9 Cherts and siliceous sediments

9.1 Introduction

Chert is a very general term for fine-grained siliceous sediment, of inorganic, biochemical, biogenic, volcanic or hydrothermal origin. It usually is a dense, very hard rock, which splinters with a conchoidal fracture when struck. Most cherts are composed of fine-grained silica, and contain only small quantities of impurities. Certain types of chert have been given specific names. For example, *flint* frequently is used as a synonym for chert and more specifically for chert nodules occurring in Cretaceous chalks. *Jasper* refers to a red variety of chert, its colour being due to finely disseminated hematite. Chert of this type is interbedded with iron minerals to form jaspilite in some Precambrian iron-formations (Section 6.5.1). *Porcelanite* refers to fine-grained siliceous rock with a texture and fracture similar to unglazed porcelain. The term porcelanite is also used more specifically for an opaline claystone composed largely of opal-CT (Section 9.3.2).

Cherts in the geological record usually are divided into bedded and nodular types. Some bedded cherts are associated with volcanic rocks and the 'chert problem' has centred on a volcanic versus biogenic origin of the silica. The modern equivalents of many ancient bedded cherts, the radiolarian and diatom oozes, cover large areas of the deep-ocean floors. Nodular cherts are developed mainly in limestones and to a lesser extent in mudrocks and evaporites. Most bedded cherts are primary accumulations; many nodular cherts on the other hand are diagenetic, having formed by replacement of the host sediment, although they commonly do still reflect deposition of silica-rich sediment. Siliceous sediments are also being deposited in lakes, and they do form soils (*silcretes*, Section 9.5).

9.2 Chert petrology

Bedded and nodular cherts consist of three main types of silica: *microquartz*, *megaquartz* and *chalcedonic quartz* (Fig. 9.1). Microquartz consists of equant quartz crystals only a few microns across. Megaquartz crystals are larger, reaching 500 μm or more in size; the crystals have unit extinction and often possess good crystal shapes and terminations. Megaquartz is often referred to as drusy quartz because it commonly occurs as a pore-filling cement, just like calcite spar. Chalcedonic quartz is a fibrous variety with crystals varying from a few tens to hundreds of microns in length. They usually occur in a radiating arrangement, forming wedge-shaped, mammillated and spherulitic growth structures (Fig. 9.2). Most chalcedonic quartz is length-fast (*chalcedonite*) but a length-slow variety (*quartzine*) also occurs. The latter is rare, but where found it is commonly associated with replaced evaporites (Section 5.5).

Radiolarians (marine zooplankton with a range of Cambrian to Recent), diatoms (marine and non-marine phytoplankton, Triassic to Recent) and siliceous sponges (marine and non-marine, Cambrian to Recent) are composed of *opaline silica*. This is an isotropic amorphous variety, containing up to 10% water. Opaline silica is metastable so that it decreases in abundance back through time and is absent from Palaeozoic cherts. Radiolarians and diatoms have disc-shaped, elongate and spherical tests with spines and surface ornamentation (Fig. 9.3). They range in size from a few tens to hundreds of microns. Sponge spicules are a similar size and up to a few millimetres in length, and have a trilete or Y-shape, giving circular and elongate sections in thin-section.

9.3 Bedded cherts

9.3.1 Siliceous oozes and bedded cherts

Radiolarian and diatom oozes are accumulating on the ocean floors at the present time. They occur especially where there is high organic productivity in near-surface waters and this is controlled largely by oceanographic factors of upwelling and nutrient supply. Diatoms dominate in siliceous oozes in the

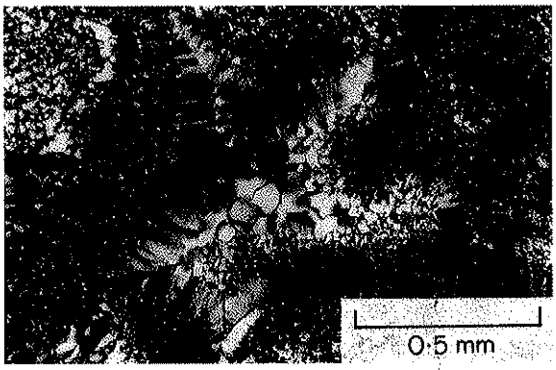

Fig. 9.1 Photomicrograph showing: microquartz—finely crystalline mosaic with pin-point extinction; megaquartz—larger quartz crystals in central part; chalcedonic quartz—in a fibrous fringe. In this case, the microquartz is a replacement of carbonate grains and the megaquartz and chalcedonic quartz are pore filling. Crossed polars. Carboniferous. Glamorgan, Wales.

