TYPE SEPTARIA-CONE IN CONE NODULES IN THE STEPHANO-PERMIAN OF THE CATALAN PYRENEES

E. Aso, T. J. Gisbert, and B. Valero Garcés

Dpto. Geologia, Universidad de Zaragoza, Zaragoza 50009 Spain

ABSTRACT: We have studied three nodules of Stephano-Permian age in the Spanish Pyrenees. These are associated with lacustrine limestone. We have determined three standard types of nodules which are described by petrographic, cathodoluminescence and ultramicroscopic techniques and carbonate composition (Edax analysis). The nodules have cumules of calcite fibres with cone in cone or fibrous-radial arrangements. Also there are septaria cracks. We dispute the nodule, septaria and cone in cone formation and suggest a development due to layering of organic gel segregated by microorganisms. We also propose a concrete meaning for the terms: Beef, feather-like cone in cone, arborescent cone in cone, card house cone in cone and planar septaria.

INTRODUCTION

The Stephano-Permian of the Pyrenees has been divided into four formations (Gisbert, 1981): The Grey Unit from the Upper Stephanian age, the Transition Unit of Stephanian-Autunian age, the Lower Red Unit of Autunian age and the Upper Red Unit of mid-late Permian age. The nodules studied are found in the upper sections of the Transition Unit.

GEOGRAPHICAL LOCATION AND GEOLOGICAL BACKGROUND

The geographical location of the region studied is shown in Figure 1 where the Transition Unit is represented by a detrital sequence increasing in coarseness downwards which ends in lutites with nodules at times surrounded by limestones. Pyroclastic layers are frequent along the whole series and in some cases have thicknesses of more than 10 m. The total thickness ranges from zero to 180 meters.

The nodules studied appear at the top of the sequence where there are no limestones, or just before the lacustrine limestones where the whole series ends with these materials.

The nodules that we present have been chosen in order to summarize the more frequent characteristics and typologies. We also indicate that type A is found in the series without carbonates or with very thin levels of these proximally while type C is associated with the series of greater thickness of lacustrine limestones further distal. Type B is found in outcrops with characteristics intermediate between type A and C.

According to Gisbert (1981) and Valero (1991), in the upper sections of the rock formation they present a great variety of colours and tones and possess important levels of lacustrine carbonates (calcitic limestones and dolomites) with frequent stromatolitic growths. These lacustrine environments, rich in allochthonous organic matter possess frequent oxidation periods as well as important yearly and multi-yearly variations of alkalinity. The paleo-climate interpreted is of the savannah type, with a fairly long dry season and a significant rainy season.

In the Transition Unit, from the wall to the top we can detect a trend indicating climatic aridification; in the wall the dry periods are short and the lake maintains conditions of sedimentation which are inadequate for the precipitation of carbonate. In these grey coloured basal sections, it is quite common to find septaria nodules with a sideritic body and cracks filled with calcite, ankerite, barite and sphalerite. The nodule can have a nucleus either in the form of an organic remain or a pyroclastic fragment. They are very similar to other sideritic nodules described in bibliography (see G. Lentsch, 1967). For this reason we have not included a detailed description of these nodules. There are also stratiform levels of cone in cone (levels ranging from 10 to 30 cm) with typical textures (see P. C. Franks, 1969 and Ws. McKenzie, 1972).

Laterally and vertically the carbonates appear in association with three different types of nodules which we shall describe in detail.

PETROGRAPHIC DESCRIPTION

General Types of Nodules

1) Type A: Septariform nodules with a kidney shaped fibrous-radial body of calcite. They are found in association with lutitas of various colours (red, green and grey) with sporadic bright spots of lacustrine limestones (25–40 cm maximum) of very little thickness and lateral continuity.
2) Type B: Septaria-cone in cone nodules with stromatolitic nucleus. They are associated with the grey series with a moderate development of the carbonated series (5 to 8 carbonate layers of thickness 0.3 to 0.6 m) and close to zones of extinction of lacustrine facies.
3) Type C: Fibrous-radial nodules. Associated to the grey series in which the lacustrine facies reach their maximum thickness and development.

