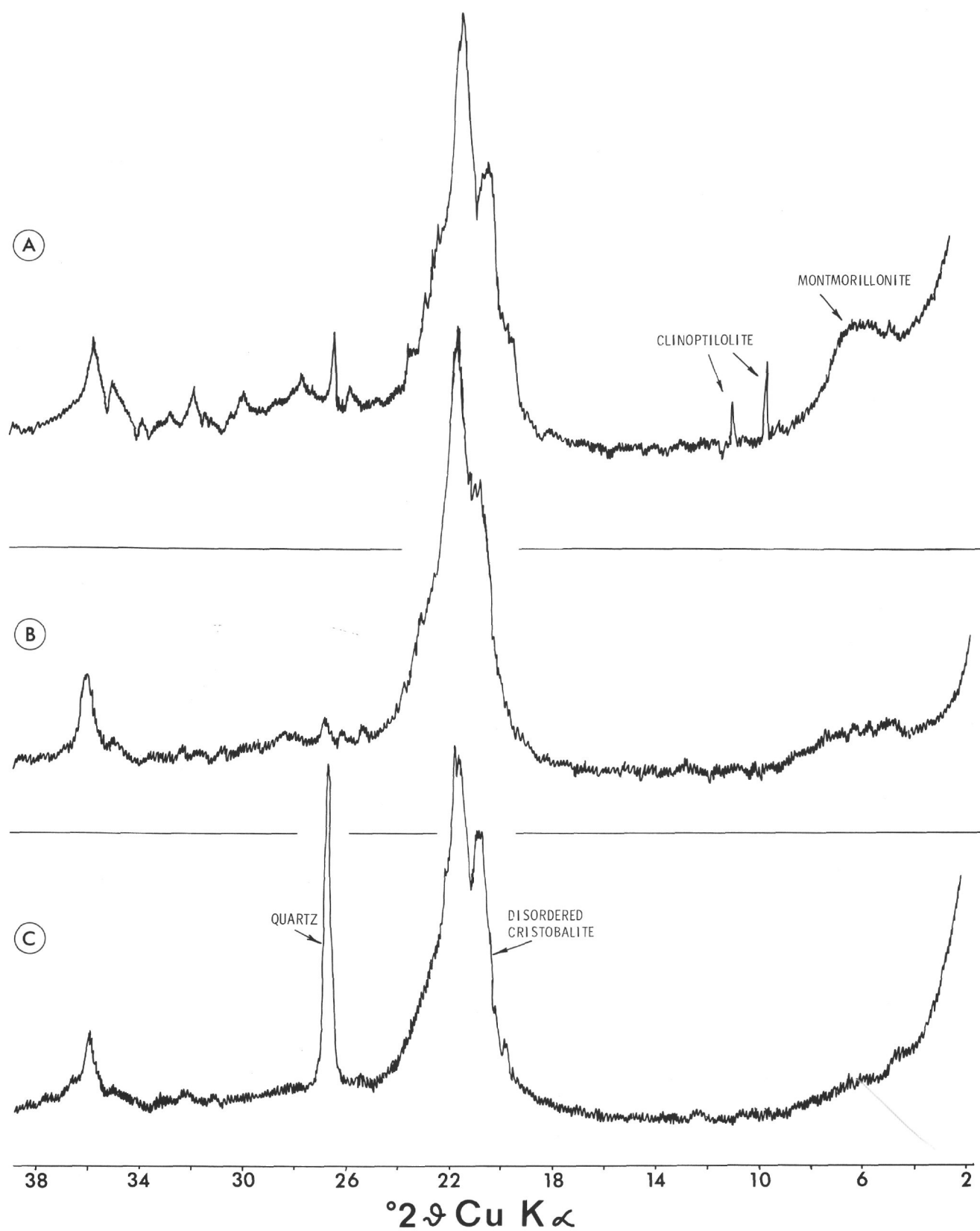


Figure 5. X-ray diffraction analysis of the transition between a porcelainitic chert nodule and the surrounding partly silicified sediment (164-4, CC). (a) Outer zone: mainly disordered cristobalite with some remnants of sediment (montmorillonite and clinoptilolite; rare quartz is here possibly detrital), (b) Intermediate zone: disordered cristobalite with rare clay minerals, (c) Inner part of nodule: disordered cristobalite and quartz (as in Figure 4).

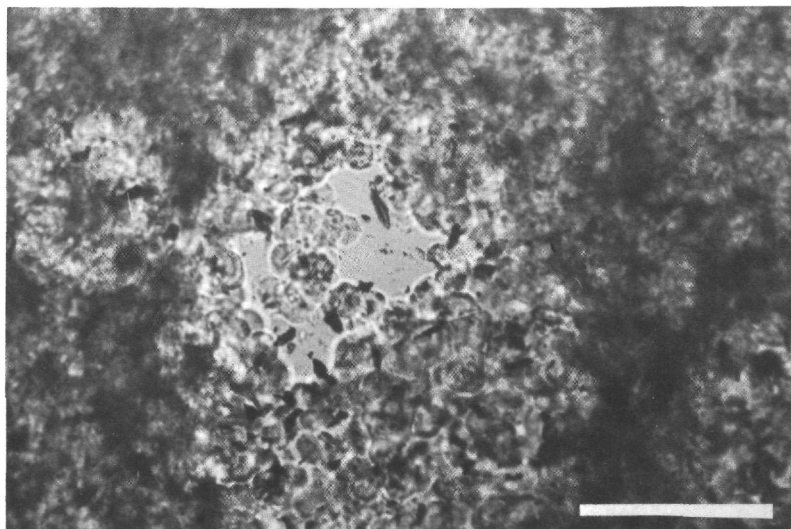


Figure 6. *Silica spherules (?disordered cristobalite) in a radiolarian mold.*
Thin section, plane polarized light; white bar = 100 μ (164-14, CC).

and the occurrence of well-preserved radiolarians in radiolarian mudstones. In the first case, the absence of remains would indicate that radiolarians were never present in the sediments, while in the second, the preservation of radiolarians would rule out the possibility that they dissolve and supply the necessary silica. At any rate it is clear that the density of chert nodules is such that their formation implies considerable concentration of silica. Obviously, as already noted by Heath and Moberly (1971), some circulation of silica-rich pore waters is required in the sediment over a range of centimeters to meters. In some cases the radiolarians might have been entirely dissolved, while in others they simply have been impregnated by silica-rich solution coming from nearby layers.

Observation of the sediments recovered from the vicinity of the youngest cherts at Site 167 strongly suggests that dissolution of radiolarians tests is the most probable source of silica. An interval of about 60 meters of radiolarian-nannofossil chalk is present above the chert-bearing layers (Cores 24-32). The Radiolarians in these late Eocene sediments are thick-walled and well-preserved. In Core 32, starting at about 1 meter above the chert, radiolarians show traces of dissolution which are observed in smear slides and in scanning electron micrographs (Figure 16). The same observation applies to sediments recovered between the chert nodules.

Radiolarians, diatoms, and spicules seem to be the most abundant amorphous silica in the sediments. Studies of solubility of silica in water show that this form of silica is by far the most soluble. Of course, in the vicinity of continents and under some particular climatic conditions, it is possible that large amounts of dissolved silica could have been delivered to the oceans. Nevertheless, as discussed later in this chapter, it appears that any primary input of silica in the water column is immediately used by siliceous organisms, and it is clear that large quantities of amorphous silica of biogenic origin are available in many deep-sea sediments. The solubility of amorphous and crystalline silica in water has been studied experimentally by Wey and

Siffert (1961), and the results show (Figure 17) that at room temperature the solubility of amorphous silica reaches 120 to 140 ppm while that of opal (disordered cristobalite), cristobalite, and quartz are very close together and much lower (6 to 15 ppm). Krauskopf (1956, 1959) has shown that at lower temperatures solubility of amorphous silica decreases slightly (50 to 80 ppm at 0°) and still remains largely above that of crystalline forms. He also demonstrated that the influence of pH was negligible below a value of around 9 which can be considered as rather exceptional in deep-sea sediments.

The silica content of sea water is extremely low (around 3 ppm), but interstitial waters in the sediments show much higher values. They range from around 10 ppm in sediments devoid of siliceous organisms and silicates to 40-50 ppm in radiolarian oozes, except in the upper few meters of sediments where the silica content decreases abruptly upward in the section and reaches sea-water values close to the sea bottom (Manheim et al., 1970; Manheim and Sayles, 1971a, 1971b; Sayles and Manheim, 1971; Sayles et al., 1972). If those values are compared to the solubility curves, it is clear that interstitial waters are generally undersaturated with respect to amorphous silica and supersaturated with respect to the crystalline forms. This implies that amorphous silica can be selectively dissolved and reprecipitated as any of the crystalline forms. As will be mentioned later, it is probable that other components of the mineral phase play an important role in the control of this transfer.

