

Mineralogy of Silica Phases in Deep-Sea Cherts and Porcelanites [and Discussion]

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MARINE MINERALOGY

Mineralogy of silica phases in deep-sea cherts and porcelanites

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[Plates 1 and 2]

Cherts and porcelanites of Late Mesozoic to Cainozoic age, recovered at many sites in all major ocean basins by the Deep Sea Drilling Project, contain both quartz and disordered cristobalite as the principal silica phases. The cristobalite is identified as opal-CT and occurs as spherical microcrystalline aggregates of bladed crystals (= *lepispheres*) that evidently formed by a solution step. This material represents a metastable intermediate stage in the conversion of amorphous biogenous and hydrothermal silica to quartz. Opal-CT also occurs in siliceous formations on land, both sedimentary and volcanic, but only in those of post-Jurassic ages. Many older cherts now composed entirely of quartz may also have formed from such an intermediate phase but all traces of such a precursor have been removed by recrystallization.

1. INTRODUCTION

Cherts and porcelanites have been recovered from many sites in all the ocean basins by the Deep Sea Drilling Project (JOIDES 1967). They occur in sequences of a wide variety of sediment and rock types and range from Pliocene to Late Jurassic in age. The composition of the silica phases in these rocks throws light on some of the diagenetic processes in oceanic sediments and in particular on the complex sequence of recrystallization of silica in such sediments.

This paper attempts to summarize the available information on the occurrences and the composition of the siliceous rocks collected from the deep sea and discusses recent work on the nature of the silica phases present and their likely modes of formation.

The principal silica phases present in the siliceous rocks considered here are quartz and opal-CT (see §4). For the purposes of this review, rocks composed of quartz are referred to as *cherts*, conforming with the classical definition (Smith 1960), and rocks composed of opal-CT are called *porcelanites*, a term originally due to Taliaferro (1934). This terminology follows that recommended by Calvert (1971) although it is recognized that many cherts contain opal-CT, and vice versa, and that the term porcelanite has had a rather loose usage in the past (Flörke, Jones & Seignit 1975).

2. OCCURRENCES

Cherts and porcelanites were recovered during the first two legs of the Deep Sea Drilling Project in the North Atlantic (Ewing *et al.* 1969; Peterson *et al.* 1970) and have been described by Calvert (1971). Siliceous rocks have been found on virtually all subsequent legs and are now known to occur in all ocean basins (figure 1). These occurrences have been discussed by Calvert (1974) and Heath (1977).

The cherts and porcelanites occur in radiolarian and diatomaceous oozes, in nannofossil

[5]

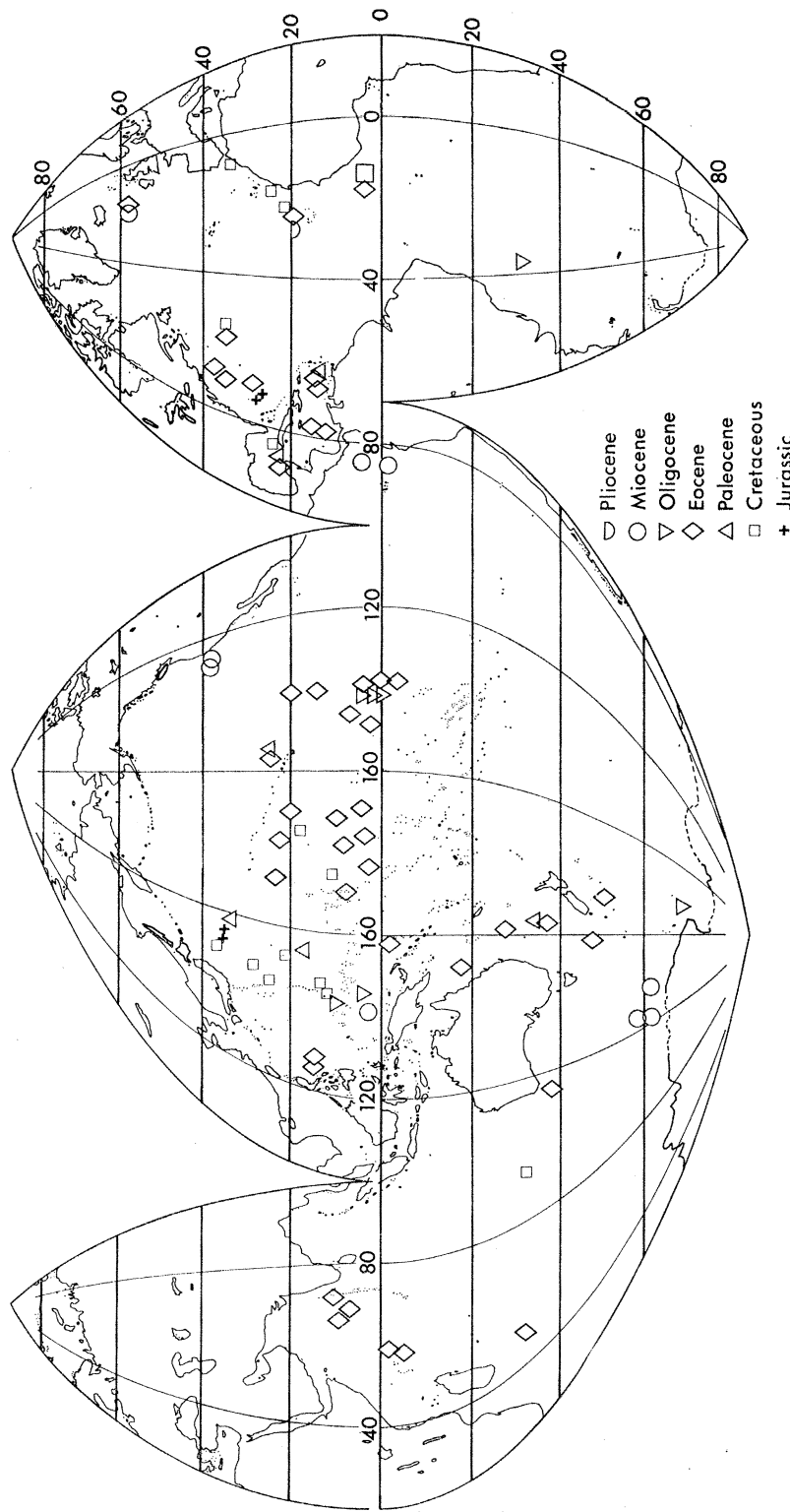


FIGURE 1. Occurrences and ages of cherts and porcelanites recovered during Legs 1-12 and 14-31 of the Deep Sea Drilling Project.

oozes, chalks and limestones, in zeolitic and palygorskite/sepiolite-bearing clays and in terrigenous silts and clays (figure 2). Middle and Late Cretaceous occurrences are found mainly in chalks and nannofossil oozes, while Middle and Late Eocene occurrences are associated with both siliceous oozes and calcareous sediments.

The chert and porcelanite horizons in the North Atlantic and in the eastern Pacific Oceans can be recognized as distinct sub-bottom acoustic reflectors (Ewing *et al.* 1969; Peterson *et al.* 1970; Heath 1973). In the North Atlantic, it has been suggested that the cherts represent Horizon A (Gartner 1970), which can be traced over a very large area. Chert horizons are therefore laterally continuous.

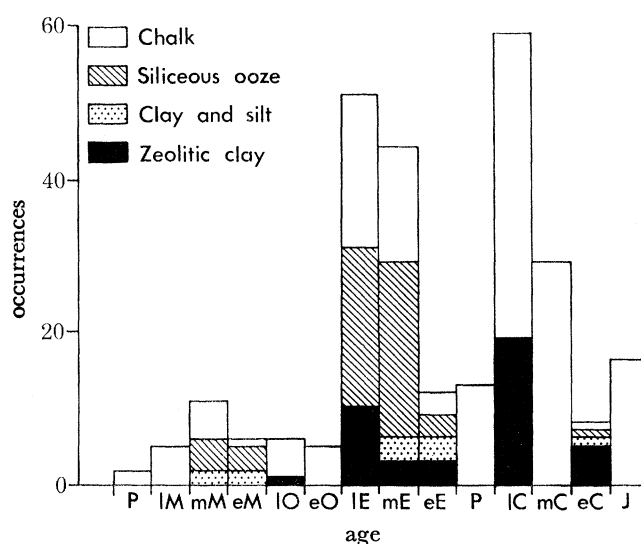


FIGURE 2. Ages and lithological associations of cherts and porcelanites recovered by the Deep Sea Drilling Project.

Chalk includes nannofossil oozes and limestones; siliceous oozes include radiolarian and diatomaceous varieties; clay and silt refers to generally fine-grained terrigenous sediments; zeolitic clay includes clays rich in clinoptilolite, sepiolite, and palygorskite. P, Pliocene; IM, late Miocene; mM, middle Miocene; eM, early Miocene; IO, late Oligocene; eO, early Oligocene; IE, late Eocene; mE, middle Eocene; eE, early Eocene; P, Palaeocene; IC, late Cretaceous; mC, middle Cretaceous; eC, early Cretaceous; J, Jurassic.

Although the coring procedures on the drilling vessel break up and often homogenize the chert and porcelanite beds, the rocks are known to occur as thin (2–5 cm), persistent beds and as irregular, nodular masses (Heath & Moberly 1971; Heath 1973). Bedded cherts occur predominantly in siliceous oozes and clays, whereas nodular cherts are found more frequently in calcareous sequences (Heath 1973; Lancelot 1973).

3. PETROGRAPHY

Deep-sea cherts and porcelanites have formed both by replacement, most commonly of calcareous material, and by alteration or inversion of amorphous silica. These two types correspond generally to the replacement nodular and primary bedded cherts of the geological literature.

The porcelanites contain very fine-grained masses of opal-CT, together with variable amounts of clay minerals, zeolites, and microfossil debris. The opal-CT often occurs as a groundmass

almost isotropic in thin section and also fills microfossil cavities (figure 3, plate 1). In the Pacific, porcelanites also contain foraminifera filled with radiating bundles of chalcedony (Heath & Moberly 1971); the calcitic microfossil walls are frequently unaltered. The zeolitic porcelanites consist of a rather featureless, very fine-grained mass of closely intermixed opal-CT and zeolites with very rare microfossil remains (figure 4, plate 1).

The cherts consist of microcrystalline quartz, including equigranular and chalcedonic varieties, whose grain size is larger than that of the opal-CT. Microfossil remains are present as areas of coarser-grained chalcedony, foraminiferal walls being preserved as radiating blades of quartz.

The sequence of formation of replacement cherts and porcelanites has been outlined by Heath & Moberly (1971). In the first stage, empty foraminiferal chambers are filled with silica, generally chalcedony but also opal-CT. The fine-grained micritic groundmass is then replaced by opal-CT and this is followed by the replacement of the microfossil walls by radiating blades of silica, frequently preserving the crystallographic orientation of the original calcite. The final stage is the filling of remaining pore spaces by silica which may also coincide with the conversion of opal-CT to quartz (see §4) to produce a true quartzitic chert.

In the case of bedded cherts, the sequence of events is much less clear. The first recognizable evidence of silicification is the development of opal-CT claystones of variable induration. In siliceous oozes, the microfossil tests become progressively more welded together and can be preserved in rocks consisting almost entirely of opal-CT (Heath 1973). Many zeolitic porcelanites, entirely devoid of microfossils, occur in sequences of unconsolidated zeolitic clays which also contain opal-CT, the variable induration of the beds most probably being due to variable cementation by the silica (Calvert 1971).