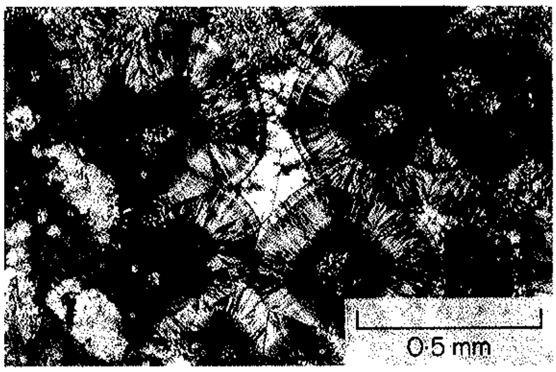

Fig. 9.2 Photomicrograph of chalcedonic quartz in spherulitic growth structure, also some microquartz and megaquartz. Crossed polars. Chert in limestone, Jurassic. Yorkshire, England.

Southern Ocean around Antarctica, and in the northern Pacific. Radiolarian-rich oozes occur in the equatorial regions of the Pacific and Indian Oceans. It is likely that prior to late Mesozoic times, radiolarians occupied the niches of diatoms and so were more widely distributed than at present. The siliceous oozes preferentially accumulate in abyssal areas where depths exceed the carbonate compensation depth (CCD, Section 4.10.7), around 4500 m in the central Pacific. Siliceous oozes form at shallower depths where surface oceanic waters are fertile and there is a paucity of calcareous plankton and terrigenous detrital material. Diatomaceous sediments accumulating at depths of less than 1500 m in the Gulf of California are of this type. The depth at which silica itself dissolves rapidly, the opal compensation depth (OCD), is around 6000 m. As a result of dissolution during settling, only a small percentage of diatoms and radiolarians actually reach the ocean floor to form sediments. Laminae within siliceous oozes are reflections of seasonal variations in plankton productivity and/or seasonal influxes of detrital clay.

Ancient bedded cherts commonly occur in mountain belts and other zones of folded rocks, many having been deposited in deeper-water basins, which are then structurally deformed. The uniform rhythmic bedding, which is a characteristic feature of these cherts, is generally on the scale of several centimetres, with millimetre-thick beds or partings of shale between (Fig. 9.4). The rhythmic bedding can be related to orbital forcing and Milankovitch rhythms, which cause periodic variations in biogenic silica precipitation and/or terrigenous influx (see Tada (1991) for a Miocene example from Japan). Other chert beds are massive with no internal sedimentary structures. Although recrystallization has commonly occurred, structureless beds may well have resulted from the slow and steady deposition of the silica. Some chert beds show graded bedding, parallel and small-scale cross-lamination, and basal scour structures. Cherts with these features have been either deposited by turbidity currents derived from some nearby topographic high where the siliceous sediments were first deposited, or reworked by contour-flowing bottom currents (Section 2.11.7). Bedded cherts locally show slump folding and contemporaneous brecciation as a result of instability and mass-sediment movement during sedimentation.

Many bedded cherts consist of radiolarians to the exclusion of other biogenic material. The radiolarians generally are poorly preserved, consisting of megaquartz-filled moulds contained in a matrix of microquartz (Fig. 9.5). Sponge spicules are common in some radiolarites. Fine clastic and carbonate sediment may be present in the cherts, and with increasing concentrations the cherts pass into siliceous shales and limestones.

Some bedded cherts are associated with volcanic rocks, others are not. Where there is a volcanic association, the cherts commonly were deposited within or