Recrystallization Processes

Environmental Conditions Versus Aging Effect

It is, of course, tempting to interpret the absence of chert in recent sediments as the result of the extreme slowness of the recrystallization of silica, but several observations lend support to the assumption that chert is a product of early diagenesis. Evidence from DSDP samples show that chert was formed in many cases prior to

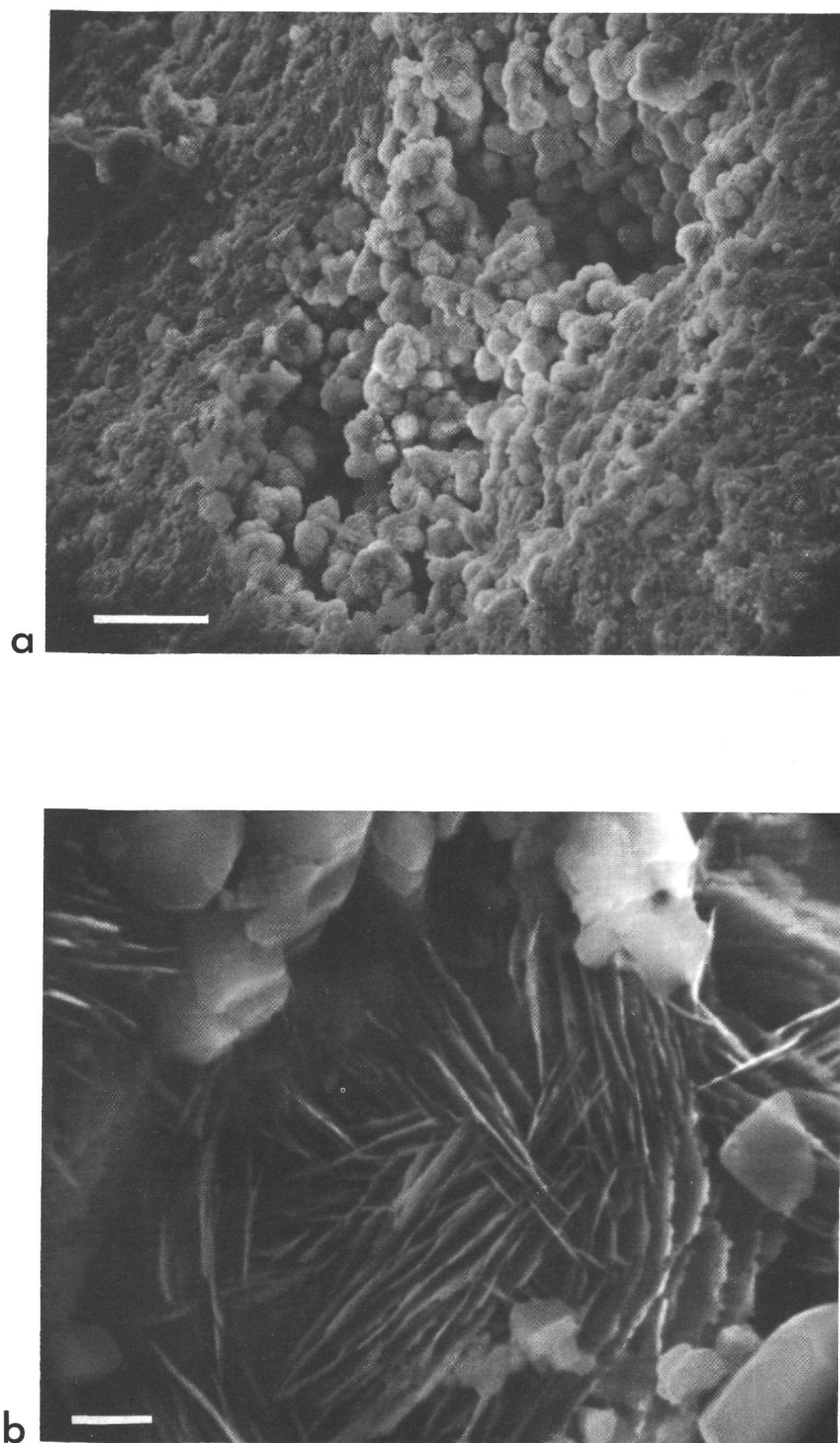


Figure 7. Scanning electron micrographs of silica spherules (?disordered cristobalite) in radiolarian molds. (a) 164-4, CC; white bar = 50 μ . (b) Detail view of similar spherules (167-33-1, 104-107 cm); white bar = 1 μ .

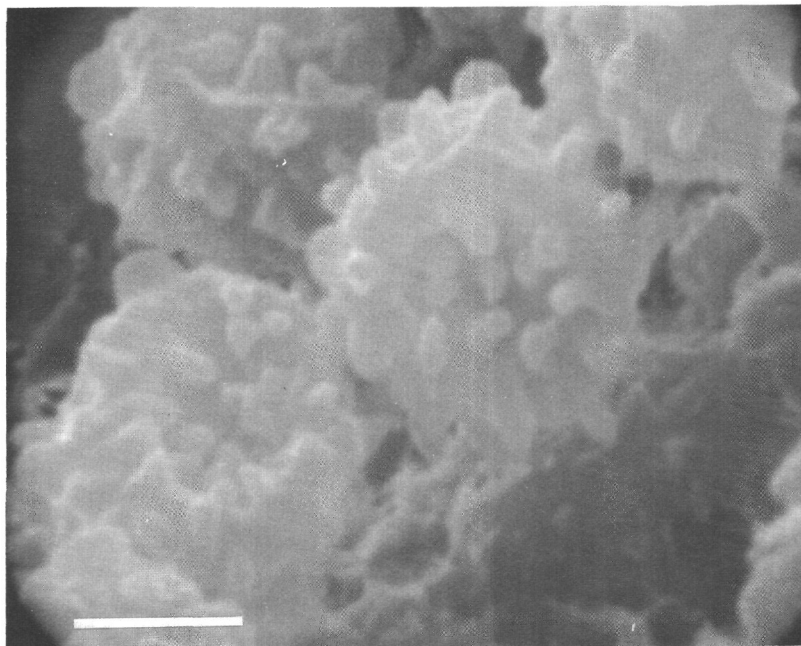
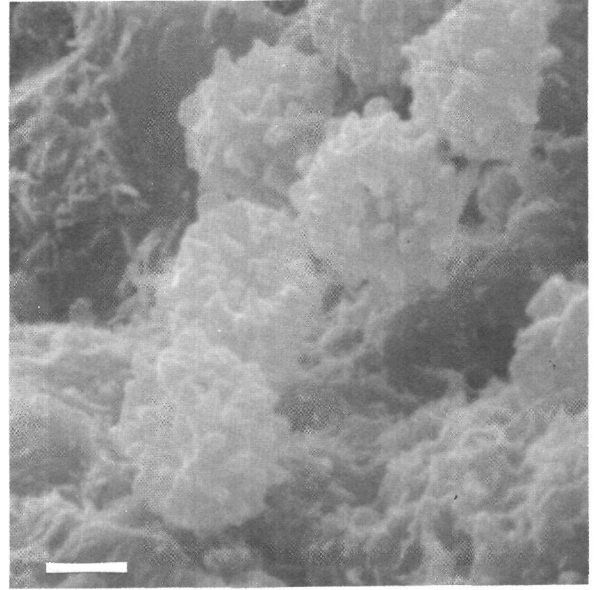
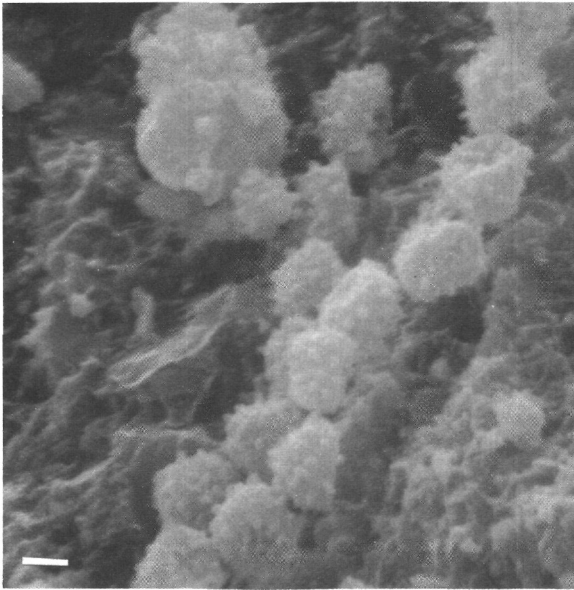


Figure 8. *Scanning electron micrographs of ?-silica spherules (164-6, CC) (cf. Fig. 7). White bar = 1 μ .*