4. MINERALOGY

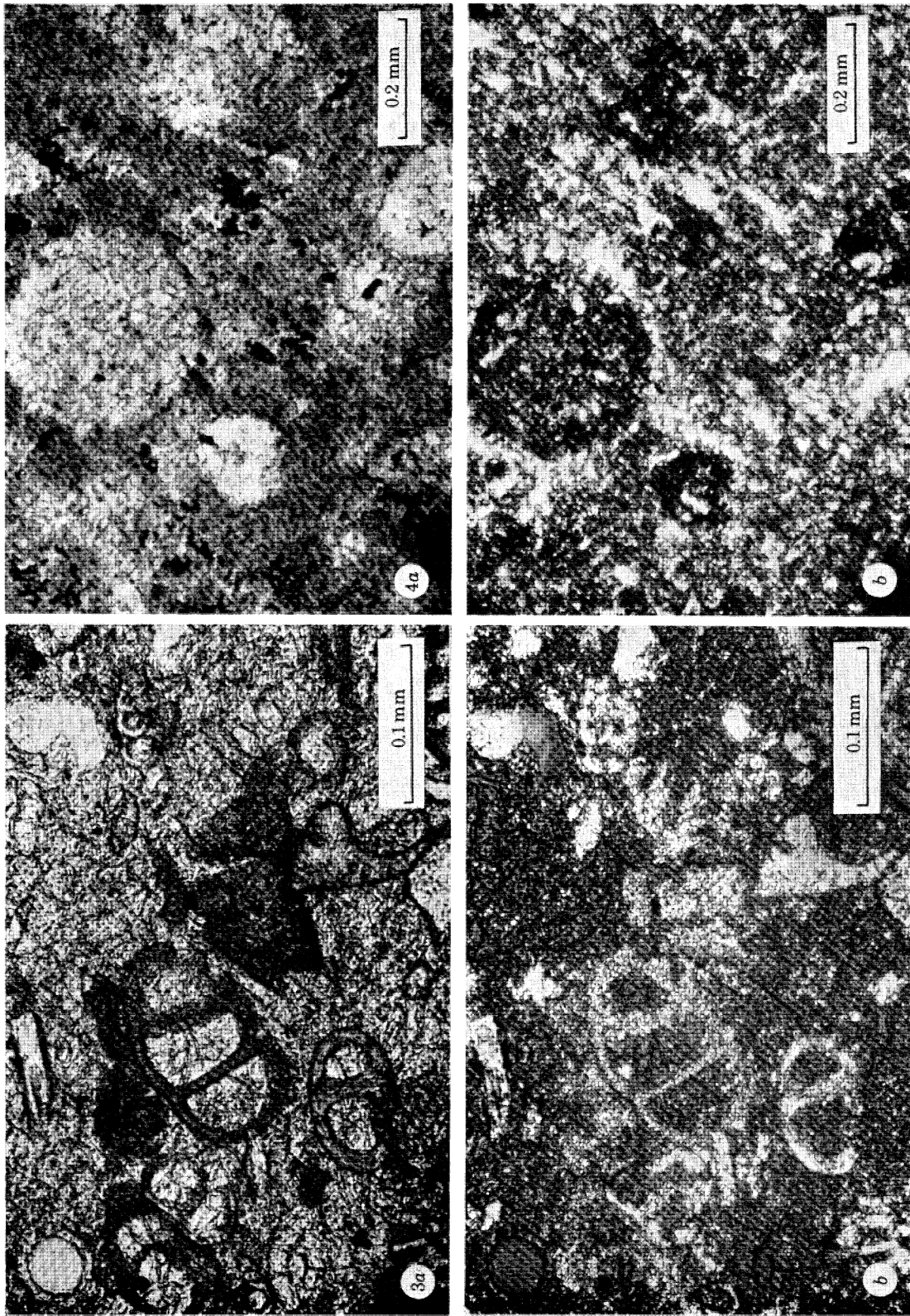
Early determinations of the mineralogy of the deep-sea cherts and porcelanites demonstrated that they were composed of more than one silica phase. Apart from quartz a second phase, which has been referred to by various authors as cristobalite, α -cristobalite, disordered cristobalite, cristobalite-tridymite, lussatite, and opal-CT, is also present.

X-ray diffraction patterns of deep-sea porcelanites are distinctive (figure 5). They show two broad reflexions at approximately 405–410 and 250 pm and a subsidiary reflexion at 425–435 pm. Although the presence of the series of peaks in the 405–435 pm region in low-temperature silicas has in the past been interpreted as β -cristobalite, the high temperature polymorph (Greigg 1932; Levin & Ott 1933; Dwyer & Mellor 1933; Buerger 1951; Omure *et al.* 1956; Buerger & Shoemaker 1972), Flörke (1955*a, b*) has shown that such patterns are produced by

DESCRIPTION OF PLATE 1

FIGURE 3. Photomicrograph of thin-section of Middle Eocene porcelanite from DSDP site 6 in the North Atlantic; upper: plain polarized light, lower: crossed nicols. Foraminiferids, glauconite, and clastic aluminosilicate grains are set in an isotropic opal-CT groundmass. Opal-CT also fills microfossil cavities, while the foraminiferal walls are composed of calcite.

FIGURE 4. Photomicrograph of thin-section of Middle Eocene porcelanite from DSDP site 9 in the North Atlantic; upper: plain polarized light, lower: crossed nicols. Circular areas are of largely isotropic silica in a brownish, very fine-grained groundmass of opal-CT and clinoptilolite.



FIGURES 3 AND 4. For description see opposite.

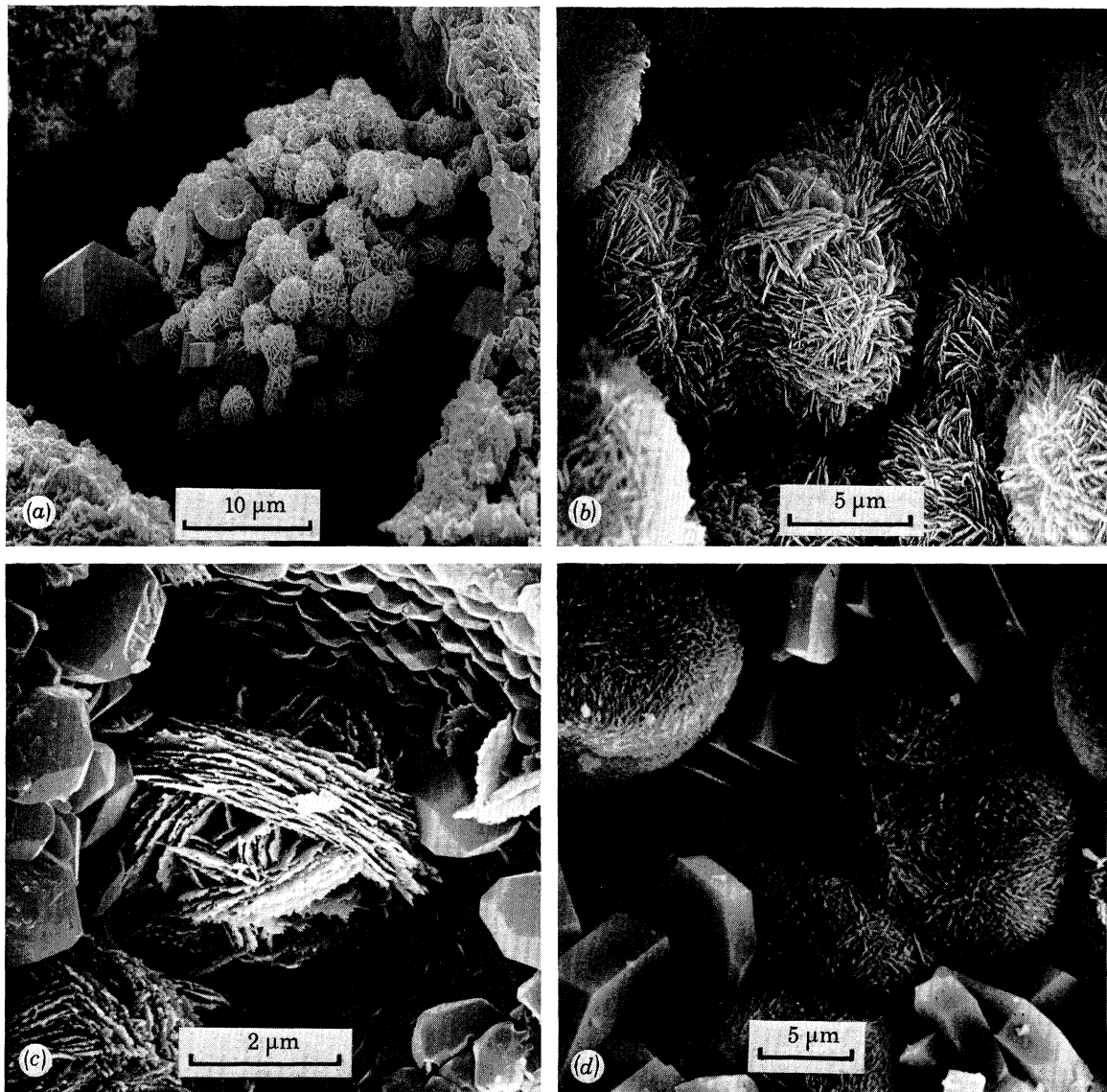


FIGURE 7. Scanning electron photomicrographs of opal-CT. (a) Cluster of lepispheres from Campanian–Maestrichtian silicified foraminiferal marlstone, Deep Sea Drilling Project Site 144, core 3, section 2, 103–104 cm, northwestern Atlantic Ocean. (b) Opal-CT lepispheres from Middle Eocene zeolitic clay and porcelanite, Deep Sea Drilling Project Site 367, core 10, section 1, 126–128 cm, northeastern Atlantic Ocean. (c) Detail of opal-CT crystals from Middle Eocene argillaceous limestone and porcelanite, Deep Sea Drilling Project Site 369A, core 35, section 1, 104–106 cm, northeastern Atlantic Ocean. (d) Opal-CT lepispheres and clinoptilolite crystals from Tertiary ashflow deposit, near Blythe, California. (a)–(c) courtesy of H. Rösch & U. von Rad; (d) courtesy of A. Tarshis.