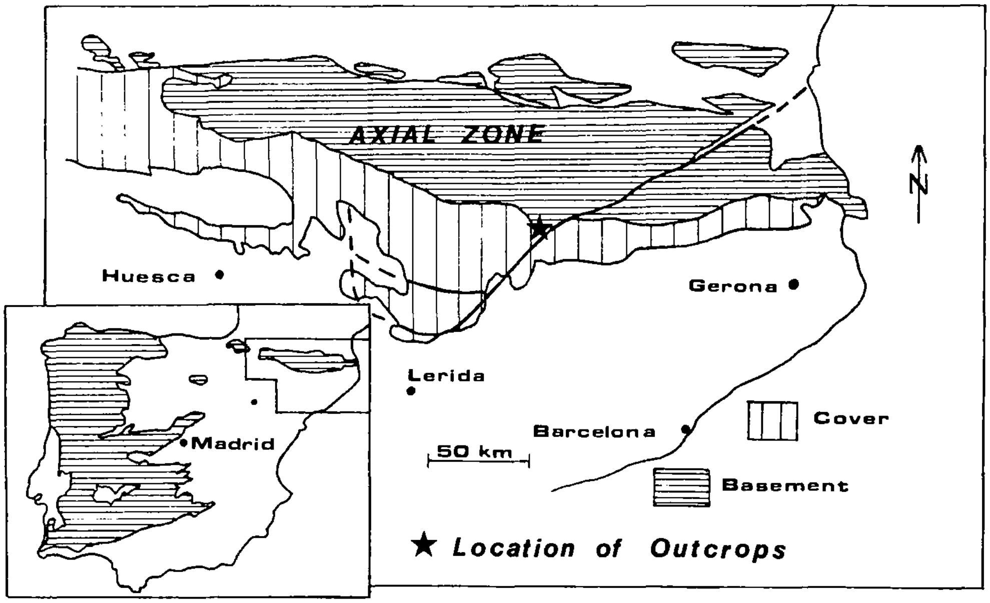

Figure 1. Location of outcrops.

Detailed Description

Type A) Septariform nodules with a kidney shaped fibrous-radial body (Fig. 2):

This type of nodule presents an external and kidney shaped reddish covering that wraps around a greenish globular nucleus. See Figure 2.

The kidney shaped reddish covering has a network of septaria cracks which run along its surface and which forms a septarian wrapping of the mass of the greenish nodule.

The kidneys have a body of calcite fibres of great length and which extend to reach the whole thickness of the septaria layer. In some cases the fibres adopt a morphology of big radiaxial calcite crystals with well marked curved lines of exfoliation and in which the lines of the individual fibres can still be recognized (Photo 1).

The composition of the fibres (the mean of 8 Edax analyses) is:

$$CO_3Ca_{0.958}Mg_{0.012}Fe_{0.004}Mn_{0.026}.$$

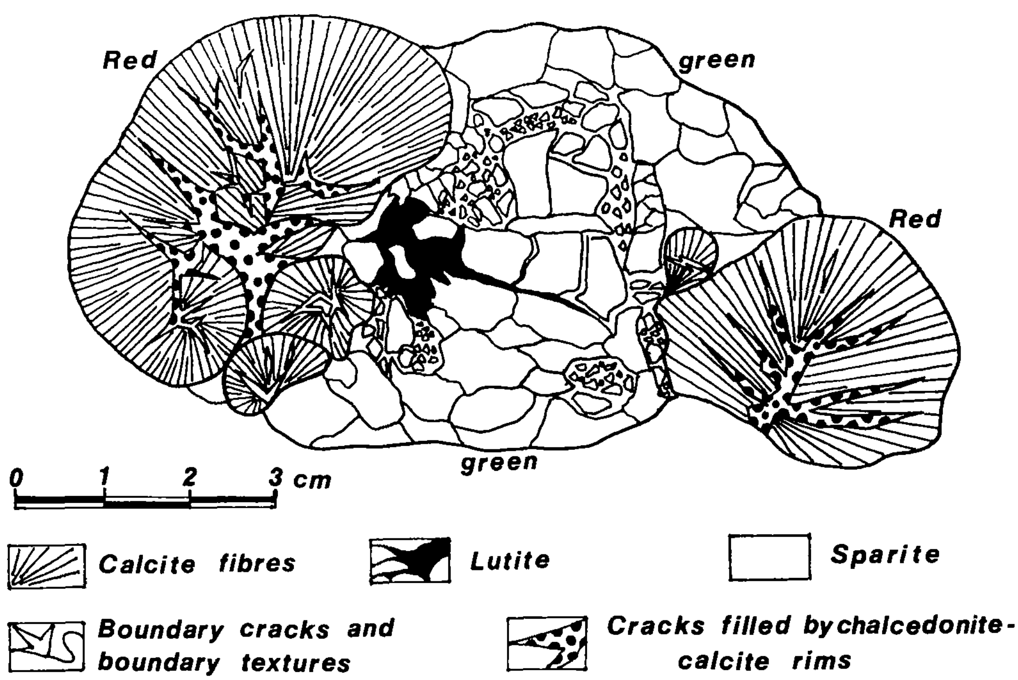

Figure 2. Textures of nodule type A: Septaria with a kidney shaped fibrous body of calcite.

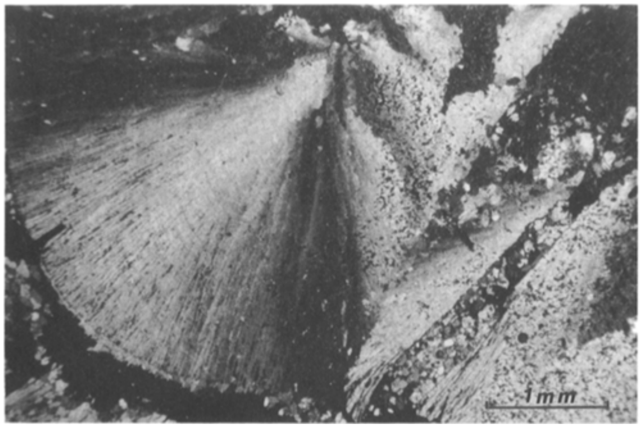

Photo 1. Bunches of fibres that make a radiaxial calcite crystal. The hematite inclusions allow identification of the fibres without cathodoluminescence techniques. Nodule type A.

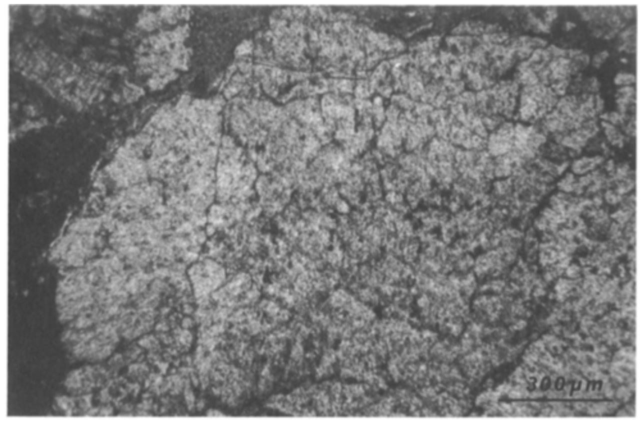

Photo 3. Petrographic microscope detail of sparitic crystal. Nodule type A.

The analysis performed with the minimum field of analysis allowed by Edax (two) gave as a result the following composition:

$$CO_3Ca_{0.968}Mg_{0.004}Mn_{0.028}.$$

Occasionally some oxides of Fe and some clay mineral accompany the fibres. In cathodoluminescence (C.L.), the calcite fibres have lenticular cracks running across. These cracks are filled with calcite that has an orange luminescence brighter than the calcite that constitutes the fibres.

These septaria cracks are filled with a first layer of sparitic subidiomorph calcite, followed by a layer of fibrous chalcedony (chalcedonite, positive elongation) that extends perpendicular to the edge of the crack with a length of 0.5 to 3 mm. Sometimes the first carbonate layer is missing and another sparitic calcite appears after the chalcedoniote (Photo 2). The surrounding carbonate layer is pure calcite without Mg, Fe or Mn (data from an Edax analysis).

