Silicification phenomena in fossil Belemnite guards

W.J.H. Schins
P. Buurman

SUMMARY

Most Belemnite guards from the Upper Senonian 'Belemnite Churchyard' (Maastrichtian Cr3b) show partial silicification. Oriented calcite that constitute the guards is partly replaced by α-quartz. Silicification appears just below the guard surface. Fine quartz needles (20 μm average in cross-section) follow the radial structure of the calcite prisms. These quartz needles are polycrystalline and consist of domains of preferredly oriented crystals, each domain having a different orientation. The crystallographic orientations of these directions are random. There is no relation between the orientation of the original calcite and that of the quartz replacements. Silicification in this case is probably not a molecule-for-molecule replacement mechanism. Replacement might have taken place by way of dissolution and subsequent filling up with quartz of larger calcite units.

1. INTRODUCTION

The Belemnites, cuttle-fish like animals belonging to the suborder Belemnoidaea (class Mollusca) lived in great numbers in the Jurassic and Cretaceous oceans. A detailed anatomic description is given by SCHINS (1976).

Belemnites have an inner shell consisting of $CaCO_3$ that is deposited radially in a sequence of organic and inorganic lammellae. This growth striation gives in cross-section the image of concentric circles.

The only part of the belemnite shell that is frequently encountered is the guard, or 'tail' which is drawn schematically in Fig. 2. Fossil guards are numerous in many strata all over the world and consequently play an important role as guide fossils (e.g. CHRISTENSEN, 1975).

The guard can undergo radical changes after deposition. It is not impossible that the original shell consisted partly or entirely of aragonite which is transformed into calcite after deposition (e.g. SPAETH, 1971b). Other possible changes are the recrystallization of small calcite crystals to large prisms (e.g. VOIGT, 1964), the filling up of cavities and pores with secondary calcite (e.g. SPAETH, 1975) and replacement of calcite by low-temperature quartz (metasomatosis, BUURMAN, 1971). The latter process is of great interest because silicified belemnite guards offer an excellent opportunity to study the relation between primary (calcite) and secondary (quartz) structures and crystallinity, a study that is not well possible in silicified limestones, or chert.

2. EXPERIMENTAL

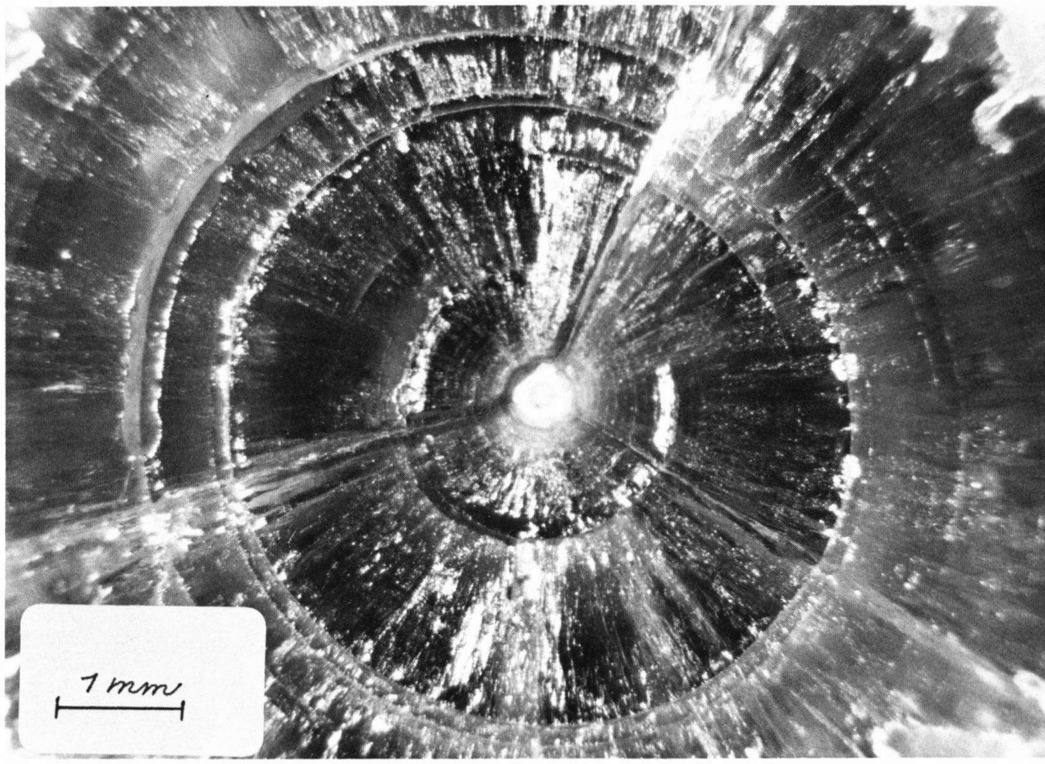
The examined silicified guards mainly originate from the glauconite containing Gulpen Chalk (Beutenaeken, Southern Limburg). The way of replacement of calcite by quartz and the occurring crystallographic structures were studied by optical microscopy and by scanning electron microscopy (SEM). For this reason appropriate samples were made by means of sawing, grinding, Al_2O_3-polishing and etching by HCl or HF. In order to determine concentration profiles of calcite and quartz and for analysis of foreign elements (e.g. Fe) an electron probe micro-analyzer was used. In order to study the crystallographic orientations of calcite and quartz and for determination of the relations between these orientations X-ray diffraction was used. Of the many X-ray techniques available at the laboratory, the recording technique by a flat camera will for instance be briefly described:*