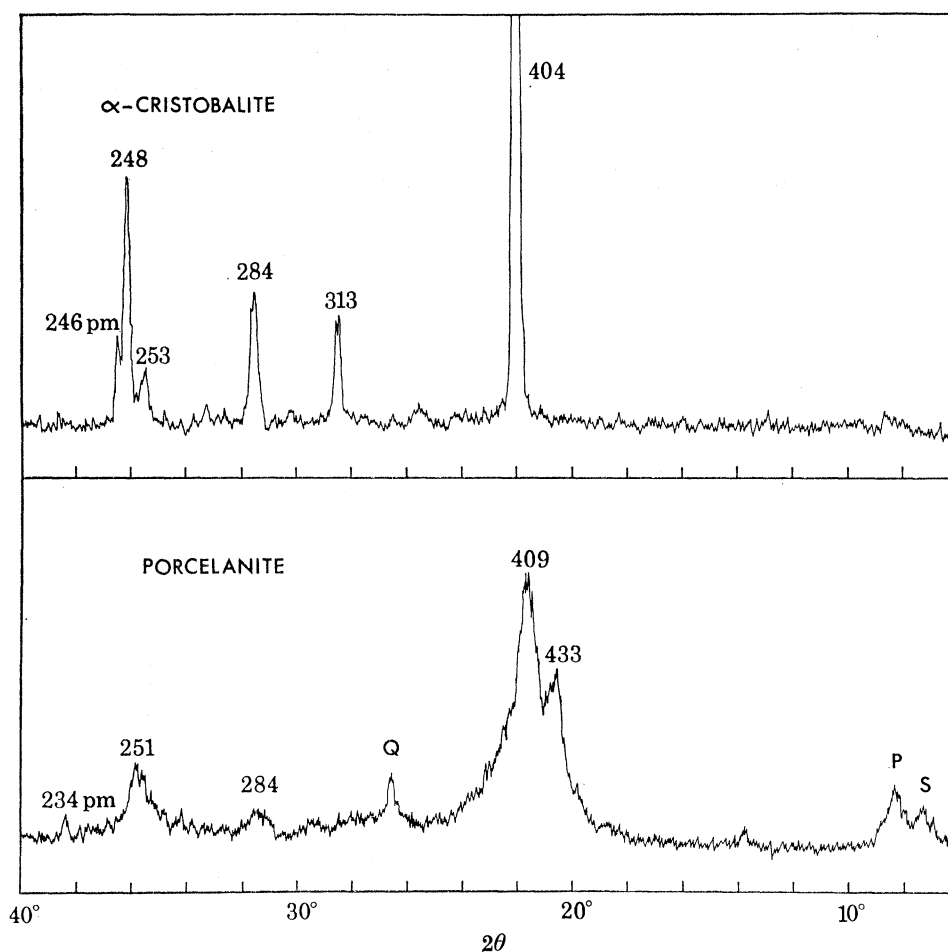


FIGURE 5. X-ray diffraction patterns of well-crystallized α -cristobalite (made by heating silica gel at 1350 °C for 4 h) and Eocene porcelanite from DSDP site 12 in the North Atlantic. P, palygorskite, S, sepiolite, Q, quartz. Peaks with spacings indicated are due to typical opal-CT.

TABLE 1. CLASSIFICATION OF NATURAL HYDROUS SILICAS ACCORDING TO JONES & SEGNI (1971)

designation	X-ray diffraction data	interpretation	occurrence
opal-A	broad, diffuse band centred at 410 pm; very low-intensity bands at <i>ca.</i> 200, 150 and 120 pm	highly disordered, nearly amorphous	precious opals; potch opals; diatom and radiolarian shells; geysersites, hyaline,
opal-CT	broad reflexions at <i>ca.</i> 410 and 250 pm; subsidiary reflexion at 425–435 pm	unidimensionally disordered cristobalite–tridymite	common opals; tripoli; opoka; porcelanites of the Monterey Formation and many others
opal-C	relatively sharp reflexions corresponding to well-crystallized α -cristobalite; some minor tridymite reflexions may occur	well-ordered α -cristobalite	opals associated with lava flows which may have been 'aged' by reheating by later flows

unidimensionally disordered low-temperature cristobalite, the random stacking arrangement of silica tetrahedral sheets producing tridymite maxima. Flörke refers to this material as *lussatite* and it is known to occur in a wide variety of low-temperature silicas, including opals, glasses, and concretions (Jones *et al.* 1964; Flörke 1955*a*; Mizutani 1966), and in bentonites and siliceous claystones (Gruner 1940; Heron *et al.* 1965).

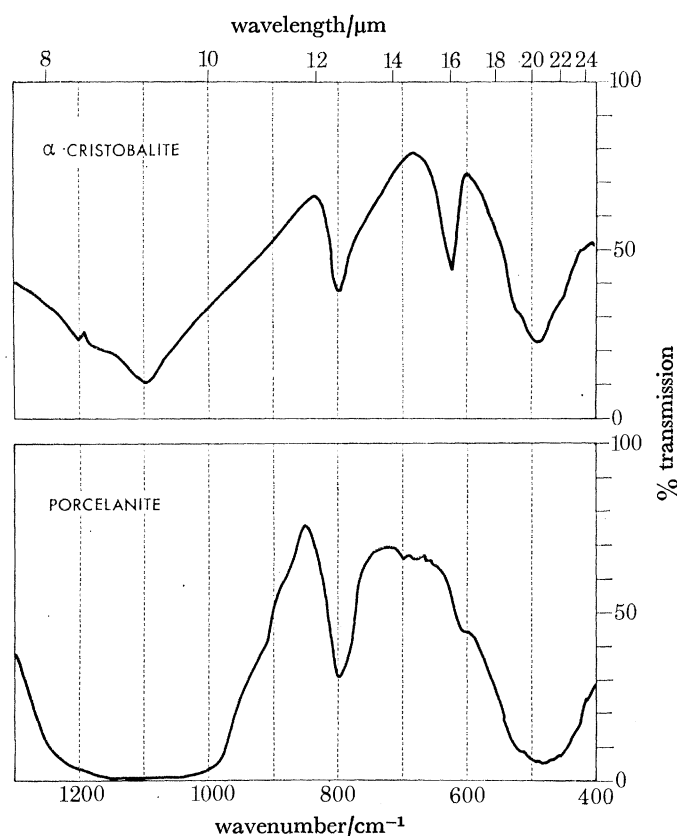


FIGURE 6. Infrared absorption spectra of the samples shown in figure 5. Note absence of band at 620 cm^{-1} , diagnostic of α -cristobalite, in the porcelanite sample.

Jones *et al.* (1964) have shown that low-temperature hydrous silicas have a wide range of structures, ranging from more or less amorphous varieties to well-crystallized α -cristobalite. On the basis of this information, Jones & Segnit (1971) have proposed a classification scheme for such phases which is summarized in table 1. All opals can be readily placed in one of the three groups shown here, while all samples of deep-sea porcelanite for which structural information is available are identified as opal-CT.

Jones & Segnit (1975) pointed out that many samples of opal-CT consist of fibrous cristobalite, which is considered to be characteristic of *lussatite* (Mallard 1890) and is in turn now known to be identical with opal-CT. Although Jones & Segnit (1971) recommended the term *lussatite* for those phases having X-ray diffraction patterns identical with that in figure 5, Oehler (1975) has pointed out, quoting a personal communication from Jones, that opal-CT is now preferred over *lussatite* by the International Mineralogical Association.

The stacking disorder in opal-CT also produces a shift in the line spacing of the cristobalite from 404 to about 411 pm (Jones & Segnit 1971). Heating opals at 1050–1100 °C results in

a decrease in the (101) spacing from 411 to 404 pm, the product showing an X-ray diffraction pattern closely similar to that of opal-C. Murata & Nakata (1974) have shown that the opal-CT in the Monterey Formation porcelanites has $d(101)$ spacings which decrease with increasing burial, implying that the opal becomes progressively more ordered with age and/or overburden pressure.

The structural interpretation of the porcelanite opal-CT is confirmed by infrared absorption data which show spectra characteristic of completely disordered low-cristobalite (figure 6). The absorption bands at 620 cm^{-1} and 560 cm^{-1} , which are characteristic of well-ordered α -cristobalite and α -tridymite, respectively (Lippincott *et al.* 1958; Rey 1966; Plyusnina *et al.* 1970; Jones & Segnit 1975) are both absent. Similar spectra to those shown in figure 6 are displayed by biogenous silica and many amorphous opals.

An alternative interpretation of the structure of opal-CT has been offered by Wilson *et al.* (1974) but rejected by Jones & Segnit (1975). Wilson and co-workers suggested that the silica phase in a deep-sea porcelanite and in a bentonite was more properly called tridymite, based on its hexagonal morphology, its hexagonal electron diffraction pattern, and on the lack of infrared absorption bands diagnostic of α -cristobalite. They suggested that the distinctive X-ray diffraction patterns of such material are produced by random transverse displacements of the silica tetrahedra normal to the c -axis, rather than irregular stacking of cristobalite and tridymite sheets as proposed originally by Flörke (1955*a*).

Jones & Segnit (1975) have pointed out that the hexagonal morphology and the electron diffraction pattern cited by Wilson *et al.* are equally well produced by disordered cristobalite. Moreover, the infrared spectra of disordered low tridymite and disordered low cristobalite are quite similar because the stacking disorder causes the disappearance of several diagnostic absorption bands in both varieties of silica. However, the X-ray diffraction pattern of opal-CT is distinctive and does not resemble either well-ordered tridymite or well-ordered cristobalite. In addition, dilatometer data for opal-CT (Jones & Segnit 1971) show clear discontinuities at temperatures corresponding to the inversions of both tridymite and cristobalite.

5. ULTRAMORPHOLOGY

Opal-CT in deep-sea porcelanites occurs as spherical crystal aggregates, of the order 3–10 μm in diameter, composed of bladed crystals 30–50 nm thick (figure 7, plate 2). The spherical aggregates were referred to as *lepispheres* by Wise & Kelts (1927), and are figured by Weaver & Wise (1972), Wise *et al.* (1972), von Rad & Rösch (1927), and Lancelot (1973). Lepispherical opal-CT also occurs in opal claystones of the southeastern U.S. (Wise & Weaver 1973), in some Australian opals (Segnit *et al.* 1973), in the Monterey Formation porcelanites (Oehler 1975), in altered pyroclastic rocks (Wise *et al.* 1973; A. Tarshis, personal communication), and in a wide variety of primary and replacement hydrous silicas (Flörke *et al.* 1975). It has also been synthesized by Oehler (1973), who refers to it as tridymite because of its morphology, and by Flörke *et al.* (1975), who have pointed out that the bladed crystal habit is also formed by low-temperature disordered cristobalite.

The bladed crystal habit of opal-CT is responsible for the lack of certain cristobalite reflexions in X-ray diffraction patterns of this material (Flörke *et al.* (1975), a characteristic feature frequently referred to in discussions of the structure of the phase (Flörke 1955*a, b*).

6. FORMATION OF DEEP-SEA CHERTS AND PORCELANITES

(a) Precipitation of opal-CT

The precipitation of disordered cristobalite–tridymite at earth surface conditions takes place in the stability field of quartz. The formation of metastable silica polymorphs during the recrystallization of glasses has been frequently reported and is discussed by Sosman (1965).

Jones & Segnit (1972) have explained this phenomenon by proposing that the first-formed product of the polymerization of silica from solution at low temperature consists of six-membered unconstrained rings which will coalesce to form extended sheets having the structure of cristobalite and tridymite. Quartz is not formed under these conditions of high silica concentrations (see §6*b*) and low energy or low ionic mobilities without breaking Si–O bonds. In addition, cristobalite will be preferred over tridymite during such a process because a lower energy structure is produced in the cristobalite as a consequence of the detailed arrangement of the silica tetrahedra (Flörke 1967).

Low-cristobalite has commonly been observed as an intermediate phase in experiments designed to study the formation of quartz from amorphous silica (Carr & Fyfe 1958; Campbell & Fyfe 1960; Heydemann 1964; Mizutani 1966; Siffert & Wey 1967). An evaluation of this literature by Betterman & Liebau (1975) has shown that other intermediate phases in this reaction, namely SiO₂-X and keatite, are formed together with cristobalite in a strict sequence under different pressure conditions and with different OH⁻ ion activities. Only at high pressures, above 3 kbar (300 MPa), or at high OH⁻ activities is an intermediate phase absent in the reaction amorphous silica → quartz.

As argued by Wise *et al.* (1972), the morphology of the opal-CT in deep-sea porcelanites indicates that the silica has precipitated from solution and is not an inversion product of opal-A nor a product of a gel. It seems reasonable to conclude, therefore, that silica is released into solution, for example by biogenous opal, clays and volcanic products, during diagenetic reactions within sediments and precipitates in available voids and pores either as opal-CT lepispheres or as intergrown masses of opal-CT and clays.

(b) Formation of chert

The Miocene Monterey Formation of California contains diatomites, porcelanites, and cherts in a stratigraphic sequence which suggests the formation of the cherts by the progressive conversion of diatomite to porcelanite and porcelanite to chert (Bramlette 1946). The presence of opal-CT in the porcelanites, and the suggestion that it represents an intermediate phase in this reaction, were reported by Ernst & Calvert (1969), while Murata & Nakata (1974) have arrived at similar conclusions.