The green central nodule has a chicken-wire texture. It is formed by sparite, often radiaxial, occasionally radiaxial macrocrystals and at times some fibrous calcite without oxides of Fe. The macrocrystals have incrustations of anhydrite of 0.3 mm maximum.

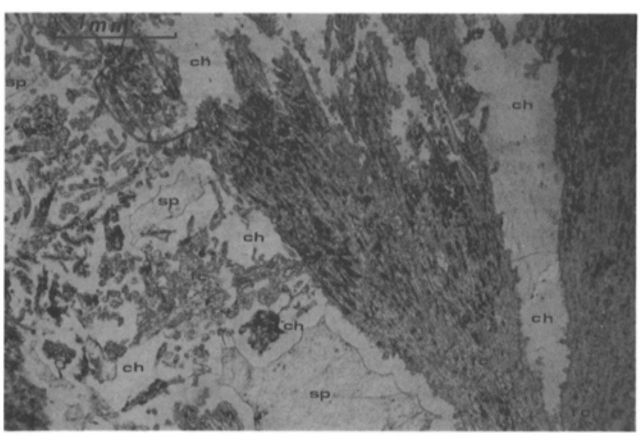

Photo 2. Bunches of fibres and chalcedonite rims in boundary septaria cracks. Nodule type A.

The sparitic calcite in cathodoluminescence (C.L.) presents a very bright orange coloured irregular lamination. This reticule is very similar to a flat septaria[3] (Photos 3 and 4). Considering radiaxial calcite, we can observe in cathodo a feather like[2] cone in cone (Photos 5 and 6). The very same bright orange calcite is found amongst the crystals of macrosparite and sparite.

The mean value of composition of the calcite from this green nucleus (4 Edax analyses) is:

$$CO_3Ca_{0.979}Mg_{0.014}Fe_{0.003}Mn_{0.004}.$$

Nevertheless, as the number of crystals used in the analyses rose, we detected and recorded an increase in Fe and Mn; based on this, and taking into consideration only the two results obtained using the minimum field sensitive to the analysis, the composition obtained is the following:

$$CO_3Ca_{0.992}Mg_{0.008}.$$

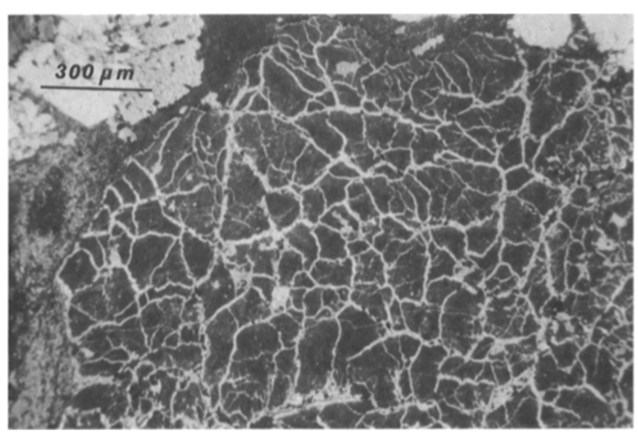

Photo 4. Cathodoluminescence microscope detail of sparitic crystal (Same Photo 3). Note a network of cracks similar to the network of planar septaria. This fact is interpreted as relict textures of organic gel before its mineralization. Nodule type A.

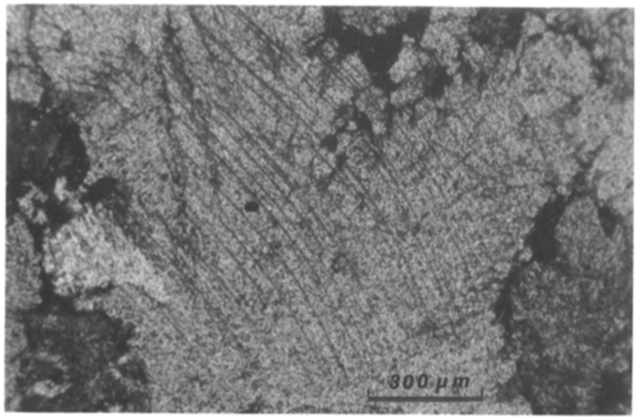

Photo 5. Petrographic microscope detail of radiaxial calcite crystal. Nodule type A.