3. RESULTS AND DISCUSSIONS

Texture of calcite in guards

Calcite prisms run radially from the apical line to the outer surface. The c-axes (<001>)of the calcite prisms are nearly perpendicular to the growth lamellae. The prisms are about 50 μm across and have irregular shapes. The a-axes (<100>) are randomly oriented.

Fig. 1 Cross-section of silicified guard after HCl-etching. Concentric growth lines are shown.



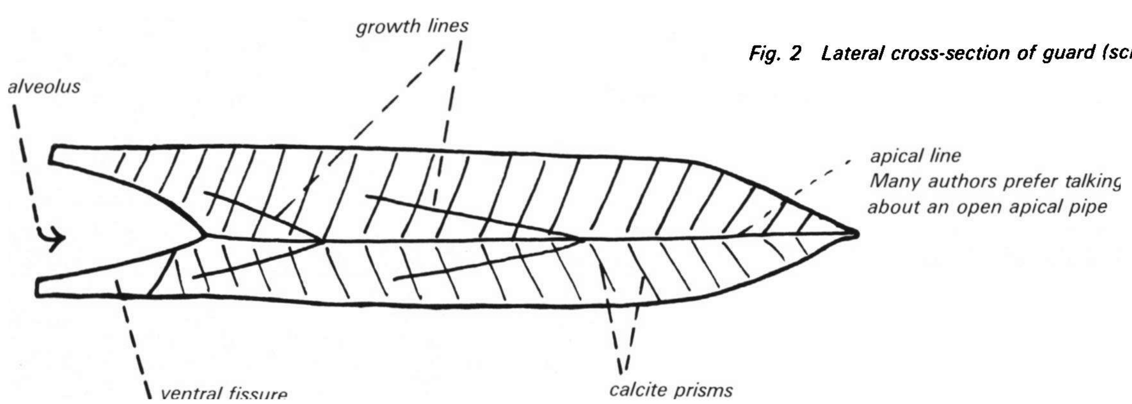


Fig. 2 Lateral cross-section of guard (schematically).