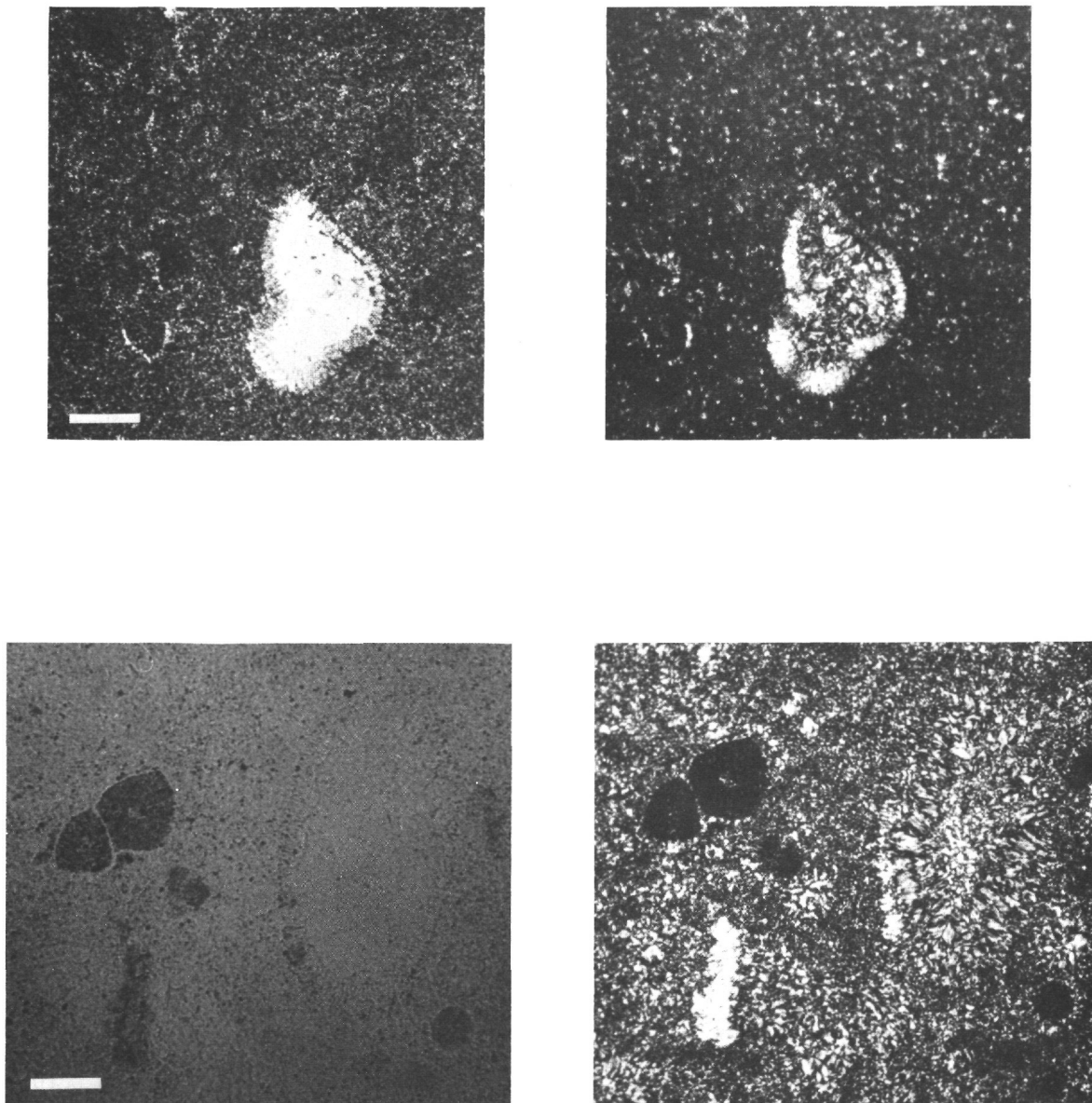


Figure 9. *Quartzose chert in calcareous sediments (thin sections).* (a) Well-preserved foraminifera (calcareous test) filled with quartz or chalcedony. Matrix is microcrystalline quartz (167-133-1, 122-126 cm). (Left: plane polarized light; right: crossed nicols; white bar = 100 μ .), (b) Large microfossil in right part of the picture has been entirely replaced by quartz while others, probably previously filled with clayey sediment, show cristobalitic filling. Near the lower-left corner a large calcite fragment is strongly etched and partially replaced by quartz. This sample came from a turbiditic section and shows a mixture of displaced elements (165A-16, CC). (Left: plane polarized light; right: crossed nicols; white bar = 100 μ).

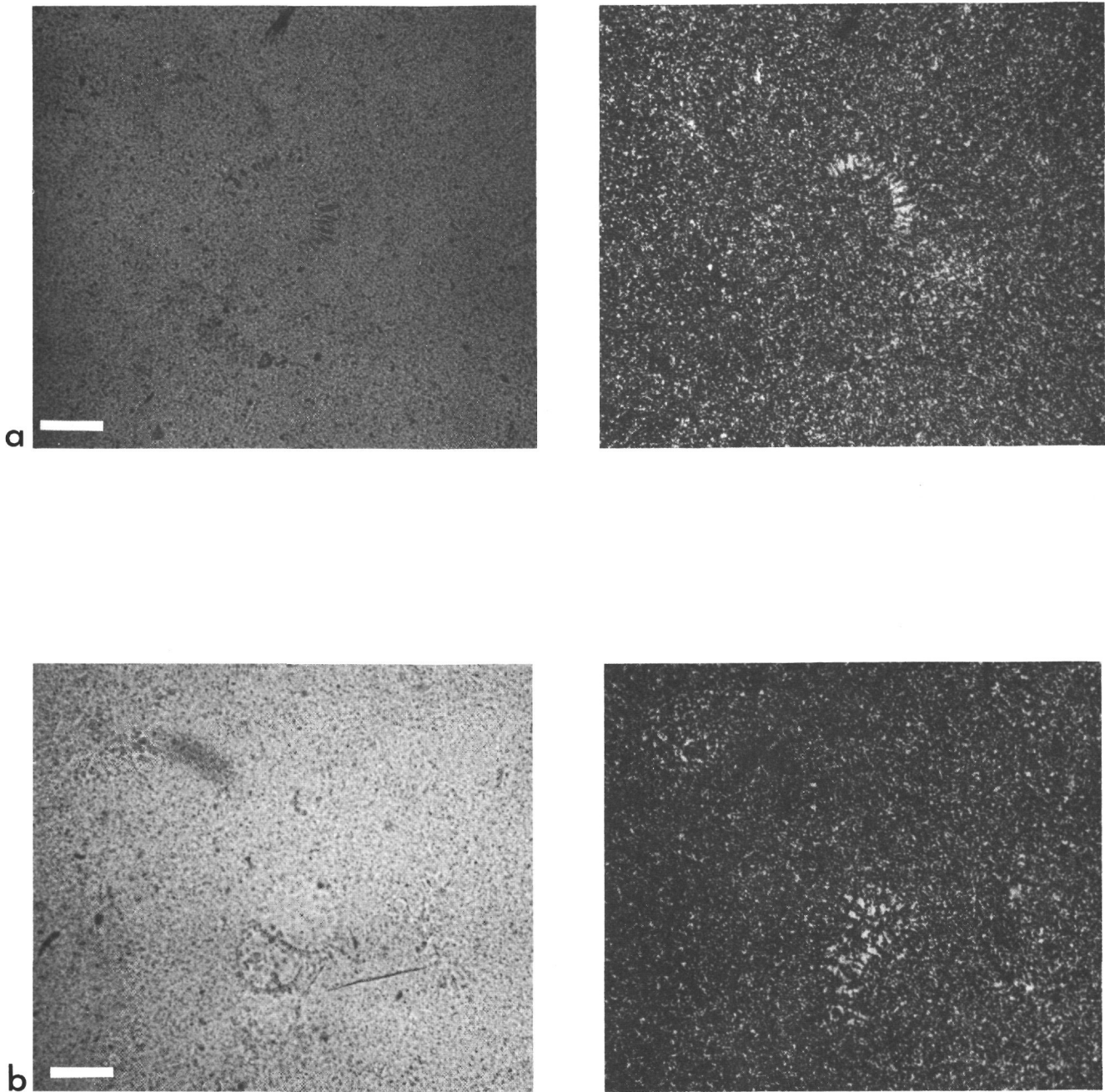


Figure 10. *Quartzose chert in calcareous sediments (thin sections).* (a) *Some remnants of a calcitic foraminifera test still visible in center of picture. Matrix is microcrystalline quartz (167-33-1, 143-145 cm: (left: plane polarized light; right: crossed nicols; white bar = 100 μ).* (b) *Completely replaced foraminifera. Detailed structure is still barely visible in plane polarized light picture (left). Only coarser crystalline quartz indicates the presence of foraminifera ghosts in crossed nicols picture (right)(167-37, CC; white bar = 100 μ).*

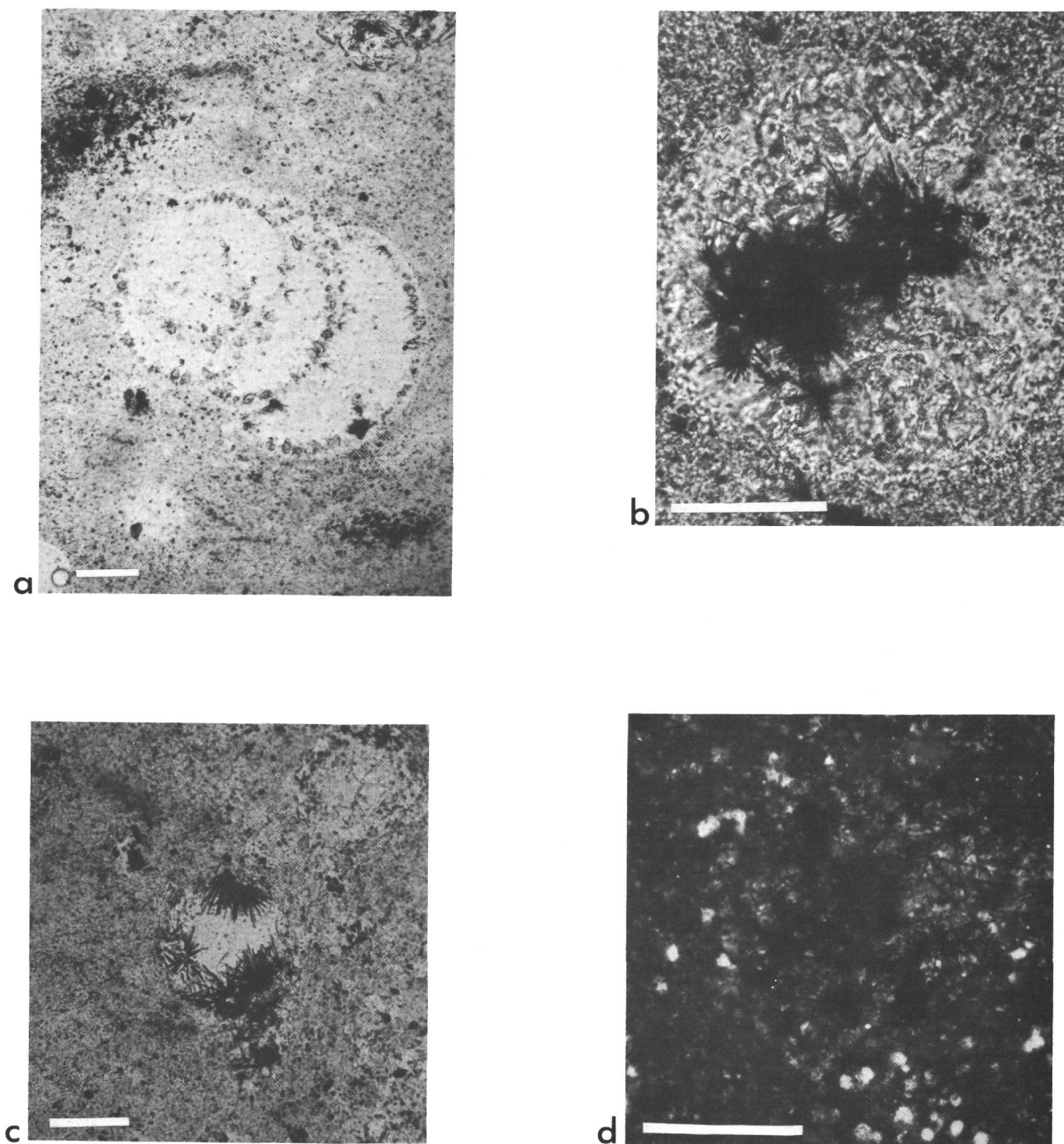


Figure 11. Dark-brown, needle-shaped minerals as inclusions in quartz and/or chalcedony-filled foraminifera (167-62-2, 138-140 cm; [a], [b], and [c]: plane polarized light, [d] crossed nicols with condensed light, white bars = 100 μ). Note that in (a) the rare small clusters seem to originate preferentially on the calcitic remnants of the foraminifera.