Experimental data on the conversion of Monterey porcelanite to quartz were obtained by Ernst & Calvert (1969) and were interpreted in terms of a zero-order reaction with an activation energy of 26 kcal/mol (100 kJ/mol). The reaction was described as a solid–solid inversion, the rate depending solely on temperature and, by inference, time.

This mechanism has been accepted by Heath & Moberly (1971), Calvert (1971), Heath (1973), and Wise & Weaver (1974) for the formation of the deep-sea cherts. It is referred to as the ‘maturation theory’ by Wise & Weaver (1974). Some evidence for the solid–solid inversion of opal-CT to quartz is reported by Heath & Moberly (1971), who have shown

distinctly irregular contacts between the two phases in a Pacific chert which are readily interpreted as inversion fronts of the two minerals.

On the other hand such evidence is rare, and cherts are generally much less porous than the accompanying porcelanites in a given sequence of siliceous rocks (see Bramlette 1946; Heath & Moberly 1971), so that some additional silicification of the original sediment, commonly consisting of biogenous silica, is required. Hence, a solution and reprecipitation step may well be implied.

Stein & Kirkpatrick (1976) have shown that the run-products from the experiments of Ernst & Calvert (1969) contain well-crystallized quartz needles and euhedral crystals of quartz with doubly-terminated prisms. Their formation therefore involved a solution step and a first-order reaction mechanism is more probable. This conclusion was also reached by Mizutani (1966) who carried out experiments on the conversion of silicic acid to quartz in KOH solutions, where solution was undoubtedly promoted by high pH.

Accepting for the moment the maturation theory of chert formation, one would expect to find that the cherts were consistently older than the porcelanites in any given drill site. Although this relation is found at some individual sites (see Calvert 1971), Heath & Moberly (1971) and Lancelot (1973) have reported that it does not exist on a regional basis. In the western Pacific, Heath & Moberly (1971) found that rocks consisting entirely of quartz, regardless of age, occurred at sites having a higher *in situ* temperature. On the other hand, the highest opal-CT/quartz ratios were found at an estimated *in situ* temperature of 15 °C, possibly a temperature at which a maximal rate of conversion of amorphous opal to opal-CT takes place. At higher temperatures, the opal-CT to quartz conversion would presumably be more rapid.

Lancelot (1973) and Greenwood (1973) discovered a relation between the occurrence of cherts and porcelanites and the composition of the host sediments which could cast doubt on the recrystallization sequences outlined above. In the central Pacific, these authors claimed that porcelanites occurred in clay-rich sediments (including zeolitic clays, clayey radiolarian oozes, marls, and marly limestones) while cherts occurred in limestone and nannofossil ooze sequences. Such lithological relations are explained by Lancelot by the preferential formation of opal-CT in environments where 'foreign cations' (see Flörke 1955 *a*) are abundant, such that the precipitated phase is a disordered SiO₂ polymorph rather than quartz. In calcareous sediments, such cations would be in low concentrations and the phase formed would be quartz. This would mean that the mineralogy of precipitated silica phases in deep-sea sediments depends on the environment of formation, and that the maturation sequence outlined by Ernst & Calvert (1969) does not apply to the deep-sea chert and porcelanite occurrences.

The observations of Lancelot (1973) and Greenwood (1973) are at variance with those of Heath & Moberly (1971) and Heath (1973), who have found abundant opal-CT in carbonate-rich sediments and quartz-rich cherts in radiolarian siltstones. Wise & Weaver (1974) have also found abundant opal-CT in clay-free nannofossil chalks from the Atlantic and from equally clay-free siliceous ooze from the Indian Ocean.

An explanation for the formation of cherts which explains this conflicting evidence has been outlined by Kastner & Keene (1975). They have pointed out that in many examples from the Pacific relatively young cherts in carbonate sediments contain much more quartz than older porcelanites in clay-rich sequences. If the temperature differences between such sites are small this implies that there may be a catalysed recrystallization of silica to quartz in carbonates or an inhibited conversion of opal-CT to quartz in clays. In hydrothermal experiments on the

solution of biogenous silica and the precipitation of secondary silica phases, Kastner & Keene (1975) observed that opal-CT lepispheres were formed only in the presence of solid carbonate (foraminiferids), implying that the presence of carbonate enhanced the solution rate of biogenous silica or the crystallization rate of opal-CT. They also surmised that the presence of other cations (i.e., other than Ca^{2+}) in clays may also stabilize the opal-CT for a longer time period, thereby retarding its conversion to quartz. Additionally, Kastner & Keene argued that direct precipitation of quartz from solution is also possible, as indicated by the experiments of McKenzie & Gees (1971), when the concentration of silica in the solution phase was relatively low. In carbonate-rich sediments, sources of silica, in the form of biogenous debris, would be low so that interstitial dissolved silica concentrations would also be low. If such concentrations were to rise above the equilibrium value with respect to opal-CT, this phase would form in preference to quartz. Both of these suggestions would offer explanations for the observations of Lancelot (1973) and Greenwood (1973) on the one hand, and Heath & Moberly (1971), Heath (1973), and Weaver & Wise (1974) on the other.

7. SOURCES OF SILICA

The main possible sources of silica for the formation of deep-sea cherts and porcelanites are biogenous opal and certain volcanic products. The importance of biogenous sources has been emphasized by Heath & Moberly (1971), von der Borch *et al.* (1971), Wise *et al.* (1972), Heath (1973), Lancelot (1973), and Keene (1975). The evidence includes the presence of corroded siliceous shells in sediments associated with cherts and porcelanites, the occurrence of moulds of siliceous microfossils in the silicified rocks, the occasional occurrence of silicified siliceous ooze in cherts and the restriction of the siliceous rocks to areas of high primary plankton production. Also mentioned is the paucity of evidence for the association of opal-CT with volcanic sediments (Lancelot 1973) and the lack of pseudomorphs of glass shards in cherts (Heath 1973).

Calvert (1971, 1974) has contended that the silica in deep-sea cherts and porcelanites has a variety of origins, including biogenous siliceous debris, the alteration of volcanic debris, and also, possibly, hydrothermal sources. Many of the porcelanites from the North Atlantic and Pacific Oceans occur in sequences of altered volcanic material consisting of zeolitic (clinoptilolite) and montmorillonite clays, or in sections containing abundant sepiolite and palygorskite. The association of clinoptilolite, montmorillonite, and opal-CT is very common in altered pyroclastic deposits on land (Bramlette & Posnjak 1933; Deffeyes 1959; Hay 1966; Reynolds & Anderson 1967; Iijima & Utada 1966; Reynolds 1970). Hemley, Meyer & Richter (1961) have shown experimentally that montmorillonite and low-cristobalite are formed during the low-temperature alteration of albite. Gruner (1940) had earlier explained the presence of opal-CT in bentonites by the alteration of ash and had argued that it represented a metastable phase, recrystallizing to quartz with time.

Recently, Guven & Grim (1972) have shown the intimate intergrowth of montmorillonite and disordered cristobalite (opal-CT) in some bentonites, and Wise *et al.* (1973) have shown that the opal-CT in one of the samples studied by Guven & Grim (1972) occurs as distinct lepispheres. An occurrence of lepispherical opal-CT and clinoptilolite in an ashflow sequence in California is described by A. Tarshis (U.S. Geological Survey, personal communication) (see figure 7*d*).

Bowles *et al.* (1971) explained the presence of abundant sepiolite and palygorskite in some north Atlantic sediments by precipitation of these phases from hydrothermal solutions migrating through the sediments. It seems reasonable to suggest that opal-A could also be precipitated by such a process, and eventually be converted to opal-CT, as is known to take place in some hot-spring deposits (White *et al.* 1964).

The source of silica in the extensive siliceous clay-rich rocks from the southeastern United States, previously considered to be altered volcanic deposits based on the presence of zeolites and montmorillonite, is considered by Wise & Weaver (1973, 1974) to be biogenous microfossil debris. This conclusion was based on the presence of moulds of siliceous fossils, now composed of opal-CT, although the abundance of such moulds is apparently quite low because the beds are believed to be highly altered, and the supposedly inadequate quantities of silica released from altered volcanic material to form extensive chert beds.

8. CONCLUSION

It is clear from this brief review of the possible modes of formation of deep-sea cherts and porcelanites that some less equivocal criteria for identifying sources of silica are required. As suggested by Calvert (1974), the oxygen isotopic composition of opal-CT in such rocks may provide such criteria, following the work of Henderson *et al.* (1971, 1972). Although Knauth & Epstein (1975) have provided some data, the sampling strategy was not designed to test this suggestion and the problem remains unresolved.

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REFERENCES (Calvert)

- Betterman, P. & Liebau, F. 1975 The transformation of amorphous silica to crystalline silica under hydrothermal conditions. *Contr. Miner. Petrol.* **53**, 25–36.
- Bowles, F. A., Angino, E. E., Hosterman, J. W. & Galle, O. K. 1971 Precipitation of deep-sea palygorskite and sepiolite. *Earth Planet. Sci. Lett.* **11**, 324–332.
- Bramlette, M. N. 1946 The Monterey Formation of California and the origin of its siliceous rocks. *U.S. Geol. Surv. Prof. Pap.* **212**, 57 pp.
- Bramlette, M. N. & Posnjak, E. 1933 Zeolite alteration of pyroclastics. *Am. Miner.* **18**, 167–171.
- Buerger, M. J. 1951 Crystallographic aspects of phase transformations. In *Phase transformations in solids* (eds R. Smoluchowski, J. E. Mayer & W. A. Weyl), New York: J. Wiley. pp. 183–209.
- Buerger, M. J. & Shoemaker, G. L. 1972 Thermal effect in opal below room temperature. *Proc. Natn. Acad. Sci., U.S.A.* **69**, 3225–3227.
- Calvert, S. E. 1971 Composition and origin of North Atlantic deep sea charts. *Contr. Miner. Petrol.* **33**, 273–288.
- Calvert, S. E. 1974 Deposition and diagenesis of silica in marine sediments. In *Pelagic sediments: on land and under the Sea*. (eds K. J. Hsü & H. C. Jenkyns), vol. 1, pp. 273–299. Spec. Publ. Int. Assoc. Sediment.
- Campbell, A. S. & Fyfe, W. S. 1960 Hydroxyl ion catalysis of the hydrothermal crystallisation of amorphous silica: a possible high temperature pH indicator. *Am. Miner.* **45**, 464–468.
- Carr, R. M. & Fyfe, W. S. 1958 Some observations on the crystallisation of amorphous silica. *Am. Miner.* **43**, 908–916.
- Deffeyes, K. S. 1959 Zeolites in sedimentary rocks. *J. Sedim. Petrol.* **29**, 602–609.
- Dwyer, F. P. & Mellor, D. P. 1933 A note on the occurrence of β -cristobalite in Australian opals. *J. R. Soc. New South Wales* **66**, 378–382.
- Ernst, W. G. & Calvert, S. E. 1969 An experimental study of the recrystallisation of porcelanite and its bearing on the origin of some bedded cherts. *Am. J. Sci.* **267A**, 114–133.