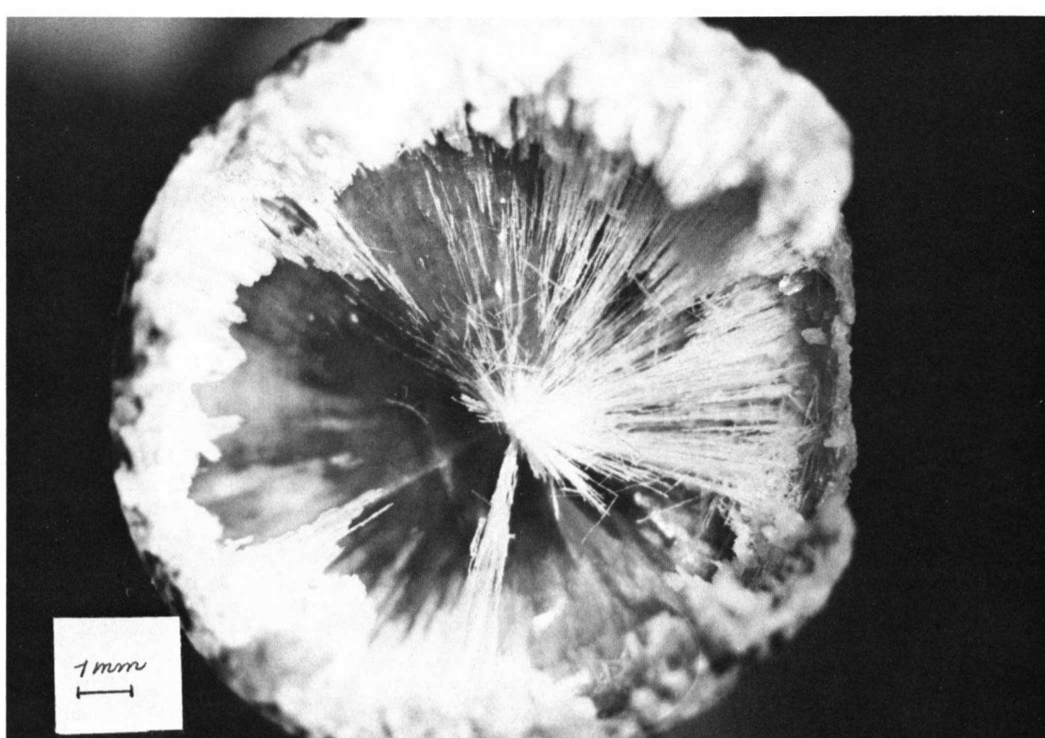


Fig. 3 Cross-section of silicified guard after HCl-treatment.

