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Partial silicification of chalk fossils from the Chilterns

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SUMMARY. The calcite of brachiopod, lamellibranch and echinoid shells from the Upper and Middle Chalk of Hertfordshire and Bedfordshire is partly replaced by chalcedonic silica. The crystallographic forms of the silica are described, and its diagenetic emplacement inferred from thin section studies.

1. INTRODUCTION

The occurrence of chalcedony in the Chalk of the Chilterns has been suspected since Avery, Stephen, Brown & Yaalon (1959) reported rod-shaped and botryoidal fragments in Chiltern soils containing insoluble residues of the Upper Chalk. Soils of the Batcombe series, which are developed in a thin silty drift (loess) overlying and incompletely mixed with plateau deposits mapped as “Clay-with-flints” or “Pebbly Clay and Sand” by the Institute of Geological Sciences, commonly contain tabular fragments of chalcedonic silica as large as 40 mm across and 5 mm thick. Some of these superficially resemble broken pieces of Inoceramus shell, because they have a faint surface pattern of parallel “growth-lines”. We confirmed the presence of silica in Inoceramus by acid treatment of shell fragments extracted from the Upper Chalk, and then investigated the extent of silicification in Chalk fossils by examining specimens from a range of fossil groups obtained from several zones of the Hertfordshire and Bedfordshire Chalk. Most of the shells were treated with 2N hydrochloric acid and their insoluble residues examined with a petrographic microscope or by X-ray methods. Thin sections were cut parallel and perpendicular to the surface of a few shells.

2. DISTRIBUTION OF THE CHALCEDONY

The replacement of shell carbonate by chalcedony is most common in lamellibranchs, especially Inoceramus spp., but also occurs in some brachiopods and echinoids. The replacement is always partial, and varies greatly in extent. We examined Inoceramus shells from the Middle Chalk at Totternhoe (SP 988220) and the Upper Chalk at Kensworth (TL 017198) and Redbourn (TL 123103) (planus zone) and at Water End (TL 230025) (coranguinum zone); after acid treatment, almost all of these left a coherent siliceous residue that commonly preserved the growth ridges of the shell. In contrast, specimens of Spondylus spinosus from Kensworth contained only small circular patches of chalcedony near their ventral margins. Echinoids (Micraster spp. and Echinocorys) from the Upper Chalk usually have small, sub-circular, unconnected patches of chalcedony; these are distributed irregularly over the shell and do not preserve the pattern of ambulacral and interambulacral plates. The extent of silicification in brachiopods is also variable. Acid
treatment of Rhynchonellidae from the Middle Chalk at Totternhoe often leaves the complete shell preserved in a delicate framework of silica, whereas most Terebratulidae from Kensworth have a more solid development of chalcedony that is restricted to the posterior (umbonal) regions. The translucent qualities of many Terebratulid shells are often spoilt in posterior parts of the ventral valve by opaque, microcrystalline silica.

We have not determined the geographic distribution of chalcedony in the Chalk. However, fragments of silica similar to those in the fossils of the Hertfordshire and Bedfordshire Chalk are widespread in superficial deposits containing other Chalk-derived material on the Chilterns (J. Loveday, unpublished Ph.D. thesis, London University, 1958) and in parts of East Anglia. We also found chalcedony in fragments of *Inoceramus* shells from the Upper Chalk at Swanscombe, Kent; Muir-Wood & Owen (1952) reported a silicified *Rhynchonella* from the Lower Chalk of Wiltshire. These occurrences suggest that the chalcedony is much more widely distributed in the Chalk than the area we studied. A macroscopically similar form of silica, known as beekite, is common in brachiopods and corals of the Carboniferous Limestone and in Jurassic lamellibranchs (Hatch, Rastall & Greensmith, 1965, p. 246).

3. FORM AND STRUCTURE

In fragments of *Inoceramus* the silica occurs mainly as rods elongated perpendicular to the surface of the shell; these are usually united on the surfaces of the fragment, but become thinner and disconnected between the surfaces. Complete shells have only the rods that extend in from the outer surface, and there is little or no replacement of the inner surfaces; this suggests that the calcite is replaced by silica derived from outside the shell. Thin sections cut perpendicular to the shell surface show that the rods form between the calcite columns, and progressively replace the calcite by the development of fibrous crystals that extend parallel to the shell surface (and therefore perpendicular to the rod axis). The fibres are length-slow and therefore elongated parallel to the *c* axis. Thin sections parallel to the shell surface show a weakly-developed radial arrangement of fibres in each rod. The polygonal outline of the original calcite columns is preserved even in layers where the silification is complete, though in many it can only be seen clearly by the use of phase contrast. The surfaces of the chalcedony corresponding approximately to the surfaces of the shell often have a macroscopic pattern of raised concentric circles, which interfere to give complex patterns.

X-ray powder patterns of crushed chalcedony specimens showed that the only crystalline component is α-quartz. Some of the rods were examined by rotation and oscillation methods, with the rod axis as the rotation axis. This confirmed that the *c* axes of the quartz fibres are perpendicular to the rod axis, and showed that the *a* axes are also ordered so that one of them is
parallel to the rod axis. The chalcedony is completely anisotropic, but its mean refractive index (1.535) suggests that it contains a little opaline silica or water in addition to quartz. Chemical analysis of the acid insoluble residue from a fragment of *Inoceramus* shell dried at room temperature gave: SiO₂ - 97.1%, H₂O⁻ - 0.4%, H₂O⁺ - 1.5%.

Some *Inoceramus* fragments contain isolated spherulitic masses of chalcedony as large as 2 mm across. These usually form approximately half way between the shell surfaces, and adjacent spherulites sometimes coalesce to form botryoidal aggregates. The silica in echinoid tests is also mainly botryoidal. Two distinct forms occur in the brachiopods. The Terebratulidae have rods perpendicular to the shell surface, but these are thinner than the rods found in *Inoceramus* and are composed of both length-fast and length-slow fibres oriented parallel to the rod axis. In contrast, the Rhynchonellidae contain lath-shaped or platy particles, which are flattened parallel to the shell surface and elongated in a posterior-anterior direction. These have a mean refractive index of 1.542, and are composed of larger quartz crystals than the chalcedony in the other fossils examined.

4. ORIGIN

Carbonate could have been replaced by silica in the fossil shells while the animals were still alive in the Chalk sea or at any subsequent time. However, biological accumulation of the silica is unlikely because it is otherwise unknown in these groups. Also, the growth of chalcedony from both surfaces of isolated *Inoceramus* fragments but from only the outer surface of complete shells suggests that the replacement occurred after the post-mortem fragmentation of the shells. A large *Inoceramus* partly enclosed in a flint nodule from the *planus* zone at Redbourn indicated that the emplacement of silica was post-depositional. In thin section it showed extensive replacement of the columnar calcite by chalcedony rods and spherulites where the shell had been covered by chalk, but where the shell was enclosed in flint there was no replacement. The flint had therefore protected part of the shell from subsequent silicification. Carozzi (1960, p. 323) and others favour a syngenetic origin of flint nodules in the Chalk, so the emplacement of chalcedony was probably a diagenetic process. Weir & Catt (1965) suggested that euhedral quartz crystals in the Upper Chalk of Sussex are evidence for the post-depositional mobility of silica in the Chalk. The forms of silica described here provide further evidence of this, because the silica they contain must have been derived from interpore solutions.

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