- Ewing, M., Worzel, J. L., Beall, A. O., Bergeren, W. A., Bukry, D., Burk, C. A., Fischer, A. G. & Pessagno, E. A. 1969 *Initial reports of the Deep Sea Drilling Project*, vol. 1. Washington, D.C.: U.S. Government Printing Office.
- Flörke, O. W. 1955a Zur Frage des 'Hoch' – Cristobalite in Opalen, Bentoniten und Gläsern. *Neu. J. Mineral. Mh.* 217–223.
- Flörke, O. W. 1955b Strukturanomalien bei Tridymit und Cristobalite. *Ber. Deutsch. Keram. Gesell.* **32**, 369–381.
- Flörke, O. W. 1967 The structures of AlPO_4 and SiO_2 . In *Science of ceramics* (ed G. H. Stewart), vol. 3, pp. 13–27. London: Academic Press.
- Flörke, O. W., Jones, J. B. & Seignit, E. R. 1975 Opal-CT crystals. *Neu. Jahrb. Mineral. Mh.* 369–377.
- Gartner, S. 1970 Sea-floor spreading, carbonate dissolution level and the nature of Horizon A. *Science, N.Y.* **169**, 1077–1079.
- Greenwood, R. 1973 Cristobalite: its relationship to chert formation in selected samples from the Deep Sea Drilling Project. *J. Sedim. Petrol.* **43**, 700–708.
- Greigg, J. W. 1932 The existence of the high temperature form of cristobalite at room temperature and the crystallinity of opal. *J. Am. Chem. Soc.* **54**, 2846–2849.
- Gruner, J. W. 1940 Abundance and significance of cristobalite in bentonites and Fuller's earth. *Econ. Geol.* **35**, 867–875.
- Guyen, N. & Grim, R. E. 1972 X-ray diffraction and electron optical studies on smectite and α -cristobalite associations. *Clays and Clay Min.* **20**, 89–92.
- Hay, R. L. 1966 Zeolites and zeolitic reactions in sedimentary rocks. *Geol. Soc. Am. Spec. Pap.* **85**, 130 pp.
- Heath, G. R. 1973 Cherts from the eastern Pacific, Leg 16, Deep Sea Drilling Project. In *Initial reports of the Deep Sea Drilling Project* (eds van Andel *et al.*), vol. 16, pp. 609–613. Washington: U.S. Government Printing Office.
- Heath, G. R. 1974 Dissolved silica and deep-sea sediments. In *Studies in paleo-oceanography* (ed W. W. Hay), *Soc. Econ. Paleont. Mineral. Spec. Publ.* **20**, 77–93.
- Heath, G. R. 1977 Processes controlling siliceous biogenous deposits. In *Marine plankton and sediments* (eds W. R. Riedel & T. Saito). U.S. Mus. Nat. History: Micropaleontology Press. (In the press.)
- Heath, G. R. & Moberly, R. 1971 Cherts from the western Pacific, Leg 7, Deep Sea Drilling Project. In *Initial reports of the Deep Sea Drilling Project* (eds E. L. Winterer *et al.*), vol. 7, part 2, pp. 991–1008. Washington, U.S.: Government Printing Office.
- Hemley, J. J., Meyer, C. & Richter, D. H. 1961 Some alteration reactions in the system $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$. *U.S. Geol. Surv. Prof. Pap.* **424D**, 338–340.
- Henderson, J. H., Jackson, M. L., Syers, J. K., Clayton, R. N. & Rex, R. W. 1971 Cristobalite authigenic origin in relation to montmorillonite and quartz origin in bentonites. *Clays and Clay Min.* **19**, 229–238.
- Henderson, J. H., Clayton, R. N., Jackson, M. L., Syers, J. K., Rex, R. W., Brown, J. L. & Sachs, I. B. 1972 Cristobalite and quartz isolation from soils and sediments by hydrofluosilicic acid treatment and heavy liquid separation. *Soil Sci. Soc. Am. Proc.* **36**, 830–835.
- Heron, S. D., Robinson, G. C. & Johnson, H. S. 1965 Clays and opal-bearing claystones of the South Carolina coastal plain. *State Devel. Board South Carolina, Div. Geol., Bull.* **31**, 64 pp.
- Heydemann, A. 1964 Untersuchungen über die Bildungsbedingungen von Quarz im Tempersturbereich zwischen 100 °C und 250 °C. *Beitr. zur Mineral. und. Petrog.*, **10**, 242–259.
- Iijima, A. & Utada, M. 1966 Zeolites in sedimentary rocks, with reference to the depositional environments and zonal distribution. *Sedimentology* **7**, 327–357.
- JOIDES 1967 The Deep Sea Drilling Project. *Bull. Am. Ass. Petrol. Geol.* **51**, 1787–1802.
- Jones, J. B. & Segnit, E. R. 1971 The nature of opal. I. Nomenclature and constituent phases. *J. geol. Soc. Australia* **18**, 57–68.
- Jones, J. B. & Segnit, E. R. 1972 Genesis of cristobalite and tridymite at low temperatures. *J. geol. Soc. Australia* **18**, 419–422.
- Jones, J. B. & Segnit, E. R. 1975 Nomenclature and structure of natural disordered (opaline) silica. *Contr. Miner. Petrol.* **51**, 231–234.
- Jones, J. B., Sanders, J. V. & Segnit, E. R. 1964 Structure of opal. *Nature, Lond.* **204**, 990–991.
- Kastner, M. & Keene, J. R. 1975 Diagenesis of pelagic siliceous oozes. *Proc. IXth Int. Cong. of Sedimentology* **7**, 89–98.
- Keene, J. B. 1975 Cherts and porcelanites from the North Pacific, DSDP Leg 32. In *Initial Reports of the Deep Sea Drilling Project* (eds R. L. Larson, R. Moberly *et al.*), vol. 32, pp. 429–507. Washington D.C.: Government Printing Office.
- Knauth, L. P. & Epstein, S. 1975 Hydrogen and oxygen isotope ratios in silica from the JOIDES Deep Sea Drilling Project. *Earth Planet. Sci. Lett.* **25**, 1–10.
- Lancelot, Y. 1973 Chert and silica diagenesis in sediments from the central Pacific. In *Initial reports of the Deep Sea Drilling Project* (eds E. L. Winterer, J. E. Ewing *et al.*), vol. 17, pp. 377–405. Washington D.C.: Government Printing Office.
- Levin, J. & Ott, E. 1933 X-ray study of opals, silica glass and silica gel. *Z. Krist.* **85**, 305–318.

- Lippincott, E. R., Van Valkenburg, A., Weir, C. E. & Bunting, E. N. 1958 Infra-red studies on polymorphs of silicon dioxide and germanium dioxide. *J. Res. Natl. Bur. Standards* **61**, 61–70.
- MacKenzie, F. T. & Gees, R. 1971 Quartz: synthesis at Earth-surface conditions. *Science, N.Y.* **173**, 533–535.
- Mallard, M. E. 1890 Sur la lussatite, nouvelle variété minérale cristallisée de silice. *Bull. Soc. Fr. Mineral. Cristallog* **13**, 63–66.
- Mizutani, S. 1966 Transformation of silica under hydrothermal conditions. *Nagoya Univ. J. Earth Sci.* **14**, 56–88.
- Murata, K. J. & Nakata, J. K. 1974 Cristobalitic stage in the diagenesis of diatomaceous shale. *Science, N.Y.* **184**, 567–568.
- Oehler, J. H. 1973 Tridymite-like crystals in critobalitic ‘cherts’. *Nature, Phys. Sci.* **241**, 64–65.
- Oehler, J. H. 1975 Origin and distribution of silica lepispheres in porcelanite from the Monterey Formation of California. *J. Sedim. Petrol.* **45**, 252–257.
- Omure, M., Ookaware, S. & Iwai, Sh. 1956 Über die Entstehung des Hoch – Cristobalits in Roseki-Schamotte. *Naturwissenschaften* **43**, 495.
- Peterson, M. N. A., Edgar, N. T., Cita, M., Gartner, S., Goll, R., Nigrini, C. & von der Borch, C. 1970 *Initial reports of the Deep Sea Drilling Project*, vol. 2. Washington, D.C.: U.S. Government Printing Office.
- Plyusnina, I. I., Maleyev, M. N. & Yefimova, G. A. 1970 Infra-red-spectroscopic investigation of cryptocrystalline varieties of silica. *Izvest. Akad. Nauk. S.S.S.R., Ser. Geol.* **9**, 78–83. (Engl. trans. 1750–1754.)
- Rey, T. 1966 Ultrarotabsorption von AlPO_4 und SiO_2 in Abhängigkeit von Fehlordnung und Temperatur. *Z. Krist.* **123**, 266–314.
- Reynolds, R. C. & Anderson, D. M. 1967 Cristobalite and clinoptilolite in bentonite beds of the Colville Group, Northern Alaska. *J. Sedim. Petrol.* **37**, 966–969.
- Reynolds, W. R. 1970 Mineralogy and stratigraphy of Lower Tertiary clays and claystones of Alabama. *J. Sedim. Petrol.* **40**, 829–838.
- Segnit, E. R., Jones, J. B. & Anderson, C. A. 1973 Opaline silicas from the Murray River region west of Wentworth, N.S.W., Australia. *Mem. Nat. Mus. Vic.* **34**, 187–194.
- Siffert, B. & Wey, R. 1967 Étude quantitative de la transformation de la silice en quartz entre 230° et 350 °C en présence de bases alcalines. *Silicates Ind.* **32**, 415–421.
- Smith, W. E. 1960 The siliceous constituents of chert. *Geol. Mijnbouw.* **39**, 1–8.
- Sosman, R. B. 1965 *The phases of silica*. Rutgers University Press. 388 pp.
- Stein, C. L. & Kirkpatrick, R. J. 1976 Experimental porcelanite recrystallisation kinetics: a nucleation and growth model. *J. Sedim. Petrol.* **46**, 430–435.
- Taliaferro, N. L. 1934 Contraction phenomena in cherts. *Bull. geol. Soc. Am.* **45**, 189–232.
- Von Rad, U. & Rösch, H. 1972 Mineralogy and origin of clay minerals, silica and authigenic silicates in Leg 14 sediments. In *Initial reports of the Deep Sea Drilling Project* (eds D. E. Hayes *et al.*), vol. 14, pp. 727–751. Washington: U.S. Government Printing Office.
- Von der Borch, C. C., Galehouse, J. & Nesteroff, W. D. 1971 Silicified limestone–chert sequences cored during Leg 8 of the Deep Sea Drilling Project: A petrologic study. In *Initial reports of the Deep Sea Drilling Project* (eds J. I. Tracey *et al.*), vol. 8, pp. 819–828. Washington: U.S. Government Printing Office.
- Warren, B. E., & Bischof, J. 1938 The structure of silica glass by X-ray diffraction. *J. Am. Ceram. Soc.* **21**, 49–54.
- Weaver, F. M. & Wise, S. W. 1972 Ultramorphology of deep sea cristobalitic chert. *Nature Phys. Sci.* **237**, 56–57.
- Weaver, F. M. & Wise, S. W. 1974 Opaline sediments of the south eastern Coastal Plain and Horizon A: biogenic origin. *Science, N.Y.* **184**, 899–901.
- Wilson, M. J., Russell, J. D. & Tait, J. M. 1974 A new interpretation of the structure of disordered α -cristobalite. *Contr. Miner. Petrol.* **47**, 1–6.
- Wise, S. W. & Kelts, K. R. 1972 Inferred diagenetic history of a weakly silicified deep sea chalk. *Trans. Gulf Coast Ass. geol. Soc.* **22**, 177–203.
- Wise, S. W., Buie, B. F. & Weaver, F. M. 1972 Chemically precipitated sedimentary cristobalite and the origin of chert. *Ecolg. Geol. Helv.* **65**, 157–163.
- Wise, S. W. & Weaver, F. M. 1973 Origin of critobalite-rich Tertiary sediments in the Atlantic and Gulf coastal plain. *Trans. Gulf Coast Ass. geol. Soc.* **23**, 305–323.
- Wise, S. W. & Weaver, F. M. 1974 Chertification of oceanic sediments. In *Pelagic sediments: on land and under the sea* (eds K. J. Hsü & H. C. Jenkyns), vol. 1, pp. 30–326. Spec. Publ. Int. Ass. Sedimentol.
- Wise, S. W., Weaver, F. M. & Guven, N. 1973 Early silica diagenesis in volcanic and sedimentary rocks: devitrification and replacement phenomena. *31st Ann. Proc. Electron Microsc. Soc. Am.* 206–207.
- White, D. E., Thompson, G. A. & Sandberg, C. H. 1964 Rocks, structure and geologic history of Steamboat Springs thermal area, Washoe County, Nevada. *U.S. Geol. Surv. Prof. Pap.* **458B**, 63 pp.