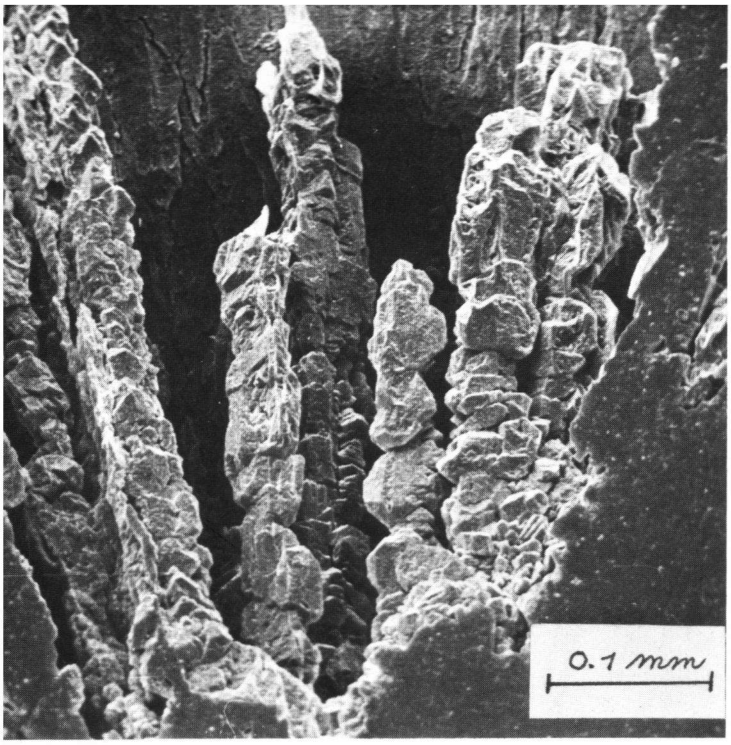


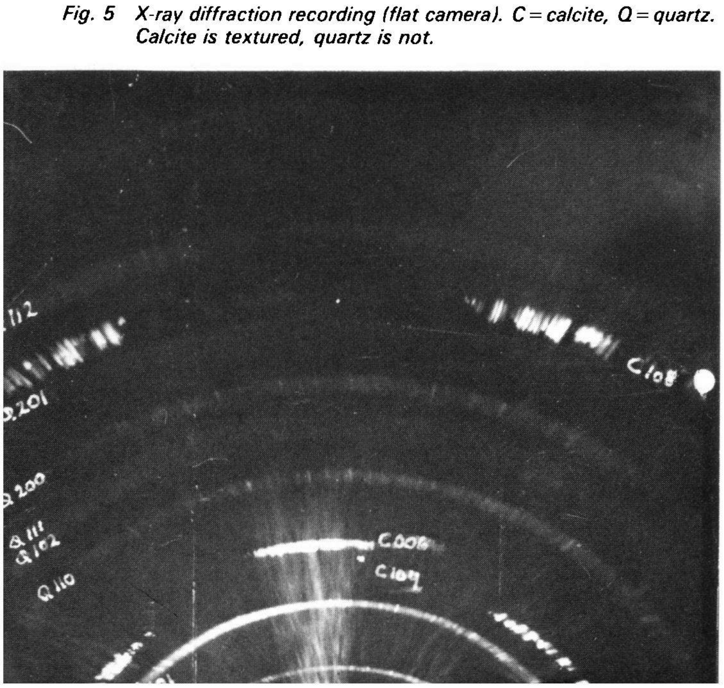
Fig. 4 Quartz needles growing from apical line. SEM-recording.

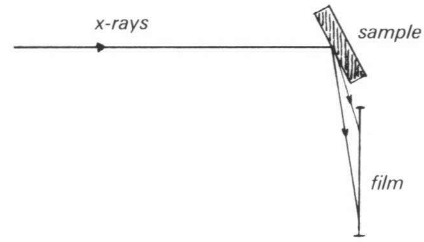
In a guard found in Maastrichtian Chalk (Nekami quarry) sharply <001> textured calcite semi-crystals of several milimeters length were found which are obviously the result of recrystallization. Despite of this recrystallization the semi-crystals still reveal very clearly the original growth lines or traces of them.

Silicification

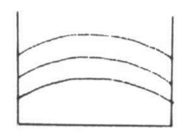
After etching with HCl of the partly silicified guards a skeleton of quartz remains. Etching shows that the outer layer of the guards consisted entirely of calcite (less than 0.1 weight % Si) with iron-rich islands in the matrix. This indicates that silicification begins below the surface at a depth of a few tens of microns. Here we find a dense wall of quartz built up in circular patterns. BUURMAN (1971) postulates that the detailed structure of these patters is mainly determined by the rate of silicification. The quartz domains are randomly oriented.
A few millimeters below the guard surface the dense quartz wall bulges out at many sites into the calcitic matrix. These quartz outgrowths (diameters of a few millimeters) develop rather abruptly into fine quartz needles which grow towards the apical line (Fig. 3). There is no growth of quartz needles on the dense wall itself. Dependent on the local degree of silicification the needles are 1-10 millimeters in length and 10-40 μm in cross-section. The needles (Fig. 4) are polycrystalline and very brittle and for this reason rather unaccessible for analysis. From the apical line in the direction of the surface the same quartz structures are found. There is clear evidence that in the examined guards an open apical pipe is present instead of an apical line as referred to in Fig. 2. The silica solution must have been supplied through the open apical pipe.
X-ray measurements (e.g. by the rotating-crystal method) on about thirty quartz needles which had to be broken out of the guards very carefully, indicated that most of the needles consist of groups of grains. Each group has a preferred grain orientation but the crystallographic directions are different for different groups. In each needle several textures are present and two identical needles have not been found.
From these observations it appears that an orientation relation between the calcite and the quartz grains is unlikely. This is illustrated conclusively by the flat camera recording technique when the quartz needles are irradiated in situ in the calcitic matrix. From Fig. 5 it is clear that the calcite is <001> oriented (symmetrically interrupted lines) while the quartz needles have all possible orientations (closed lines).