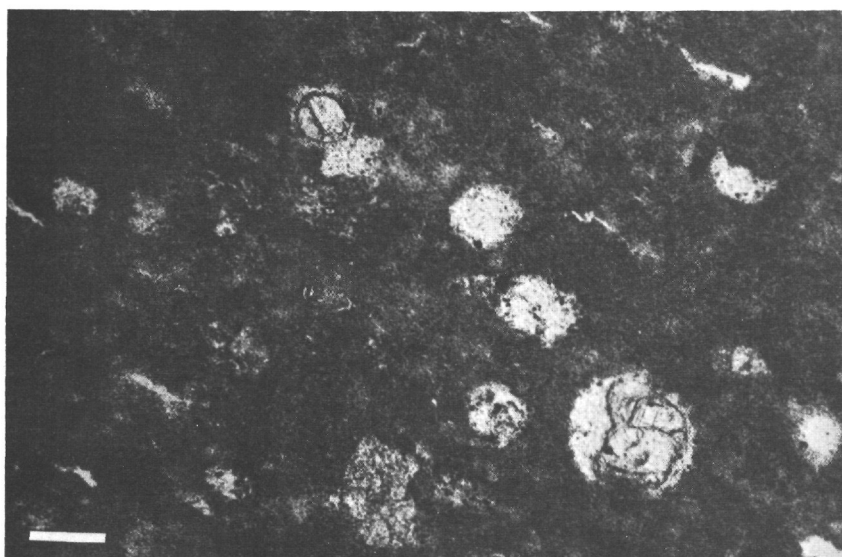


Figure 12. *Partial calcite filling (coarsely crystalline sparry calcite) in microfossils (?radiolarian molds). The larger mold is filled with both silica (on the left side) and calcite (rest of chamber). Others are filled with either silica (center of picture) or calcite (uppermost and lowermost molds). (167-61-2, 43-47 cm; thin section; crossed nicols; white bar = 100 μ).*

compaction of the sediments. Figure 18 shows that small quartz veinlets in limestones from Site 167 were already hard when the compaction took place. In some cases they resisted compaction, and in others they were broken by the compaction effects and partially stacked in an "en accordéon" manner. Furthermore, field evidence has been provided by Bernoulli (1972) that suggests very early diagenetic chert formation in upper Cretaceous limestone from Greece. Plates of broken chert occur in a slumped bed, while the overlying layers are undisturbed (Figure 19). The sharpness of the edges of the broken chert fragments suggests an early diagenetic solidification rather than a post-deformational selective silicification.

Several authors have proposed that chert formation undergoes several phases beginning with precipitation of cristobalite and slowly "maturing" into quartz (Heath and Moberly, 1971; Berger and von Rad, 1972). Although a very slow inversion from disordered cristobalite to quartz cannot be completely ruled out, some evidence found during the study of Leg 17 chert shows that it is probably only of secondary importance compared to the influence of the lithology of matrix sediments on the mineralogy of the chert. It should be pointed out that if the relationship between carbonate and quartzose chert, as well as between clayey or marly sediments and porcelanitic chert, as described here is valid, it is quite obvious that there will be statistically more quartz in the old sediments than in the more recent ones simply because most of the older sediments are rich in carbonates. This is a consequence of the sea-floor spreading mechanism and associated subsidence which brings carbonates deposited on the midoceanic ridge flanks to deeper parts of the basins where they receive a cover of noncalcareous sediments. Most of the chert-bearing carbonate layers lie presently in deep water below the carbonate compensation depth, and the majority of the

calcareous deposits presently above that level are of post-Eocene age and are, therefore, generally devoid of chert. Whenever chert is reported in these younger sediments, the patterns described earlier in this report can be observed, and the lithology of the host sediments seems to provide the main control upon its mineralogical nature. For example, at Site 76 from Leg 9 (Hays et al., 1972) chalcedonic chert occurs in calcareous sediments possibly as young as Pliocene. At Site 164 porcelanitic chert present in clays is as old as lower Cretaceous. Also the occurrence of chalcedony in the radiolarian molds of the Oligocene cherts of this same site indicates that quartz or chalcedony can primarily precipitate even in youngest chert, given the proper environmental conditions. Similar deduction can be made from Sites 62 and 63 (Winterer et al., 1971). At Site 62 Oligo-Miocene chert associated with calcareous sediments is made of chalcedony, and at Site 63 Tertiary calcareous oozes contain quartzose chert, while it is cristobalitic in the marls of the older parts of the section.

Role of Foreign Cations

The possible influence of cations able to cause disorder in the crystalline structure of silica during the growth of crystals has been summarized very well by Millot (1964). Analysis of natural opals (made of disordered cristobalite) has shown that they contain regularly an appreciable amount of alkaline and alkaline-earth elements (Buerger, 1954). Weil (1926), Flörke (1955), and Millot (1960, 1964) indicate that the disorder in the structure of cristobalite-tridymite layers found in disordered cristobalite is open enough to accommodate large cations, while the electrostatic balance is obtained by Al ions replacing Si in tetrahedrons. Millot (1964) points out that if no foreign cations are available, only quartz can precipitate, and

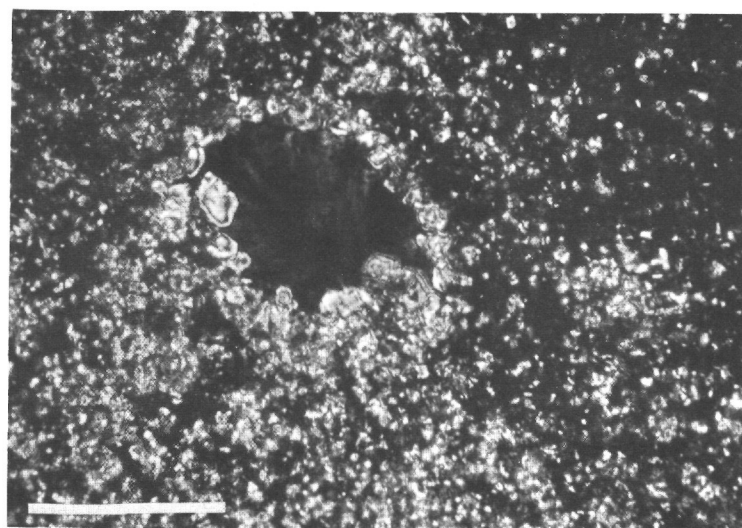
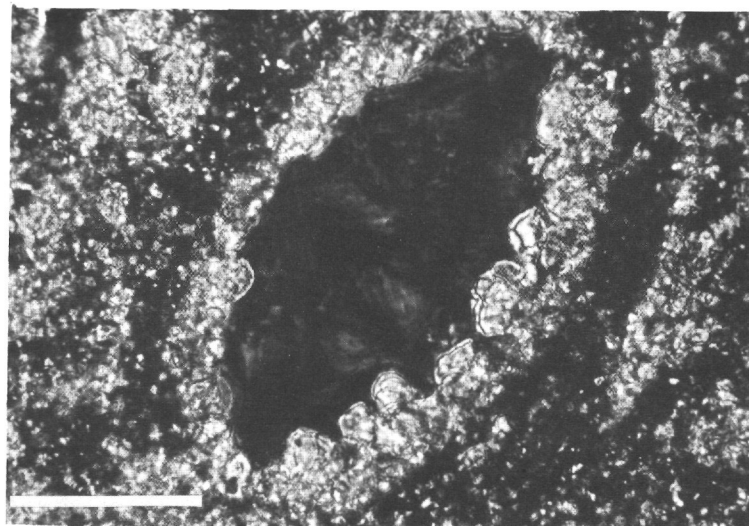


Figure 13. Possible secondary calcite recrystallization in silica-filled microfossil molds. Calcite crystals seem to grow from the walls toward the inside and may partially replace chalcedony filling (167-75, CC). Compare to the aspect of partially replaced foraminifera from Figures 9 and 10 (thin section; crossed nicols; white bar = 100 μ).

conversely only disordered cristobalite can precipitate if these cations are present in sufficient amounts.

Of course, clay minerals are the most likely source for easily exchangeable cations. It is thus proposed here that they are responsible for the diagenetic precipitation of disordered cristobalite in clayey sediments, while only quartz can precipitate in a carbonate environment.

Role of Permeability

Disordered cristobalite is confined to sediments in which clay minerals represent a major obstacle to circulation and

create a microenvironment in which pore spaces are small enough to keep the ratio of silica to metallic cations at relatively low values. Whenever the permeability increases, such as in a large void, chalcedony and quartz can precipitate because of a sharp increase of this ratio. This is well illustrated in Figure 20, where a radiolarian mold shows geopetal partial filling with sediment. The part filled with clayey sediments has been silicified by disordered cristobalite, while the void in the upper part has been filled with chalcedony.