Type B) Septaria-cone in cone nodules with a stromatolitic nucleus (Fig. 3):

Nodule with a 30 cm diameter in which three areas can be identified (Fig. 3):

1) Central nucleus with a kidney-shaped concentric lamination and beef[1] type fibres (6–9 cm diameter).
2) Fibrous internal covering and millimetric cones of the arborescent type (2–3 cm thickness).
3) External fibrous covering and centimetric cones of the card house[2] type (0–3 cm thickness).

The network of septariform cracks (1–6 mm thickness) affects zones 1 and 2 and appears filled with sparitic calcite in a mosaic form ($\phi_m = 0.3$ mm).

The nucleus is formed by micritic and microsparitic calcite, the changes in the shape of the crystals being responsible for the concentrically layered outline. Generally speaking, the micritic carbonate are predominant in the interior while the microsparitic are predominant in the outer layers. In the outer layers, beef type cumules of parallel calcite which extend perpendicularly to the kidney-shaped concentric sections are also common. Occasionally, and in the outer zones there is also an aggregate of fibres with a fibrous-radial or feather-like[2] texture.

Zone 2 is separated from the nucleus either by a layer of clay (0.5–3 mm thickness) or by a layer of sparitic calcite or by an important change in texture (fibrous-radial or feather-like). It is composed of bunches of calcite fibres of millimetric size (1–8 mm), the cones are displayed in an irregular fashion and are to be found only locally as an harmonious arrangement. Thus, it has a cone in cone texture of the arborescent type[2]. The cones are always open towards the external part of the nodule while the vortex points to the interior. There is also micritic carbonate and clay, either disperse or concentrated in a concentric crack (0.3–0.9 mm thickness).

Zone 3 is separated from the latter by little cracks filled with clay that on some occasions present a reticule of a flat septaria developed from a micritic or microsparitic layer. In terms of texture it presents a bunch of fibres with either a cone in cone organization in card house form or a more irregular texture with large long fibres. The main difference with zone 2 lies in a greater organization of the cones and in an increase in size of the cones and fibres (0.9–3 cm). At one point the nodule presents a protuberance in the shape of a horn (not shown in Fig. 3) which is formed by big bunches of fibres (4–7 cm) that would obviously be included in zone 3.

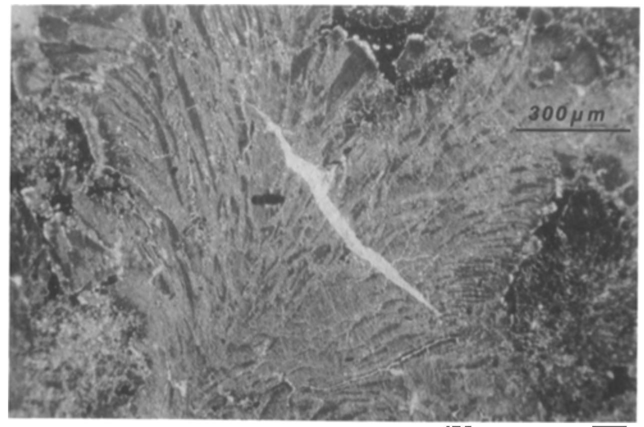

Photo 6. Cathodoluminescence microscope detail of radiaxial calcite crystal (Same Photo 5). Note a featherlike[2] cone in cone. This texture is interpreted as the primary, and after a small diagenetic arrangement of rhombohedron fibres, they have form the radiaxial calcite crystal.

With an electron microscope we can observe how the fibres are composed of aligned rhombohedrons. The Edax analysis proved that some of these rhombohedrons were replaced by silica, while the rhombohedral form prevailed in the replacement.