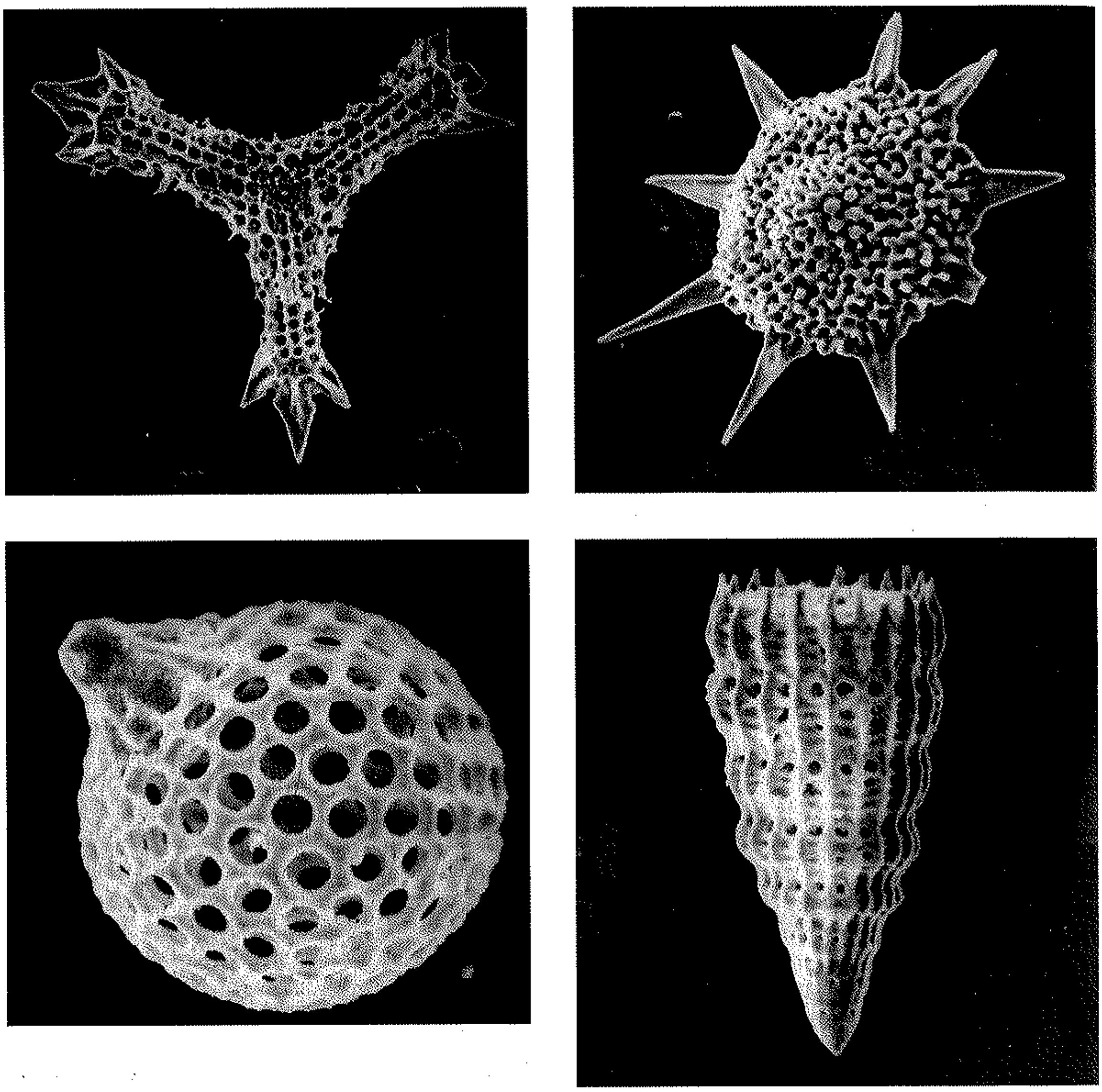

Fig. 9.3 Scanning electron micrographs of radiolarians, illustrating variety of shape. All from the Upper Cretaceous of Cyprus and between 200 and 300 μm across. (a) *Paronaella* sp., (b) *Pseudoaulophacus* sp., (c) *Cryptamphorella* sp. and (d) *Dictyomitra* sp.

above pillow lavas. Lava flows and volcaniclastic sediments may be intercalated, as well as horizons of black shale and pelagic limestone. In some cases ultramafic rocks and dyke complexes also are present, so that the whole igneous–sedimentary assemblage constitutes an *ophiolite suite*, generally accepted as a fragment of ocean floor. The chert may be derived from devitrification of volcanic ash or a biogenic source. Classic Mesozoic volcanic–chert associations occur in the Franciscan rocks of the Californian Coast Ranges (Robertson, 1990), in the Apennines of Italy (Barrett, 1982) and in the Troodos Massif, Cyprus (Robertson & Hudson, 1974). A Tertiary example occurs in Japan (Hattori *et al.*, 1996) and Cambro-Ordovician chert is found in Newfoundland and Maine (Pollock, 1987), also Girvan–Ballantrae, southwest Scotland, where REEs have helped identify the plate-tectonic setting (Armstrong *et al.*, 1999).

Bedded cherts independent of volcanics usually are associated with pelagic limestones, and siliciclastic and carbonate turbidites. Such deposits are typical of ancient passive continental-margin successions and commonly rest upon foundered shallow-water platform carbonates. Examples occur in the Mesozoic of the Tethyan–Alpine region and the Lower Carboniferous of western Europe, in southwest England and central Germany especially.