In carbonates, both the lack of aluminum and metallic cations (except Ca and Na) and the high permeability favor

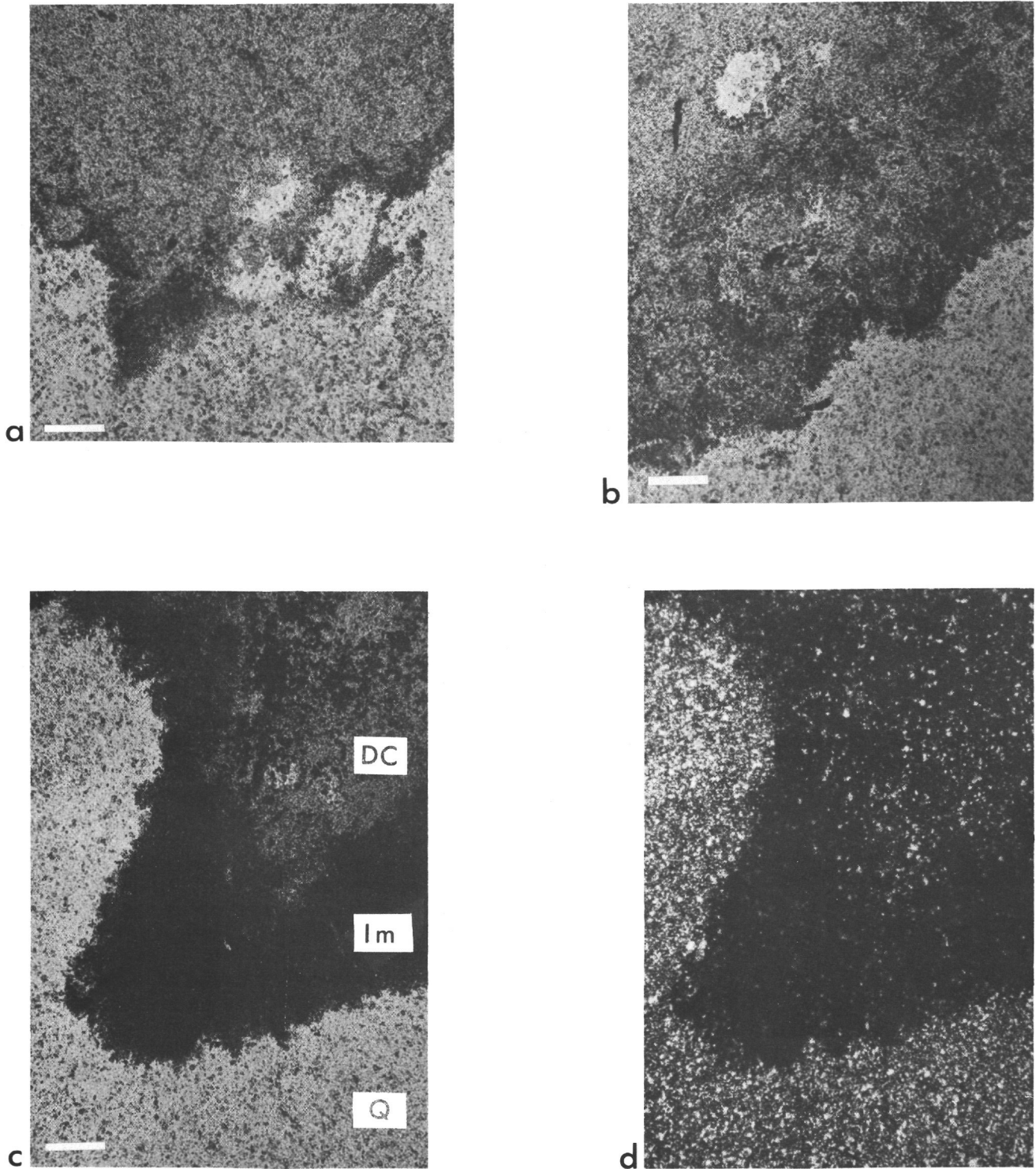


Figure 14. Concentration of dark impurities at boundary between quartz and disordered cristobalite (thin sections). (a) and (b): 167-33-1, 121-122 cm; quartz is in lower part, disordered cristobalite in upper part (plane polarized light; white bar = 100μ). (c) and (d): 167-35, CC; Q = quartz, DC = disordered cristobalite, Im = impurities ([c]: plane polarized light; [d]: crossed nicols; white bar = 100μ).

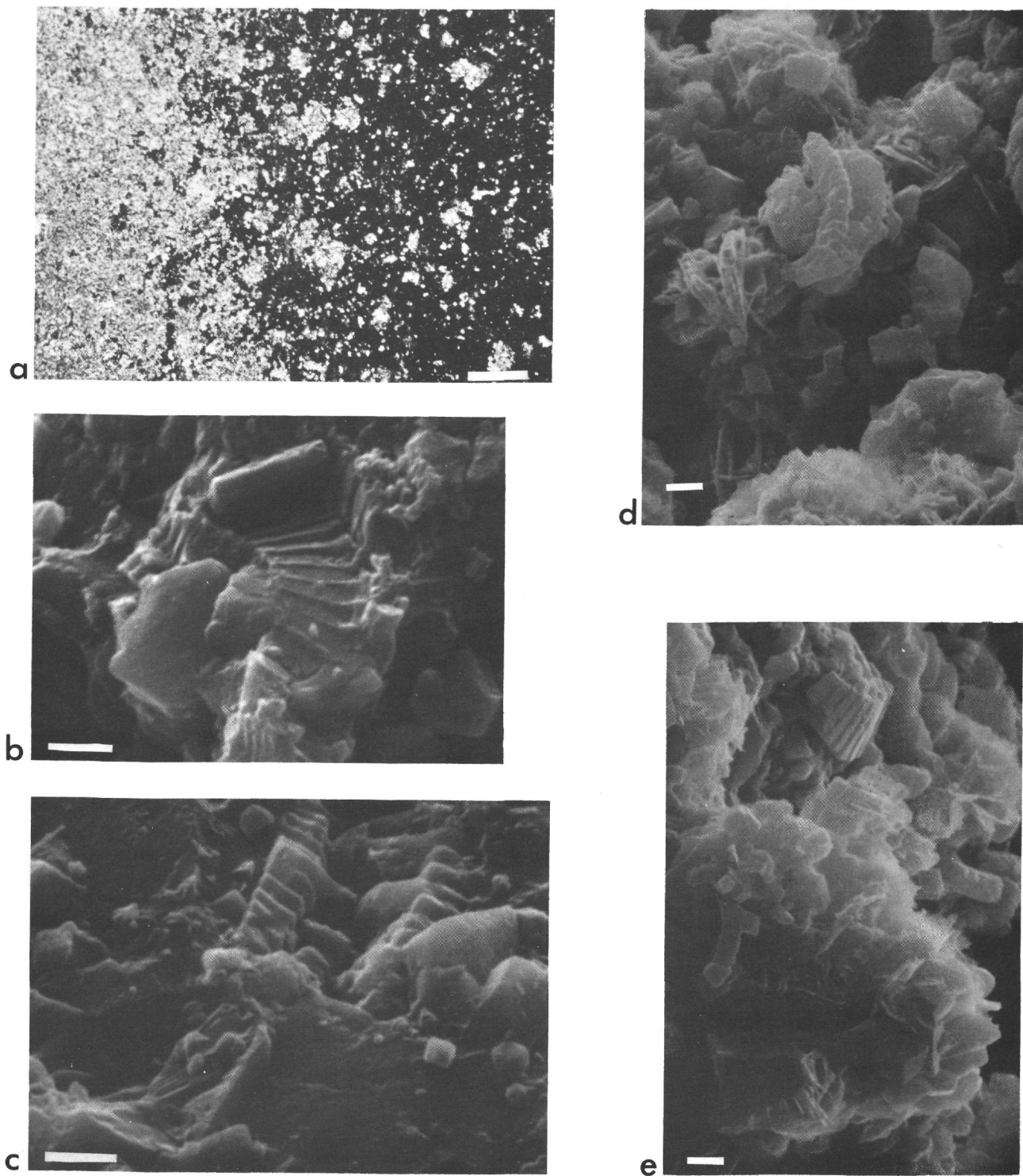


Figure 15. *Boundary between opaline rim and calcareous sediment at the periphery of quartzose chert nodules. (a): 165A-15, CC; thin section; crossed nicols; white bar = 100 μ ; calcite is at left, disordered cristobalite at right. (b), (c), (d), and (e); 167-33-1, 104-107 cm; scanning electron micrographs showing partial cementation of the calcareous elements by silica. Silica is either cryptocrystalline and structureless (b) and (c) or in the spherulitic form (d) and (e), white bar = 1 μ .*