The composition of the calcites is shown in Table 1. As is shown in this table, the calcite composition shows an increase in Fe and Mn when we move from the nucleus to the outer zone. This trend in the mean values is undeniable, but it could be open to argument for zone 3, if one considers only the analyses performed using the minimum field available for Edax analysis, which are the most reliable. However, this effect could be the result of the actual meteoric oxidation which is reflected on the nodule with several limonitic rims and which affects mainly the most external cortex of zone 3.

Type C) Fibro-radial nodules

Their structure is relatively simple: They are formed by calcite fibres from the nucleus of the nodule to the outer zone. Amongst the fibres there are small holes filled with sparitic calcite. On the external edge of the nodule there are two thin layers. The first layer, of the beef[1] type (2.5 mm) calcite is separated from the radial fibres by a stilolitic surface. On top of this layer there is a marlous zone (6–8 mm), arranged in cone in cone fashion.

Their size ranges from 0.5 cm and 100 cm; the example studied has a diameter of 60 cm. Because of its size, a systematic investigation of the nuclei has not

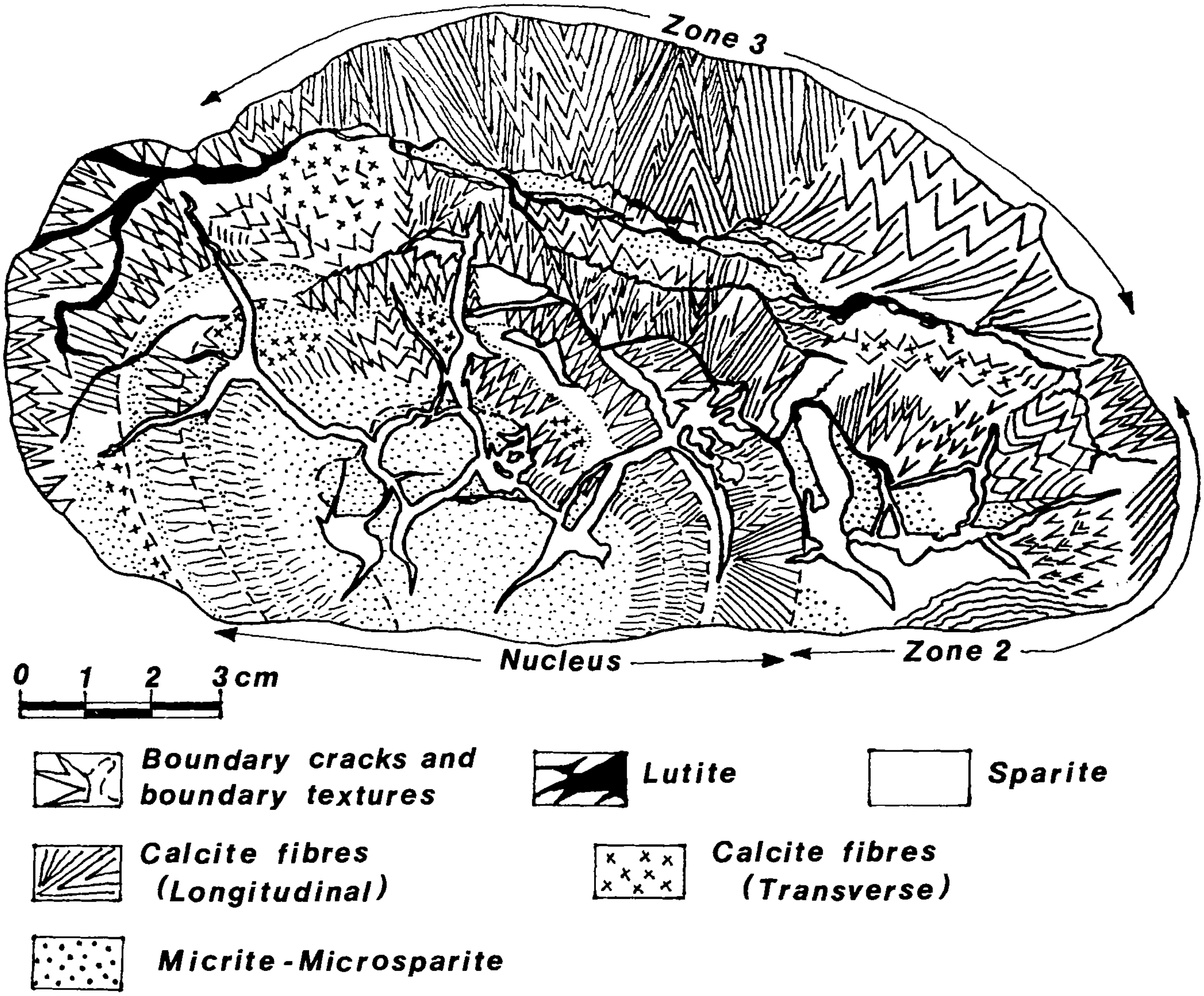

Figure 3. Textures of nodule type B: Septaria-cone in cone with stromatolitic nucleus.

been possible, but it is plausible that some of them could be type B nodules with a very well developed zone 3.

With Edax we can observe that the fibres are composed of aligned rhombohedrons (Photo 7). We can also detect small quantities of pseudomorphic chalcedony that takes a rhombohedral shape and ferrous dolomite but these cannot be distinguished with the petrographic microscope.

The composition of the calcite fibres is, according to the five Edax analyses (confirmed also by chemical analysis Gisbert, 1981):

$$CO_3Ca_{0.974}Mg_{0.004}Fe_{0.016}Mn_{0.006}.$$