By analogy with modern siliceous oozes, many ancient radiolarian-rich bedded cherts are interpreted as very deep-water in origin, having been deposited below the carbonate compensation depth (CCD), at depths of several kilometres. Although this may be so for some cherts, they could have been deposited at much shallower depths if there was no calcareous plankton available for sedimentation. This may well have been the case during the Palaeozoic and well into the Mesozoic, because the main calcareous planktonic organisms, coccoliths and foraminifers, did not evolve

Fig. 9.4 Rhythmically bedded chert, with thin shale partings. Carboniferous. Montagne Noire, southern France.

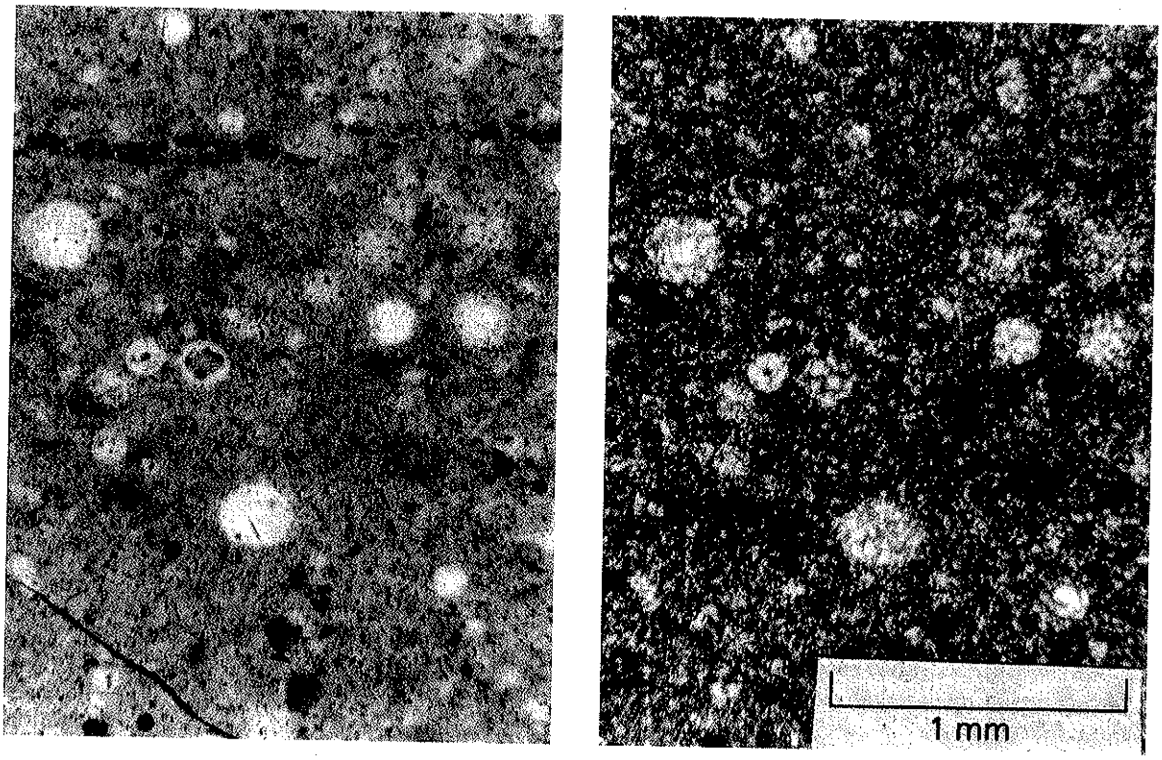

Fig. 9.5 Photomicrographs of bedded chert, composed of microquartz, with radiolarians preserved as microquartz and megaquartz: (a) plane-polarized light; (b) crossed polars. Ordovician. Ballantrae, Scotland.

until the Mesozoic. Variations in the CCD also could have permitted siliceous sediments to form in shallower water.

Cherts are relatively common in Precambrian successions but it is thought generally that siliceous organisms evolved later, in the Palaeozoic. The most likely sources of silica are volcanic material and hydrothermal fluids. The early Proterozoic from eastern Canada contains chert-cemented sandstones and thin chert beds, and intraclasts of these facies suggest very early precipitation of the silica (Simonson, 1985). It is thought that the silica was derived from hydrothermal waters migrating up through the sediments and discharging onto the sea floor. It is very likely that seawater had higher concentrations of silica in the early Precambrian than in the Phanerozoic, and a lower pH, so promoting primary silica precipitation (see Sugitani *et al.* (1998) for an Australian Archaean case study). See Zhou *et al.* (1994) for a description of hydrothermal cherts from China, interpreted on the basis of REE patterns.