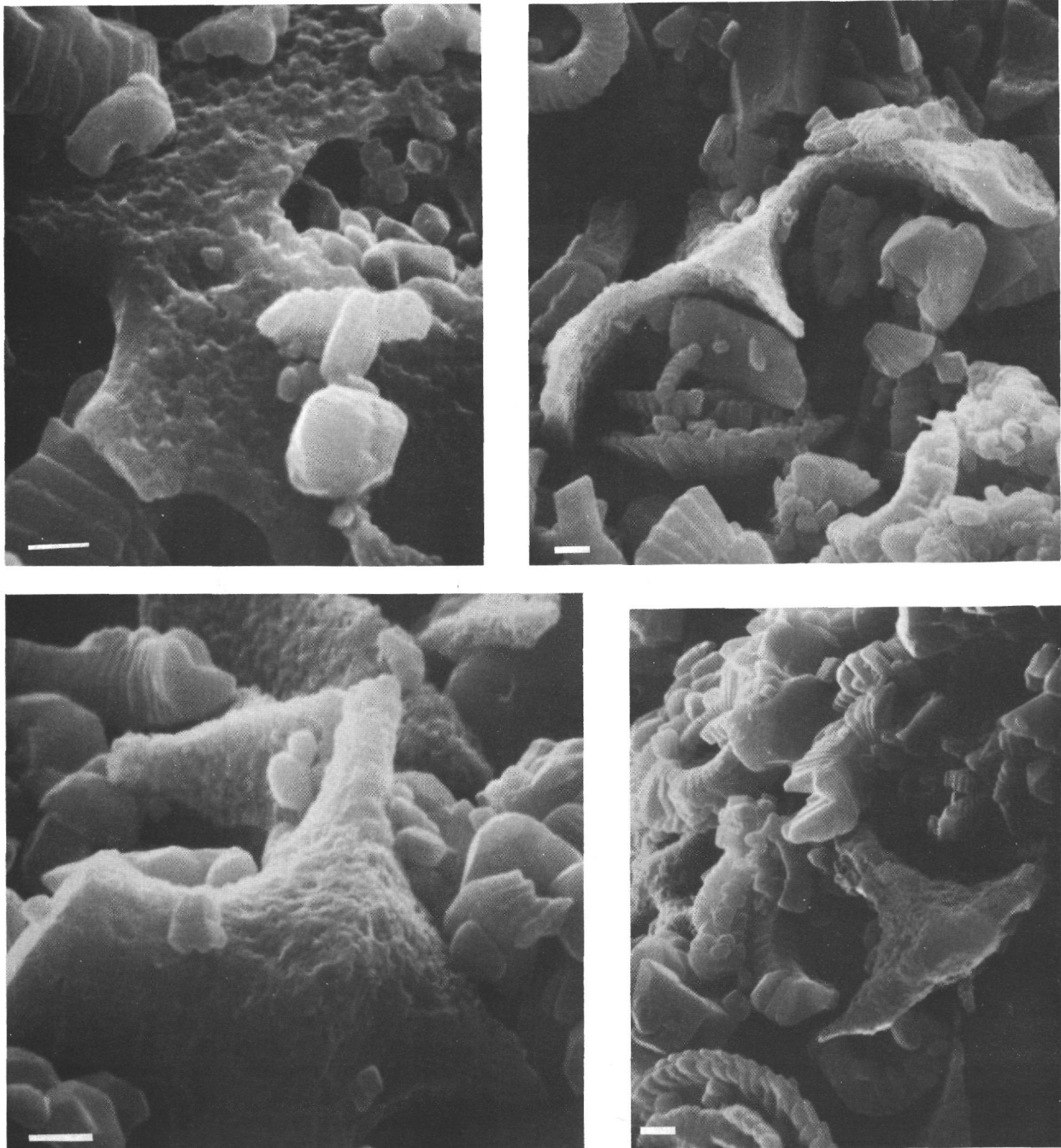


Figure 16. *Dissolution of radiolarian fragments in the vicinity of chert (167-32-3, 150 cm). Scanning electron micrographs; white bar = 1 μ . Note the strongly etched surface of the fragments and their partial dissolution.*

direct precipitation of microcrystalline quartz. A good example of such a process can be observed at Site 165-16, CC where relatively coarsely crystalline quartz has precipitated in a coarse-grained limestone consisting of displaced shallow-water elements (Figure 21). The role of permeability is also emphasized by the occurrence of small silica spherules precipitating directly in the carbonate matrix (Figure 15), while in the clays they appear restricted only to the radiolarian molds. The zonation observed at the periphery of nodules in carbonates can be the result of the relatively high permeability of the sediment. It is

suggested that the development of a quartzose chert nodule in a calcareous ooze can be explained in the following way:

- 1) Quartz precipitates directly in the carbonate matrix where clay minerals are rare and dispersed.
- 2) The nodule develops outwards by accretion, and in the process all the clay minerals and dissolved cations that cannot be accommodated in the quartz structure are excluded and move along a "quartzification front." This can be achieved only because of the high permeability of the sediment, allowing relatively free circulation of the interstitial waters.

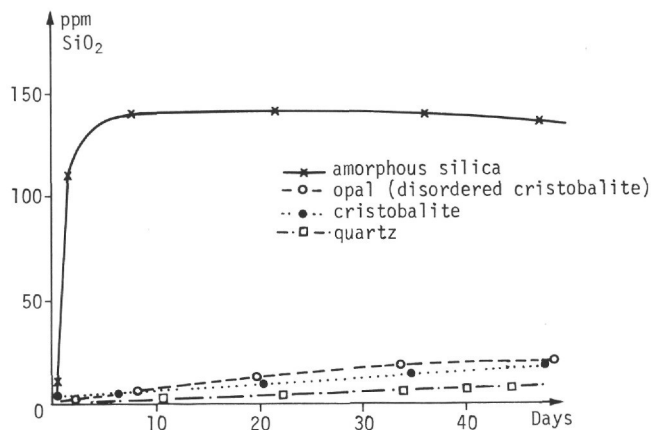
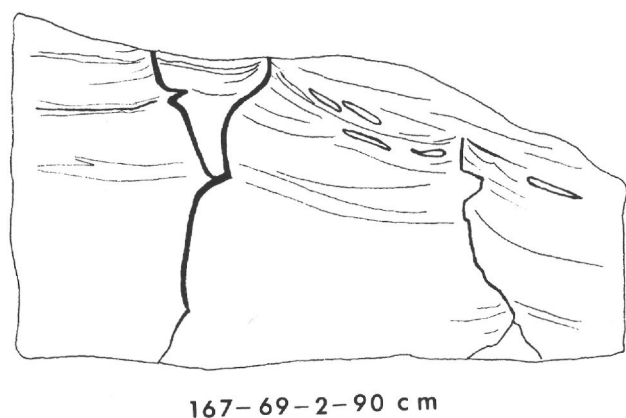
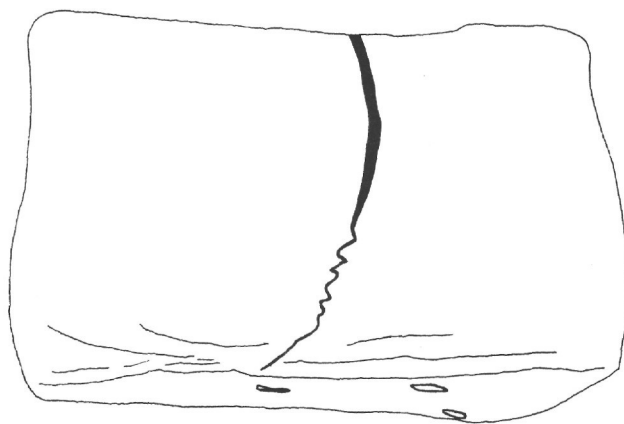


Figure 17. Solubility of amorphous silica, opal, cristobalite, and quartz in water at room temperature (after Wey and Siffert, 1961).



0 1 2 3 cm



167-69-2-105 cm

Figure 18. Compaction effect on quartz veinlets. Upper: note the compaction of sediments around the veinlets which were already hard at the time of compaction. Lower: the hard quartz veinlet has been broken and folded during compaction.

3) At the periphery of the quartz nodule the concentration of clay minerals and foreign cations increases, while that of dissolved silica decreases because of limited supply. These conditions favor precipitation of disordered cristobalite that makes the rim commonly observed around the nodule.

This concentration process can be visualized in thin sections by observing the distribution of dark impurities near the contact between quartzose chert and cristobalitic rim.

Role of Crystal Nucleation

In many samples where permeability appears high, it seems that crystal growth is favored by the presence of crystalline nuclei. This might explain the ease with which quartz seems to spread in a carbonate ooze.

Such nucleation processes that seem to characterize the most permeable environments can be observed in thin sections from brecciated cherts from Site 167 and from a "septarian nodule" from Site 166. Large quartz crystals and chalcedony seem to develop from a generation of small crystals along the edges of chert fragments (Figure 22).

Role of Time

Concepts which require that the mineralogical nature of chert is controlled by age-related "maturation" processes are not supported by the observations described here. However, it is possible that time plays a subsidiary role in the quartzification of the cherts. This process involving conversion from metastable forms of silica (disordered cristobalite) to most stable forms (quartz) could probably be favored by high temperatures found under great sediment overburden (see discussion in Heath and Moberly, 1971). The role of silica solution in that case is emphasized by the observations made on the brecciated chert from Site 167 (Core 63-1, 60-67 cm) (see color frontispiece of this volume). Brecciation is believed to have occurred after some lithification of the sediment, since no sediment filling has been observed in the fractures. Furthermore, the precipitation of large sparry calcite crystals in these fractures certainly results from late diagenetic processes since (1) it correlates with the youngest occurrence of sparry calcite inside foraminifera chambers at the same site (167, Core 62); (2) in some other samples fractures previously filled with chalcedony have been broken, and calcite has precipitated in the voids associated with this second generation of fractures (Figure 23); and (3) oxygen isotope analyses performed on the calcite crystals cementing the brecciated chert (courtesy of R. Letolle, University of Paris-VI, France) indicate a temperature of crystallization of about 30°, which can be reasonably estimated as indicative of the present in situ temperature under 870 meters of overburden, as comparable thermal gradients have been observed in sediments during Leg 19 of the Deep Sea Drilling Project (G. Bryan, personal communication). It is then remarkable to observe that some of the chalcedony has precipitated after calcite. This is suggested by the pattern of chalcedony fibers that seem to mold the large calcite crystal edges (Figure 24). It indicates that solution and reprecipitation of silica can occur very late in already lithified sediments. It is possible that, given the

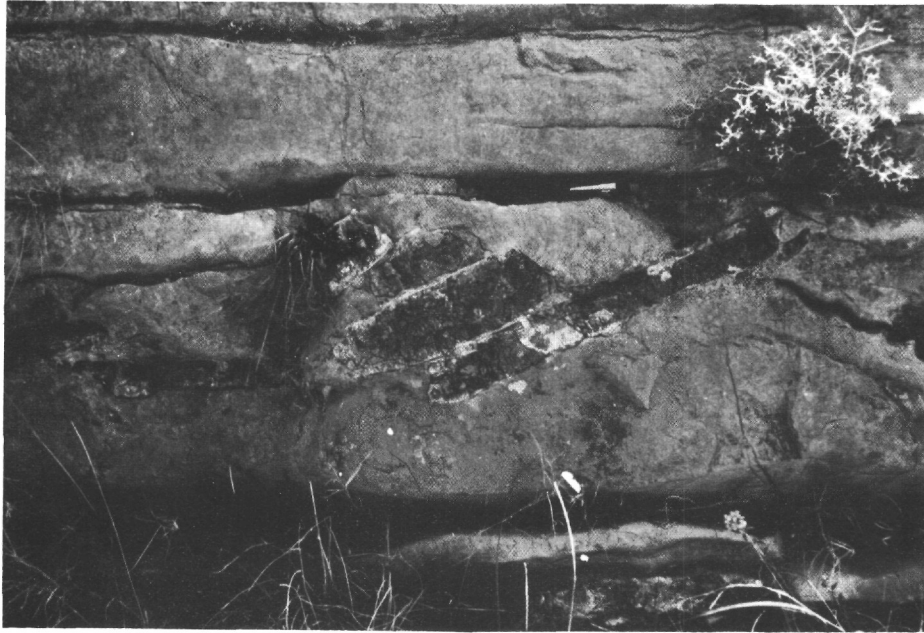


Figure 19. Broken chert layer in slumped upper Cretaceous limestones from Vigla, Western Greece (from Bernoulli, 1972). See text for explanation.