Discussion

R. G. BURNS (*Department of Earth and Planetary Sciences, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, U.S.A.*). The scanning electron photomicrographs of spherical microcrystalline aggregates of bladed opal-CT crystallites shown by Dr Calvert resemble certain textures observed inside manganese nodules, particularly those collected from siliceous oozes in the equatorial North Pacific. Such clusters in nodules, however, are coated with manganese oxides and give X-ray diffraction patterns of δ -MnO₂ or incipient todorokite. Has Dr Calvert observed opal-CT in manganese nodules or associated siliceous oozes?

S. E. CALVERT. No.

J. V. SMITH (*Dept. of the Geophysical Sciences, University of Chicago, Chicago, Illinois 60637, U.S.A.*).

(a) Clinoptilolite is a high-silica zeolite, and zeolites with lower silica content occur on the sea-floor. Is clinoptilolite the only zeolite occurring together with the silica phases, as might be expected for equilibrium?

(b) Tridymite and cristobalite are polytypes and if fully ordered should have respectively hexagonal and isometric symmetry. Does the morphology of the silica phases in deep-sea cherts give any clue to their polytypic variety?

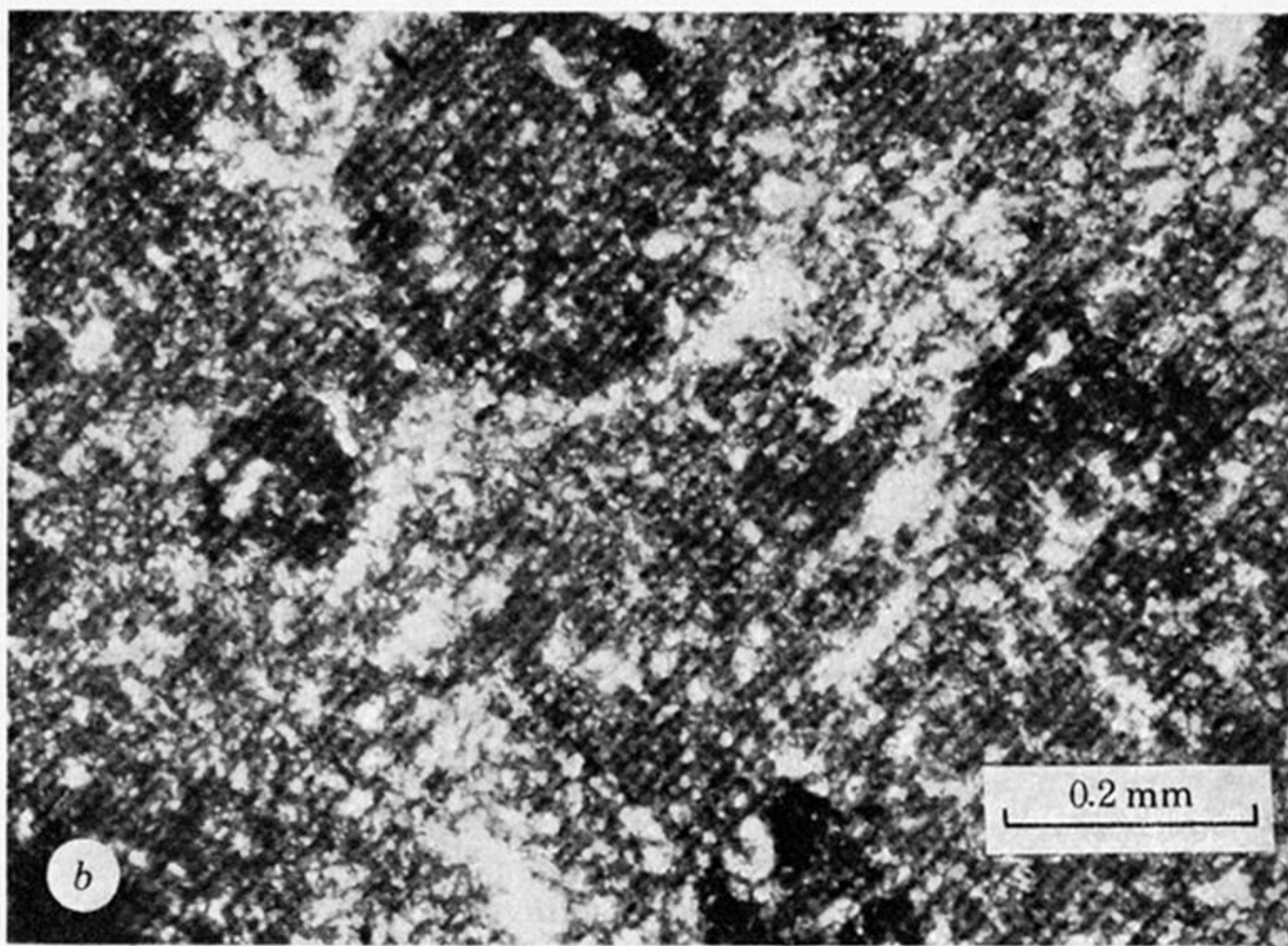
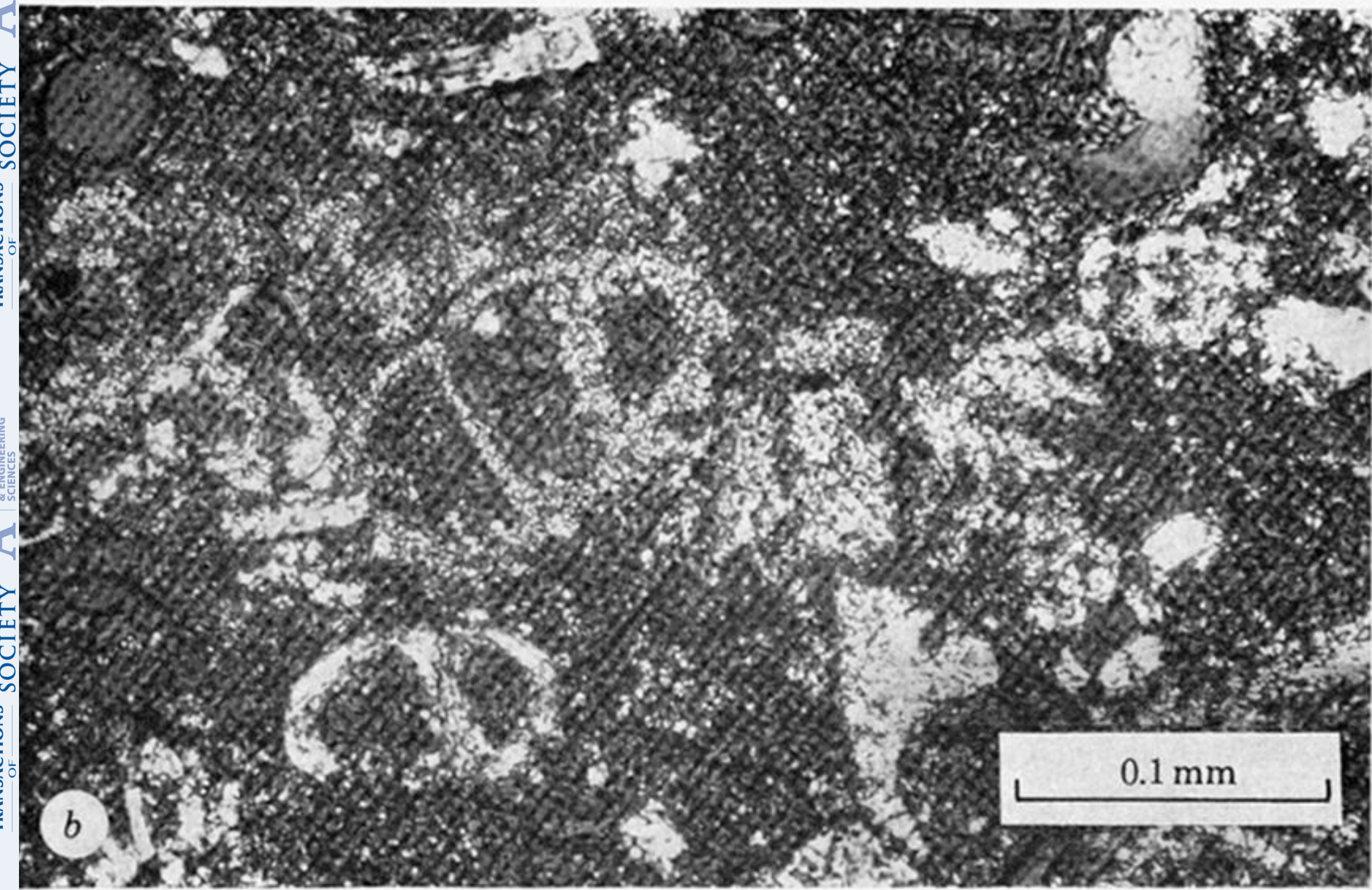
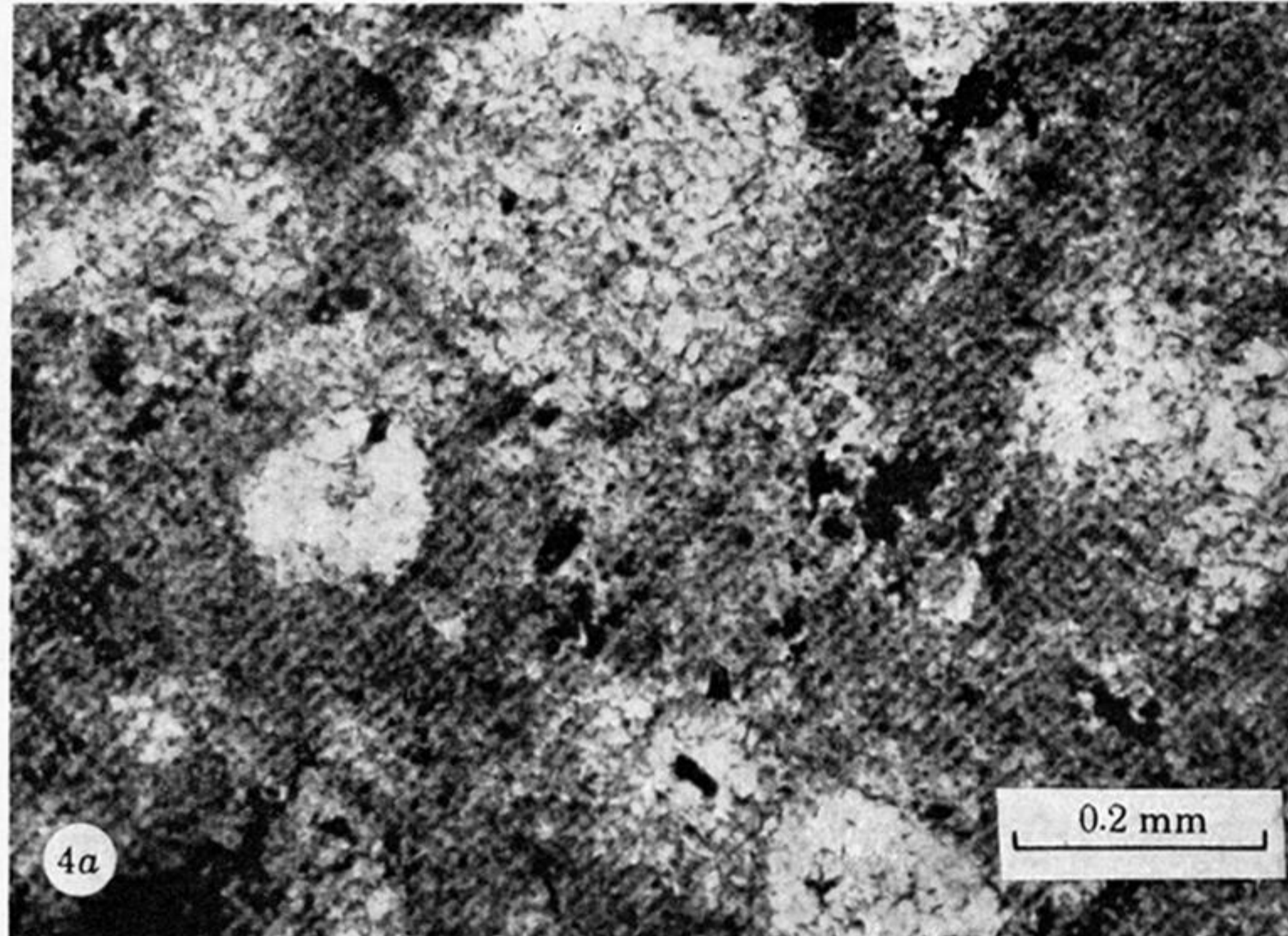
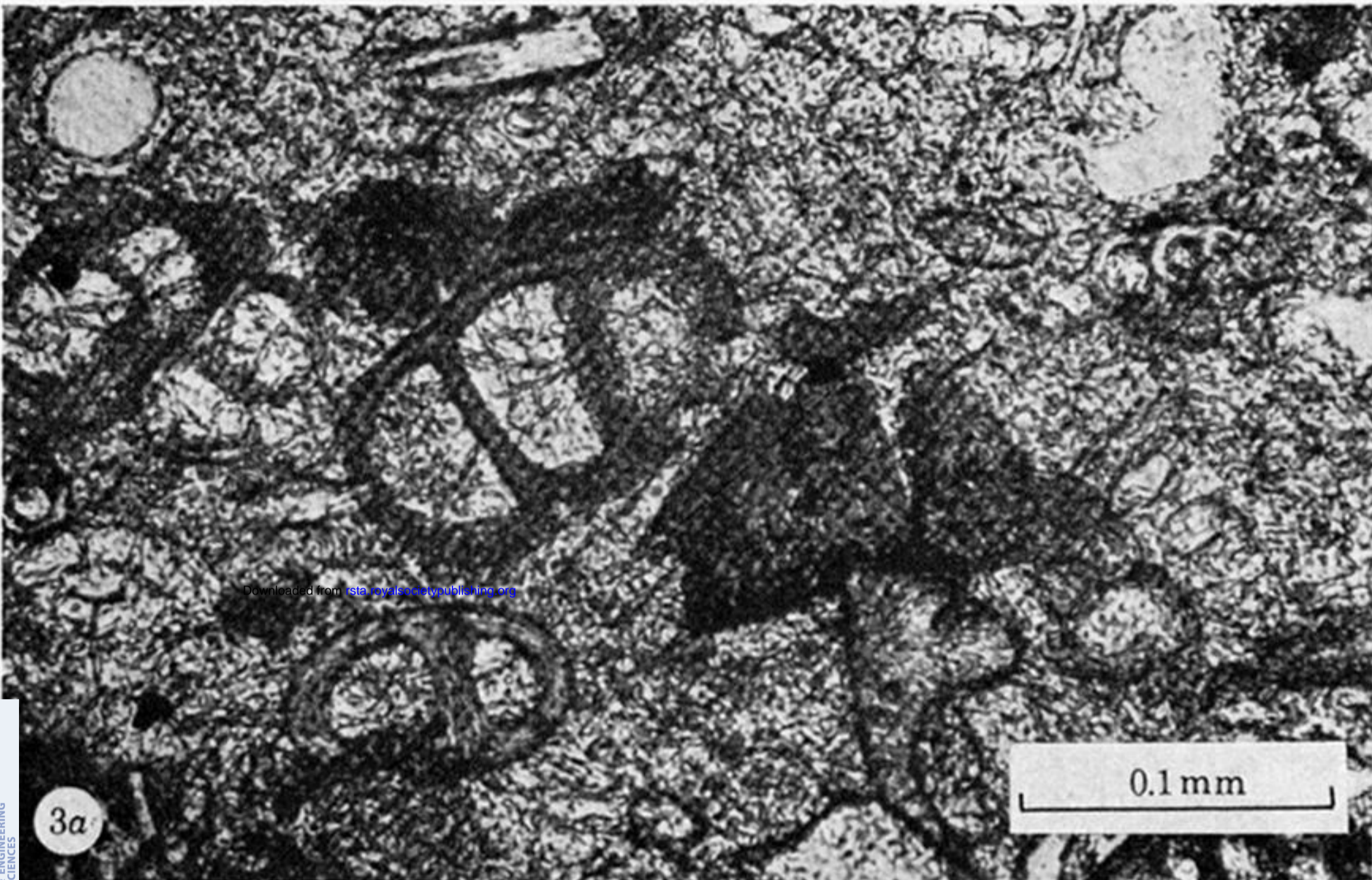
S. E. CALVERT.