Siliceous sediments rich in diatoms are common in the Miocene and Pliocene of the circum-Pacific area and in localized regions of the Mediterranean (papers in Iijima *et al.*, 1983; Hein & Obradovic, 1989). These *diatomites*, which locally are bituminous and phosphatic, formed in relatively small back-arc and rifted basins that were starved of terrigenous sediment but were the sites of vigorous upwelling and thus phytoplankton productivity. Diatomites of the Monterey Formation, California, are of this type (Beil & Garrison, 1994) and the diatom oozes of the Gulf of California are a modern analogue. Diatomites were deposited in small restricted basins in the Mediterranean region, just before the Messinian salinity crisis, towards the end of the Miocene (Bellanca *et al.*, 1986).

9.3.2 The origin of chert

Broadly there are two alternative views for the formation of chert:

1 that the cherts are entirely biogenic in origin, unrelated to any igneous activity;

2 that the cherts are a product of submarine volcanism, either directly through inorganic precipitation of silica derived from subaqueous magmas and hydrothermal activity or indirectly through plankton blooms induced by submarine volcanism.

A better understanding of submarine volcanism, in recent years, through plate-tectonic theory, has made a volcanic–sedimentary origin of cherts less likely. Seafloor volcanism is restricted to oceanic ridges and localized 'hot-spots' and so is unlikely to give rise to regionally extensive cherts. In fact, hydrothermal silica is precipitated close to vents, but it is quantitatively insignificant. In addition, the occurrence of radiolarian cherts in non-volcanic successions and the dominantly biogenic origin of modern siliceous sediments, controlled by oceanographic factors, indicate that the formation of cherts is not related to contemporaneous volcanism. The situation may well have been different in the early Precambrian, however.

Cores collected during deep-sea drilling have permitted detailed studies of the siliceous ooze to chert transformation. Cores from the ocean floors of the Pacific and Atlantic have encountered well-indurated cherts in Pliocene and older sections. Chert is particularly widespread in the Eocene of the North Atlantic. Contributions to silica diagenesis also have come from studies of cherts exposed on land.

From the biogenic amorphous opal, frequently referred to as *opal-A*, the first diagenetic stage is the development of crystalline opal, identified by X-ray diffraction (Fig. 9.6) and referred to as *opal-CT*, also called disordered cristobalite, alpha-cristobalite or lussatite. Opal-CT consists of an interlayering of cristobalite and tridymite, and its disordered nature probably results from the small crystal size and incor-

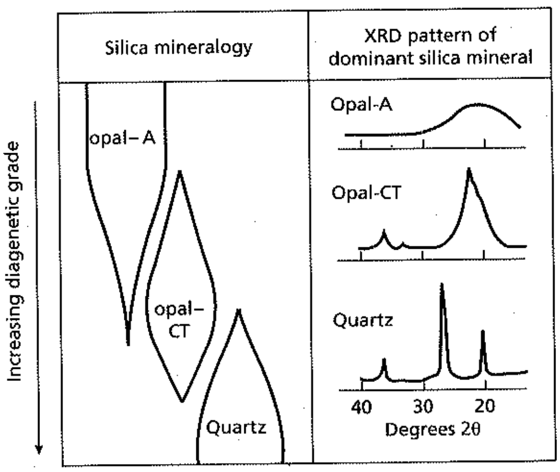

Fig. 9.6 Schematic changes in silica mineralogy with increasing diagenesis, and X-ray diffraction patterns for opal-A, opal-CT and quartz showing the increasing crystallinity. After Pisciotto (1981).

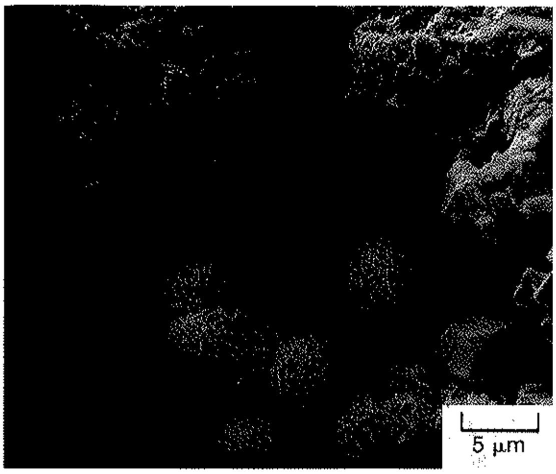

Fig. 9.7 Lepispheres of opal-CT growing in voids in silicified Eocene chalk from the Arabian Sea. Sample from 630 m below sea floor. Prismatic crystals are clinoptilolite (a zeolite). Scanning electron micrograph.