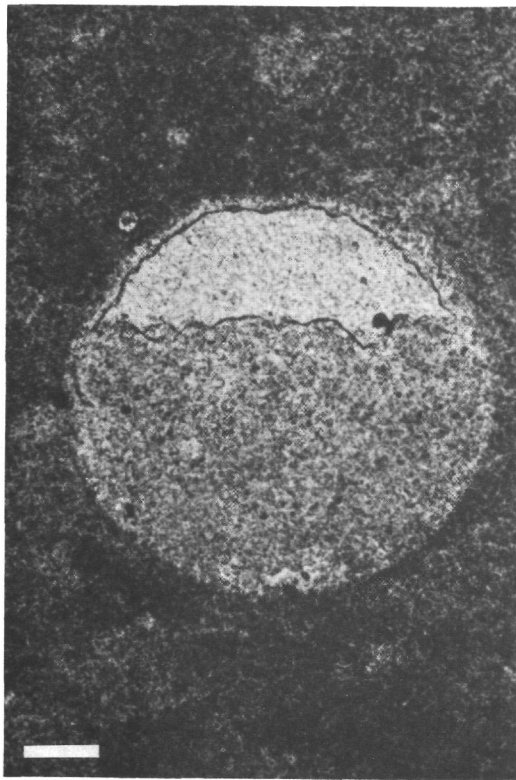


Figure 20. Differential silica recrystallization in a partially filled radiolarian mold (thin section; 164-4, CC, left: plane polarized light; right: crossed nicols; white bar = 100 μ). The partial filling gives a good geopetal indication as the upper surface is parallel to the bedding observed in the sample. The sediment-filled part has been replaced by disordered cristobalite and only the upper part, devoid of sediment, has been filled with chalcedony.

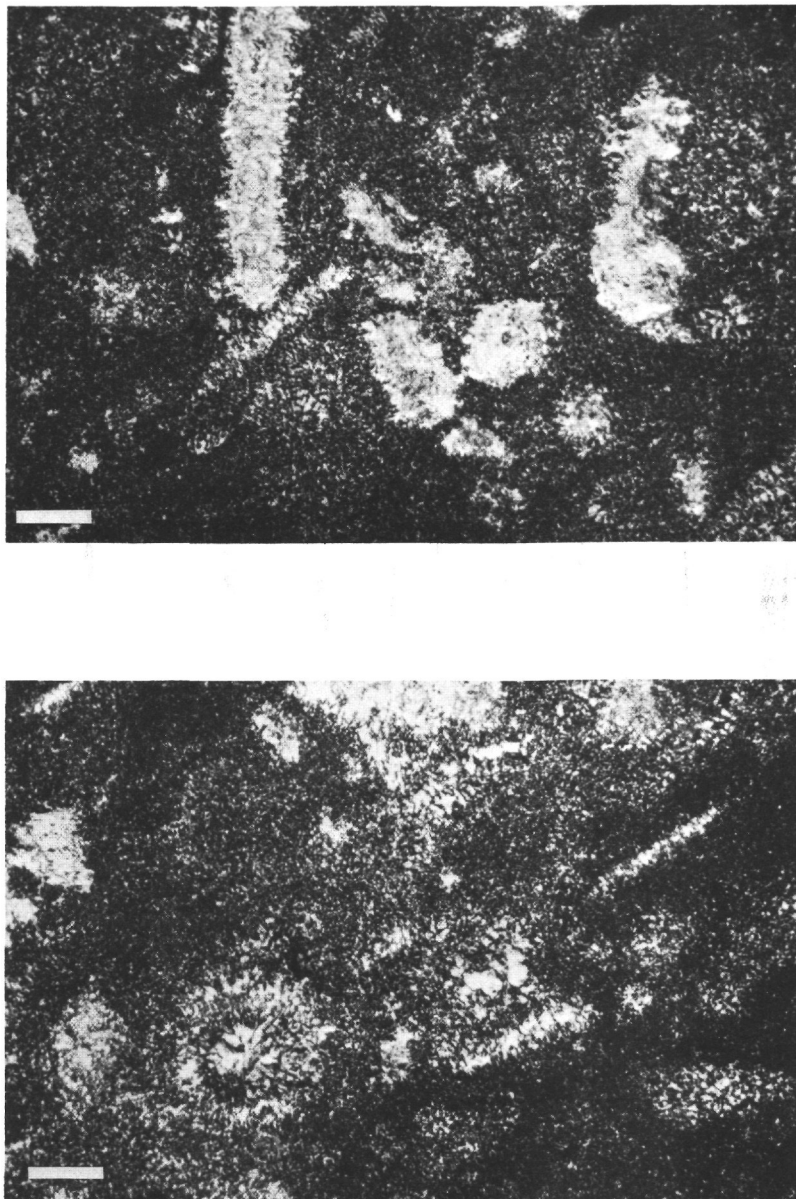


Figure 21. *Etching and replacement of large calcite fragments by quartz in a highly permeable calcareous sediment (base of a turbidite sequence, 165A-16, CC; thin section; crossed nicols; white bars = 100 μ).*

necessary permeability, all the silica could be able to slowly invert to quartz by solution and reprecipitation.

The maturation ("quartzification") of chert that can be observed on chert nodules from outcrops on land has been often attributed to age effects. It is noteworthy that no cristobalitic rim can be observed on the quartzose chert nodules from the Upper Cretaceous chalks of the Paris Basin (F. Mélières, personal communication). If a rim of light-colored material is indeed present, it is exclusively made of microcrystalline quartz. As cherts from the same age recovered by deep sea drilling do not show this complete quartzification, it is believed that the age effect was not predominant and the transformation of cristobalite into quartz on land might have been caused by weathering after the sediments had been exposed subaerially.

Possible Primary Causes of Chert Formation

Although it is possible to imagine some of the processes that might have led to the recrystallization of silica in the sediments, knowing what caused this recrystallization is still an open question.

The most puzzling observation, leading to many controversies, is that apparently no chert is being formed in recent sediments. This observation has been accounted for in two different ways: (1) chert is not presently forming because environmental conditions are now different from the ones existing during early Tertiary time; and (2) formation of chert is such a slow process that it has not had enough time to form since the Oligocene. For reasons mentioned earlier, it seems that the former explanation is the most plausible.