(a) The data from deep-sea drilling indicate that the zeolite occurring most commonly with the silica phases is indeed clinoptilolite. There is, however, some evidence to suggest that phillipsite is more common in younger sea-floor sediments, whereas clinoptilolite occurs most frequently in older horizons where the cherts and porcelanites are also more abundant. Whether this distribution is a reflection of the instability of phillipsite or of different environments of formation of the two minerals is unknown at the present time.

(b) Synthesized opal-CT has been described as tridymite due to the formation of what appear to be hexagonal plates. It has been argued, however, that this morphology can be equally well developed by low cristobalite and that the unusual morphology of the lepispheres, shown in plate 2, represents interpenetrating twinned groups of hybrid cristobalite-tridymite blades with stacking disorder (see Flörke, O. W. *et al.* (1976) *Contrib. Mineral. Petrol.* **58**, 235–242).

D. R. C. KEMPE (*British Museum (Natural History), Cromwell Road, London SW7 5BD*). Is there evidence that palygorskite, like clinoptilolite, accompanied the growth of cristobalite and tridymite in the formation of porcelanites?

S. E. CALVERT. Both palygorskite and sepiolite accompany opal-CT in deep-sea sediments. At DSDP site 12, in the northeastern Atlantic, this association occurs in Eocene sediments over a depth interval approaching 200 m.



FIGURES 3 AND 4. For description see opposite.