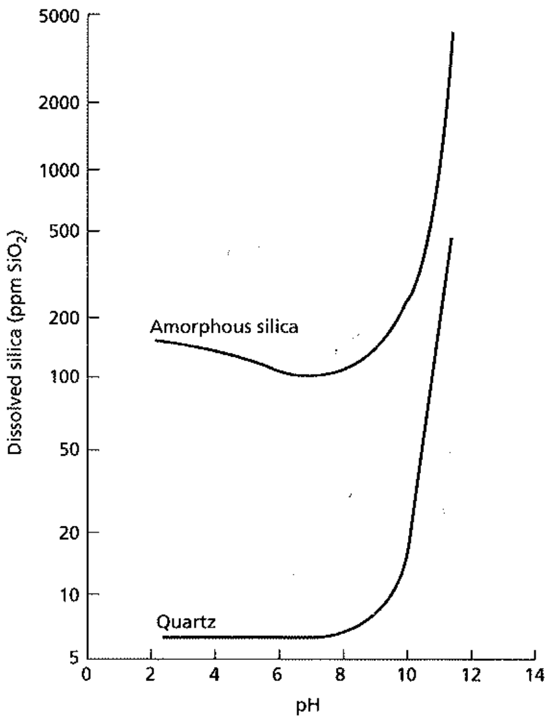

Fig. 9.8 The solubility of quartz and amorphous silica at 25 °C. At pH values less than 9, the silica is in solution as undissolved orthosilicic acid (H_4SiO_4); above pH 9, this dissociates into $H_3SiO_4^{2-}$ and $H_2SiO_4^{2-}$.

poration of cations into the crystal lattice. Opal-CT replaces radiolarian and diatom skeletons and is precipitated as bladed crystals lining cavities and forming microspherules (5–10 µm diameter) called *lepispheres* (Fig. 9.7). Further diagenesis results in the metastable opal-CT being converted to quartz chert, mostly an equant mosaic of microquartz crystals but also chalcedonic quartz. This recrystallization of opal-CT to quartz obliterates the structure of many diatom and radiolarian tests.

The driving forces behind chert formation from biogenic opal-A are the solubility differences and the chemical conditions. Biogenic silica has a solubility of 120–140 p.p.m., cristobalite of 25–30 p.p.m. and quartz of 6–10 p.p.m. in the pH ranges of marine-sediment pore water (Fig. 9.8). Once the metastable opal-A dissolves, the solution is saturated with respect to opal-CT and quartz. The precipitation of opal-CT in preference to quartz probably results from the more internally structured nature of quartz, which would require slow precipitation from less concentrated solutions. Temperature also is involved; with a rise in temperature, as through increasing depth of burial, the rate of transformation of opal-CT to quartz increases substantially. The formation of chert from opal-CT has been referred to as a 'maturation' process and in the Miocene Monterey Formation of California, the term porcelanite or opaline claystone is used for the metastable precursor to chert. Further studies have shown that the maturation of opal-A to quartz depends on the nature of the host sediment and on the chemical conditions. The presence of excess alkalinity in the sediments, as occurs where there is much calcareous material, favours the initial opal-CT precipitation and enhances the rate of transformation of opal-CT to quartz. Where there is much clay in the sediment, opal-CT contains abundant impurities, mainly foreign cations, which retard the maturation to quartz. The end-product of these processes of silica dissolution, reprecipitation and replacement is a mosaic of microquartz and chalcedonic quartz, with relatively few of the biogenic particles identifiable, although the original ooze was wholly composed of them. The maturation of siliceous sediments also leads to a decrease in porosity. In the Monterey Formation diatomites have porosities of 50–90%, porcelanites up