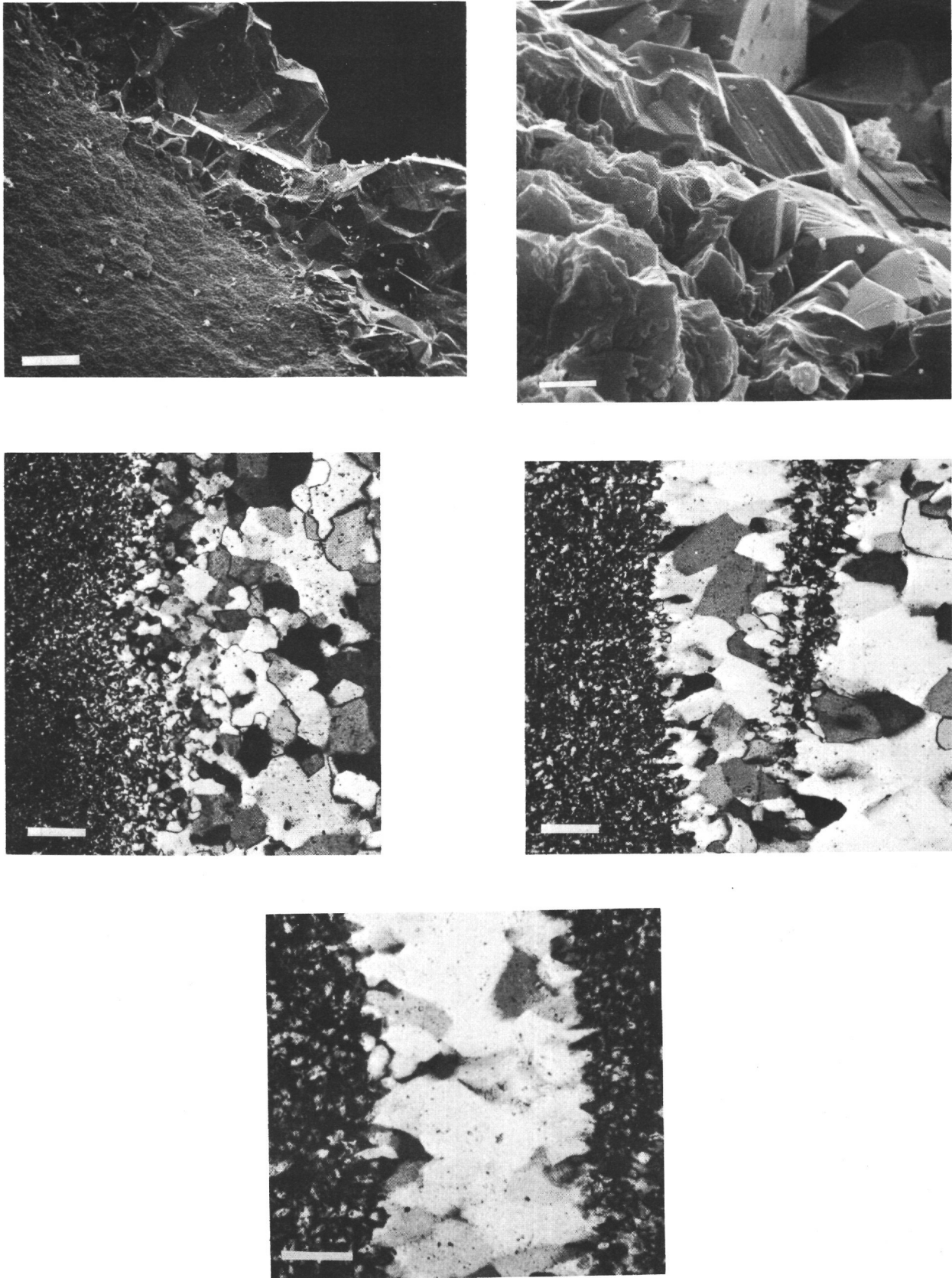


Figure 22. Nucleation of large quartz crystals from the edges of chert fragments (166-28, CC). (a) and (b): Scanning electron micrographs; white bar = 100μ in part (a), = 1μ in part (b). (c), (d), and (e): Thin sections; crossed nicols; white bars = 100μ . Note the continuity between some quartz crystals in the veins and those in the chert fragments.

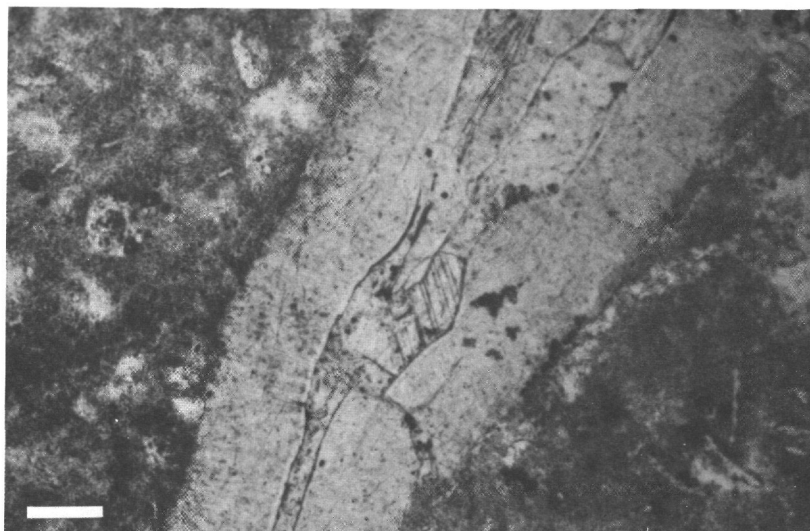


Figure 23. Broken chalcedonic double veinlets showing post-fracturing precipitation of sparry calcite cement (especially in lower center part of the picture); 167-69-1, 58-61 cm, thin section; upper: plane polarized light; lower: crossed nicols; white bar = 100 μ).

The mechanism of silica transfer from amorphous siliceous tests to crystalline forms by solution and reprecipitation according to a differential solubility pattern is theoretically possible in recent sediments. The dissolved silica content of the interstitial waters is such that, apart from the few upper meters of sediments, where it is close to that of sea water, the transformation should indeed occur. However, it does not, at least on a scale large enough to produce appreciable concentrations of recrystallized silica. It is possible that the main control of the process lies in the nature of the silicates, and especially the aluminosilicates, present in the sediments. Such an explanation is suggested by the fact that, as far as can be seen from the rather scanty analyses of chert-bearing sediments recovered from the

deep basins, the chert seems to be generally accompanied by an association of silicon-rich silicates which are not prevalent in the recent sediments. Some examples are given by the composition of sediments at Site 164 where it is clear that chert is mostly restricted to layers where clinoptilolite predominates over phillipsite, K-feldspars over plagioclases, and palygorskite over other clay minerals. These minerals are indicative of a silica-rich environment. Although not much is known of the possible diagenetic processes that could lead to transformation of phillipsite into clinoptilolite and montmorillonite into palygorskite in a silica-rich environment, it is unlikely that K-feldspar could be derived from alteration of plagioclase. It is more probable that these relatively Si-rich minerals are merely

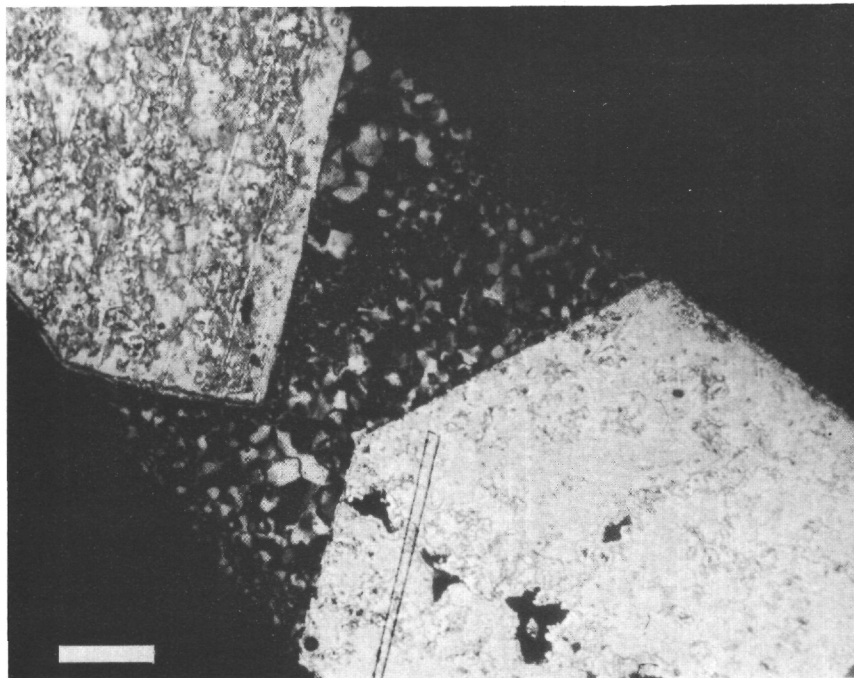
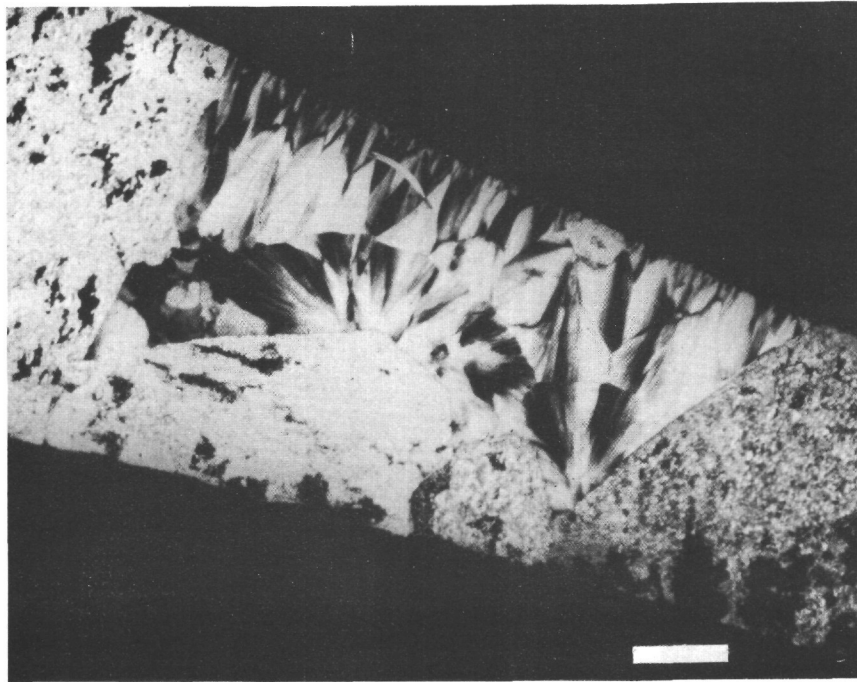


Figure 24. Late precipitation of chalcedony (upper) and quartz (lower) as filling of voids left open by precipitation of sparry calcite in the fractures of a brecciated chert. The pattern of chalcedony fibers in the upper picture indicates that silica precipitated after calcite (167-63-1, 64 cm; thin sections; crossed nicols; white bars = 100 μ). (See also color frontispiece, this volume.)

indicative of an originally different oceanic environment that was more silicic than today. The origin of silica could be found in a different type of volcanism, as suggested, for example, for certain areas of the Indian Ocean by Venkatarathnam and Biscaye (in press), or by a large output of dissolved silica from the continents under particular climatic conditions as suggested by Millot (1964) for the peri-African realm during Eocene time.

Broecker (1971) has shown that the main control of the silica content of sea water is achieved by siliceous organisms. Any influx of dissolved silica in the water is immediately compensated by biogenic precipitation of amorphous silica in the form of radiolarians, diatoms, and sponges. A large part of that silica is rapidly dissolved and permanently recycled in the water column provided the water circulation is able to recycle enough nutrients to keep biologic productivity at a high level. The remaining silica is sedimented and buried. In the sediments, the siliceous tests dissolve slowly and release monomeric silica into the interstitial waters. The excess silica is trapped in the sediments and is available for subsequent diagenetic processes. It is possible that in post-early Tertiary sediments, Si-poor silicates could buffer this excess silica by the processes determined experimentally by MacKenzie et al. (1967) so that the silica content of interstitial waters would reflect equilibrium with the alumino-silicates present in the sediments. If, during the early Tertiary and before, most of the alumino-silicates sedimented together with siliceous organisms were already Si-saturated, the excess of silica may have been available for direct reprecipitation into chert.

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