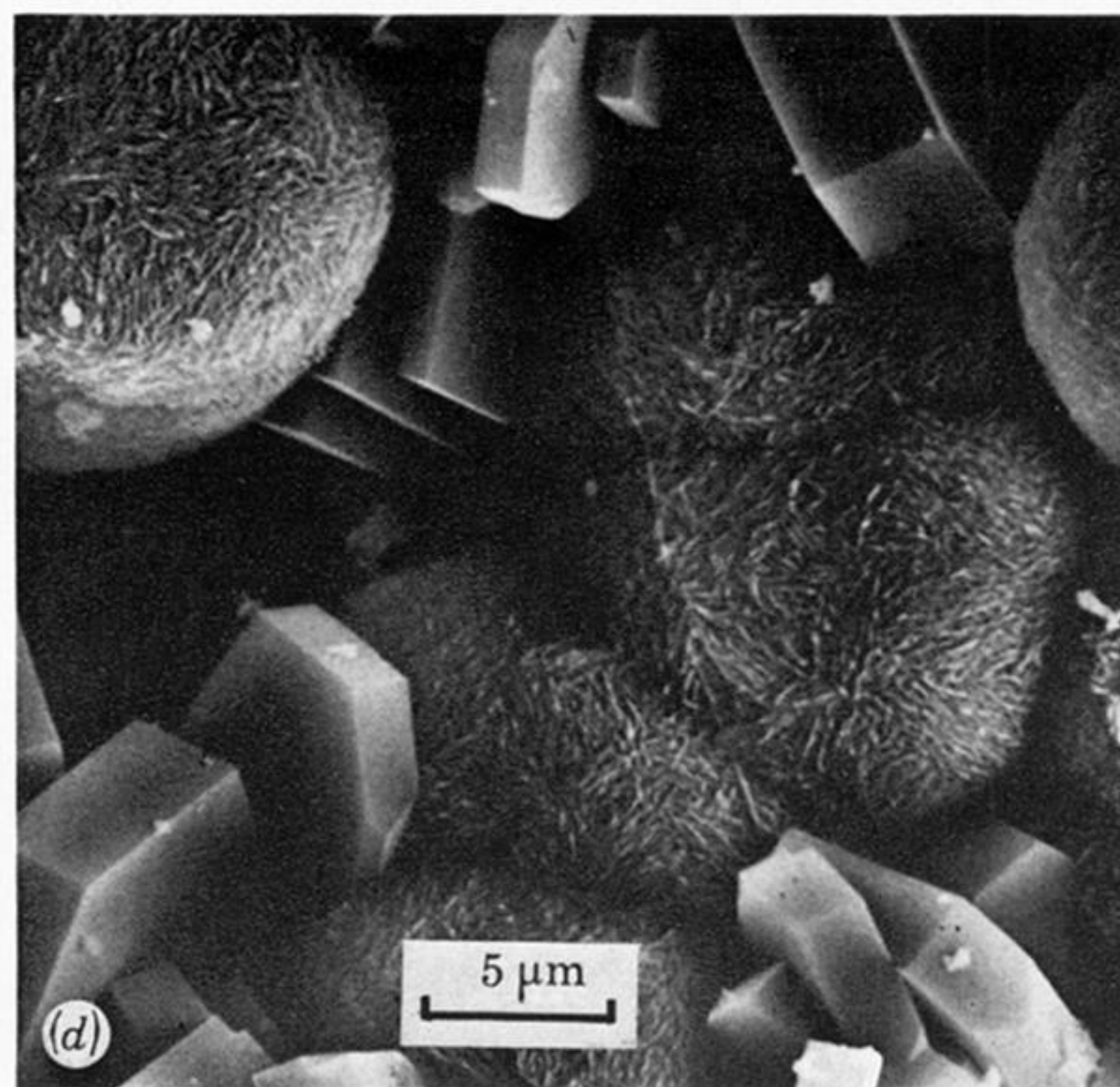
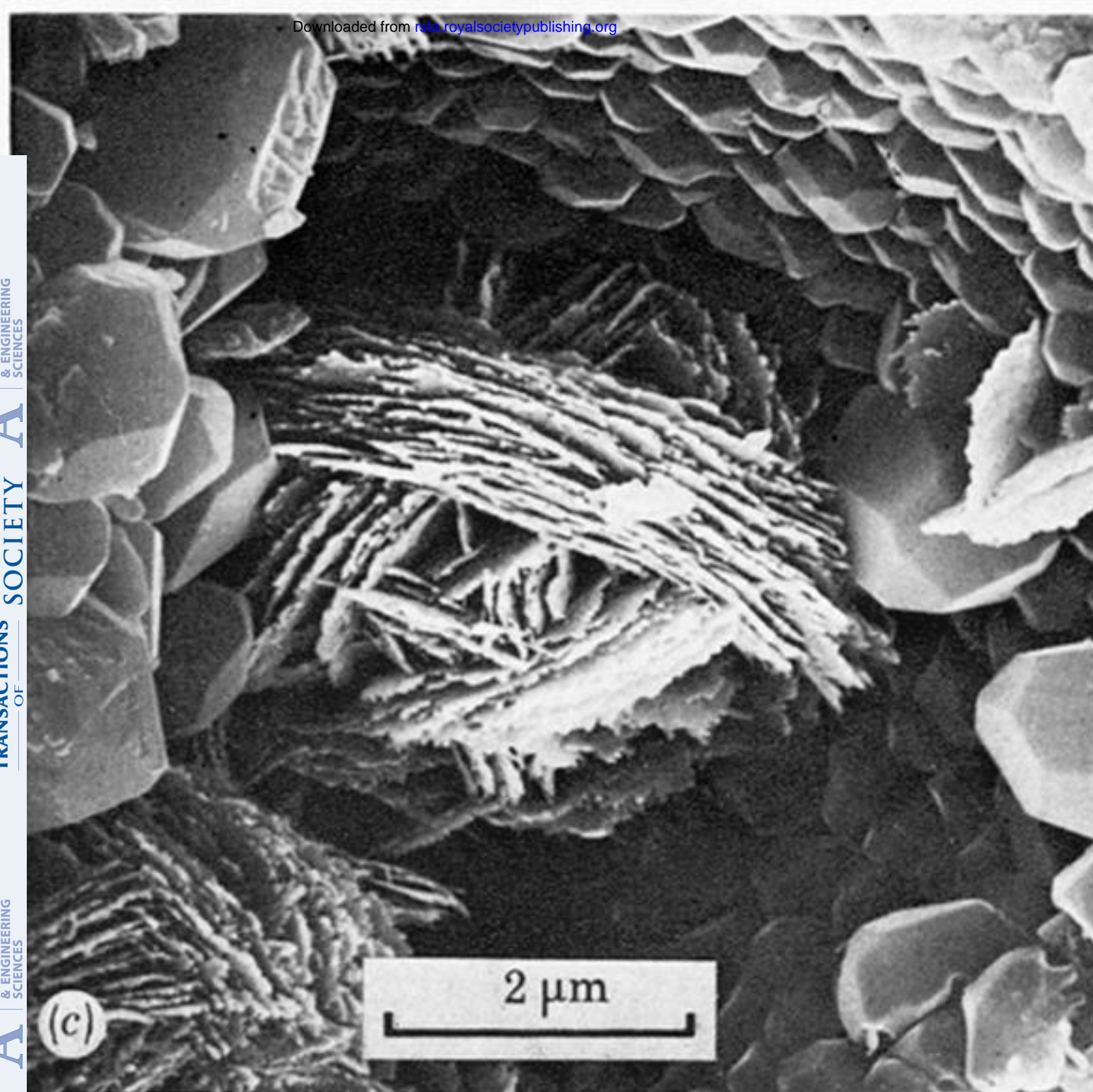
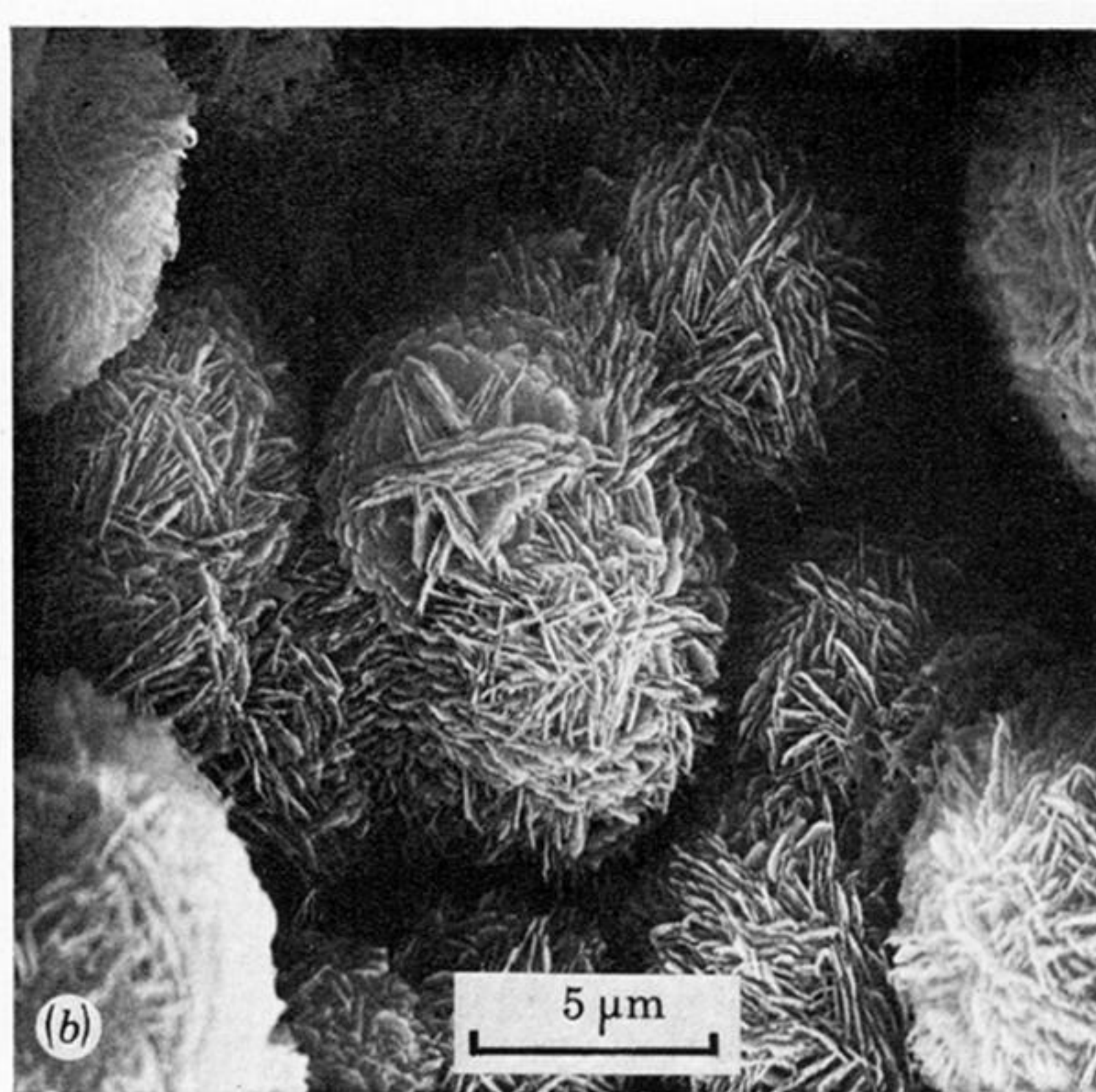
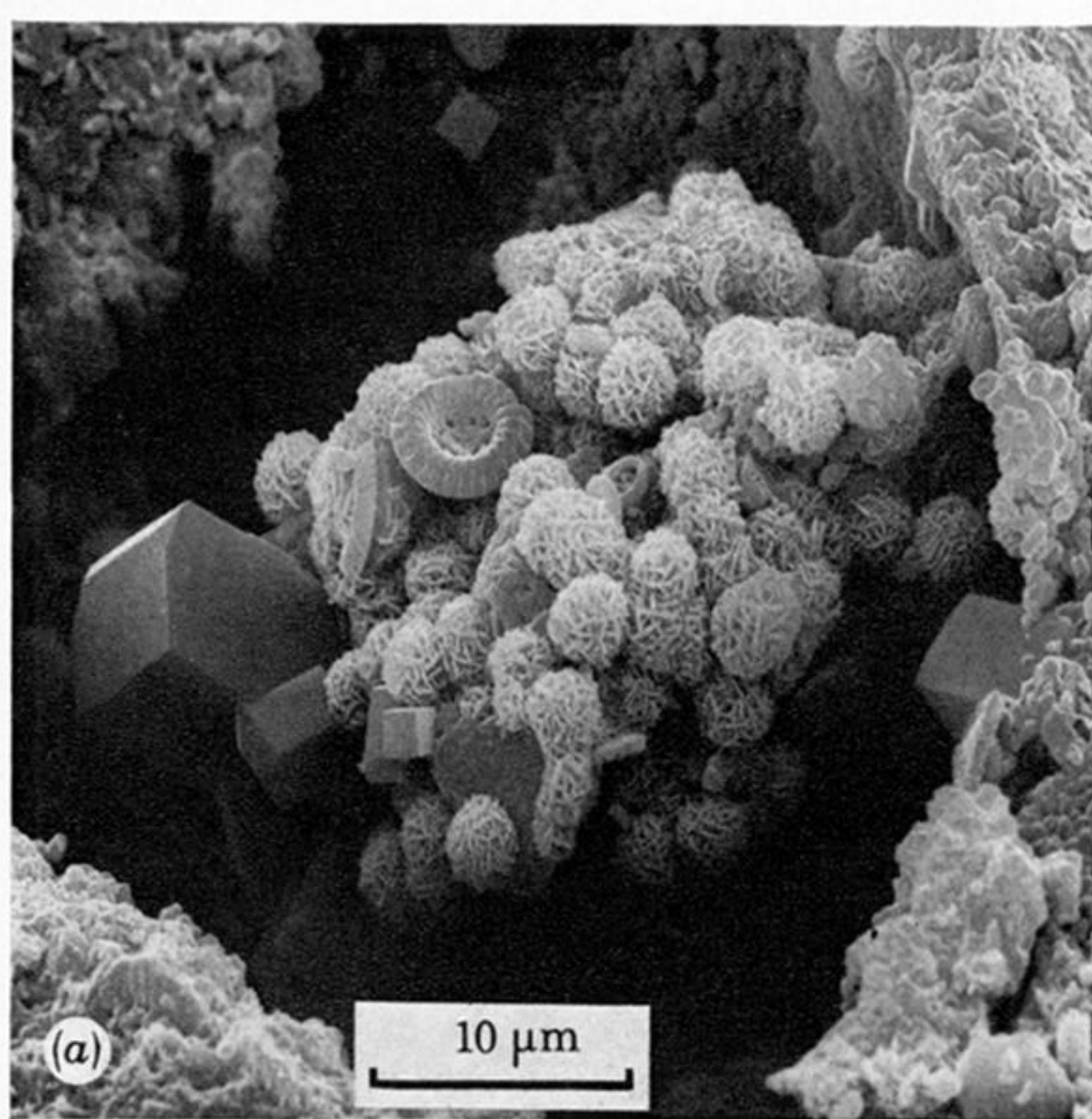


FIGURE 7. Scanning electron photomicrographs of opal-CT. (a) Cluster of lepispheres from Campanian–Maestrichtian silicified foraminiferal marlstone, Deep Sea Drilling Project Site 144, core 3, section 2, 103–104 cm, northwestern Atlantic Ocean. (b) Opal-CT lepispheres from Middle Eocene zeolitic clay and porcelanite, Deep Sea Drilling Project Site 367, core 10, section 1, 126–128 cm, northeastern Atlantic Ocean. (c) Detail of opal-CT crystals from Middle Eocene argillaceous limestone and porcelanite, Deep Sea Drilling Project Site 369A, core 35, section 1, 104–106 cm, northeastern Atlantic Ocean. (d) Opal-CT lepispheres and clinoptilolite crystals from Tertiary ashflow deposit, near Blythe, California. (a)–(c) courtesy of H. Rösch & U. von Rad; (d) courtesy of A. Tarshis.