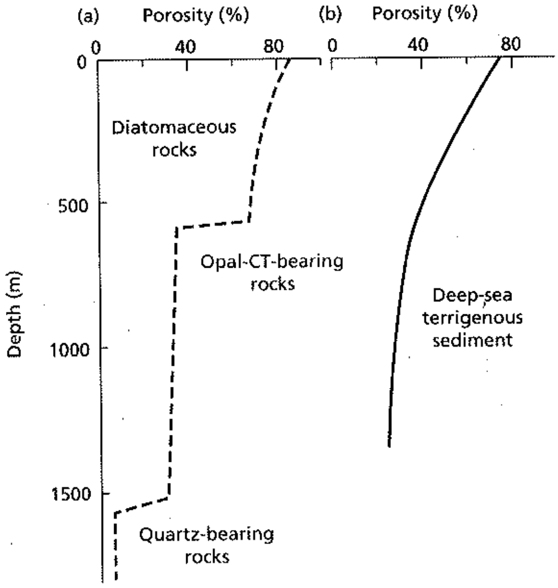

Fig. 9.9 Porosity reduction with depth for (a) diatomaceous oozes to opal-CT porcelanites to quartzose cherts, compared with (b) deep-sea terrigenous sediment, where porosity loss is gradual rather than stepwise. After Isaacs (1981).

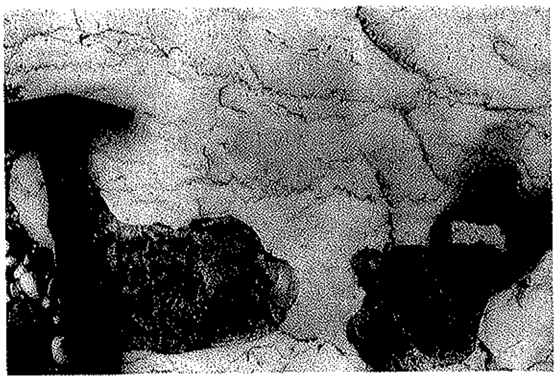

Fig. 9.10 Chert nodules (flint) in Cretaceous chalk of Yorkshire, England. Sutured stylolites are present in the chalk.

to 30% and cherts less than 10% (Fig. 9.9). This is a result of the silica-mineral transformations rather than compaction (Isaacs, 1981).

Although most Phanerozoic bedded cherts are now regarded as biogenic, some contain minerals thought to be volcanic alteration products, e.g. montmorillonite, palygorskite, sepiolite and clinoptilolite. The devitrification of volcanic glass and clay transformations, such as montmorillonite to illite, do liberate silica. In most, if not all Phanerozoic bedded cherts, however, there is at least some preservation of siliceous microfossils. This can be taken to indicate a dominantly biogenic origin, with most microfossils destroyed through the dissolution–reprecipitation of the maturation process.

Many papers on chert diagenesis are contained in Hsü & Jenkyns (1974), Iijima *et al.* (1983, 1994), Hein & Obradovic (1989), Heaney *et al.* (1994) and Knauth (1994).

9.4 Nodular cherts

Nodular cherts occur predominantly in carbonate host rocks. They are small to large, subspherical to irregular nodules, commonly concentrated along particular bedding planes; they may coalesce to form near-continuous layers, when they resemble bedded cherts. Nodular cherts are common in shelf limestones such as the Lower Carboniferous limestones of Britain and North America. They are also common in pelagic carbonates, with many examples occurring in the Cretaceous and Tertiary of the Alpine–Mediterranean–Tethys region. In the Cretaceous Chalk of western Europe and southeastern USA, nodules of chert (flint) are common (Fig. 9.10) and many have developed in burrow fills and nucleated around fossils. Flint pebbles derived from the Chalk are a major constituent of Tertiary and Quaternary gravels. Nodular cherts have been recovered from Miocene and older deep-sea chalks and pelagic limestones in cores from the ocean floors.

As with bedded cherts the origin of nodular cherts also has been much discussed. The older view involved the direct precipitation of silica from seawater to form blobs of silica gel on the sea floor that hardened into chert nodules. Nodular cherts in limestones, however, contain much evidence to demonstrate a replacement and thus diagenetic origin. Within the nodules, originally calcareous grains such as ooids and skeletal debris are preserved in silica (Fig. 9.11). Bedding structures such as lamination may be preserved in the nodules. The diagenetic processes involved in chert-nodule formation are thought to be similar to those operating in bedded cherts. Biogenic silica disseminated in the sediment dissolves and is reprecipitated in the form of opal-CT at nodule growth points.

Fig. 9.11 Silicified oolite. Ooids have been replaced by microquartz and are enclosed in a megaquartz mosaic. Crossed polars. Cambrian. Pennsylvania, USA.