Fig. 5 X-ray diffraction recording (flat camera). C = calcite, Q = quartz. Calcite is textured, quartz is not.

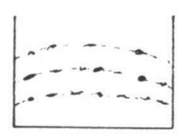




On the flat film the crystal plane reflections are recorded as arcs of circles. In principle three kinds of diagrams can be obtained:



closed lines; no preferred grain orientation



interrupted lines; no preferred orientation but material is coarse-grained

symmetrically interrupted lines; grains are preferredly oriented

Flint in the alveolus

Guards with similar silicification phenomena were obtained from a limestone quarry in Boirs (Belgium) from the III^{w}-zone. However, the alveoli of these guards are partly filled up with dark flint consisting of chalcedony with small inclusions. Furthermore, between this flint and the top of the alveolus cone fine quartz powder was found. Obviously the limestone material which had filled up the alveoli after deposition of the guards is replaced by silica.
Interesting is the appearance of two forms of silicification, dependent on the density of the calcite to be replaced. In the flint close to the alveolus wall is found a concentric band, which contains iron-rich islands.

CONCLUSIONS

There is no relation in the crystallographic orientation of the calcite in the guard and the grown-in α-quartz needles. Therefore a molecule-for-molecule replacement is not very likely. Replacement of calcite by quartz may have taken place by dissolution and subsequent filling up.

ACKNOWLEDGEMENTS

The authors are indebted to dr. F.J.J. van Loo of Eindhoven

University of Technology (Lab. for Physical Chemistry) for help and stimulating discussions and to Werner M. Felder of the Geologisch Bureau Heerlen for cooperation.

REFERENCES

SCHINS W.J.H., 1976, Belemnieten, de bouw van de schaal en mogelijke diagenetische veranderingen daarin, Grondb. & Hamer, *no 4, 106-122.*

CHRISTENSEN W.K., 1975, Upper Cretaceous Belemnites from the Kristianstad area in Scania, Fossils and Strata 7, *Universitetsforlaget Oslo.*

SPAETH Chr., 1971b, Aragonitische und calcitische Primärstrukturen im Schalenbau eines Belemniten aus der englischen Unterkreide, Paläont. Z., 45, *1/2, 33-40, Stuttgart.*

VOIGT E., 1964, Zur Temperatur- Kurve der Oberen Kreide in Europa, Geol. Rundschau, 54, *270-311, Stuttgart.*

SPAETH Chr., 1975, Zur Frage der Schwimmverhältnisse bei Belemniten in Abhängigkeit vom Primärgefüge der Hartteile, Paläont. Z., 49, *3, 321-331, Stuttgart.*

BUURMAN P., 1971, Verkiezelingsverschijnselen bij belemnieten uit het Zuidlimburgse Krijt, Grondb. & Hamer, *no 1, 13-18.*

*W.J.H. Schins**
Physical Laboratory, State University of Utrecht
P.O. Box 80.000 Utrecht
P. Buurman
Dept. of Soil Science & Geology, Wageningen University of Agriculture P.O. Box 37 Wageningen

* *This work was performed at the Laboratory for Physical Chemistry of the Eindhoven University of Technology.*