Pore spaces are first filled with opal-CT lepispheres and then carbonate-skeletal and matrix replacement by opal-CT follows. Maturation of the opal-CT to microquartz and chalcedonic quartz takes place from the nodule centre outwards. It often can be demonstrated that the microquartz has formed by replacement of carbonate and that the chalcedonic quartz and megaquartz are dominantly pore-filling (Figs 9.1 & 9.11). Quartz authigenesis in Silurian limestones of eastern Canada apparently is related to bacterial sulphate reduction and oxidation of organic matter (Noble & Van Stempvoort, 1989). Nodular chert in Ordovician Arbuckle Limestones of Oklahoma apparently formed from dissolution of sponge spicules during shallow burial in marine waters, but the silica recrystallized in meteoric water during exposure of the platform (Gao & Land, 1991). Near-surface direct precipitation of quartz from meteoric water produced metre-sized chert nodules in the Eocene of Egypt (McBride *et al.*, 1999).

The source of biogenic silica in shelf limestones is largely sponge spicules, whereas in deeper-water pelagic limestones, the silica is largely supplied by radiolarians and diatoms. With the Cretaceous chalks of western Europe, a relatively shallow-water pelagic carbonate, silica for the flint nodules was derived mainly from sponges.

Chert nodules also can form by the replacement of evaporites, particularly anhydrite. Length-slow chalcedonic quartz is common in these occurrences (Section 5.5).

9.5 Non-marine siliceous sediments and cherts

Biogenic and inorganic siliceous sediments can form in lakes and ephemeral water bodies and in soils. Diatoms, which can occur in great abundance in lakes, form diatomaceous earths or *diatomites*. Such sediments are accumulating in many sediment-starved, higher-latitude lakes such as Lake Luzern, Switzerland and Lake Baikal, Siberia. During the Pleistocene, diatomites were deposited in many late-glacial and post-glacial lakes in Europe and North America.

Inorganic precipitation of silica can take place where there are great fluctuations in pH. Quartz, with its low solubility in most natural waters, is not affected by pH until values exceed 9, and then with increasing pH, the solubility increases dramatically (Fig. 9.8). In ephemeral lakes of the Coorong district of South Australia, pH values greater than 10 are reached seasonally through photosynthetic activities of phytoplankton. Detrital quartz grains and clay minerals are partially dissolved at these high pH values so that the lake waters become supersaturated with respect to amorphous silica. Evaporation of lake water and a decrease in pH cause silica to be precipitated as a gel of cristobalite, which would give rise to chert on maturation. A Cretaceous example of Coorong-type chert has been described by Chough *et al.* (1996). Another related inorganic process has been described from East African lakes. In very alkaline, sodium carbonate-rich lake waters, silica is leached from volcanic rocks and rock fragments. Exceptionally high concentrations of silica (up to 2500 p.p.m.) are attained, and then lowering of pH by freshwater influxes causes the silica to be precipitated as *magadiite*, a metastable hydrated sodium silicate. This is converted to chert in a relatively short time. Cherts in ancient ephemeral lake successions, such as the Eocene Green River Formation of Wyoming, may well have formed via a sodium silicate precursor, and a Permian example from Italy is described by Krainer & Spötl (1998).

Silica also may be precipitated from hot springs through evaporation and rapid cooling of spring waters to form *sinter*. Silicification of microbes may take place by impregnation of organic tissue (e.g. Renaut *et al.*, 1998). Preservation of microbes in Precambrian cherts also may have occurred in thermal spring environments (e.g. Schopf, 1993), and the famous Rhynie Chert of the Lower Devonian in eastern Scotland, which contains some of the oldest preserved land plants, is also a hot spring deposit (Trewin, 1994).

Silicification of lacustrine (and marine) limestones without any biogenic or detrital silica also may take place through ground-water flow, with silica derived from dissolution of quartz in adjacent formations. Porous zones in the limestones then will be silicified preferentially. See Thiry & Ribet (1999) for an example from the Tertiary of the Paris Basin.

Chert also is precipitated in some soils and *silcrete* is one particular type occurring especially in parts of Australia (e.g. Webb & Golding, 1998) and southern Africa (e.g. Summerfield, 1983). Silcretes mostly appear to form under arid/semi-arid climates, where ground waters are alkaline with a pH above 9, but they can form in humid areas too. Silcretes usually consist of a microquartz cement between sand grains, and microquartz mosaics where they have formed within finer-grained sediments. Megaquartz and fibrous quartz occur within vugs. There may be small canals and tubes from the decay of rootlets. Ancient silcretes have been reported from the Proterozoic of northwest Canada, where they occur upon weathered rhyolite lava flows and volcaniclastic sediments (Ross & Chiarenzelli, 1985).

Further reading

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