The composition of the existing sparite amongst the fibres was the following; (two Edax analyses):

$$CO_3Ca_{0.95}Mg_{0.01}Fe_{0.04}.$$

The beef' that surrounds the nodule appears to be (one Edax analysis):

$$CO_3Ca_{0.96}Mg_{0.01}Fe_{0.017}Mn_{0.014}.$$

DISCUSSION AND INTERPRETATION

The genesis of septaria and cone in cone is a problem yet to be resolved in detail by the scientific community. Our team has been investigating the hypothesis that they are in effect structures of mineralized organic gel (J. Gisbert and F. Gascon, 1985; J. Gisbert *et al.*, 1987; E. Aso, 1991).

Recently, E. Aso (1991) has performed several experiments in which he has grown calcite crystals on organic gel and has obtained fibres from this mineral oriented in two directions that form similar angles to the ones found in cone in cone fibres (Photo 8). These fibres obtained in the laboratory are formed by alignments of calcite rhombohedrons oriented according to

Table 1. Results of Edax analysis for nodule type B.

	Policrystalline analysis (2500 $m\mu^2$)					Monocrystalline analysis (4 $m\mu^2$)				
	Ca	Mg	Mn	Fe	*	Ca	Mg	Mn	Fe	*
Zone 1 (in-boundary)	0,942	0,025	0,018	0,014	3	0.957	0.019	0.022	0,002	3
Zone 2 (in-boundary)	0,937	0,023	0,023	0,016	8	0.947	0,019	0,029	0,005	9
Zone 2 (out-boundary)	0,886	0,038	0,030	0,045	2	0,937	0,022	0,032	0,008	3
Zone 3	0,862	0,025	0,068	0,045	3	0,955	0,016	0,025	0,004	8
Filling cracks	0,957	0,026	0,015	0,002	1	0,948	0,032	0,017	0,003	3

* Number data of points analysis

MEAN VALUES

	Ca	Mg	Mn	Fe	*
Zone 1 (in-boundary)	0,955	0,022	0,020	0,002	6
Zone 2 (in-boundary)	0,947	0,021	0,026	0,005	17
Zone 2 (out-boundary)	0,913	0,030	0,031	0,026	5
Zone 3	0,909	0,020	0,046	0,024	11
Filling cracks	0,952	0,029	0,016	0,002	4

the C axis and with an order and a morphology similar to that found in the fibres of natural nodules (at least the ones studied here) (Photos 7 and 9).

This same author, using his own experimental data together with the description of natural nodules (Photo 1) concludes that the radiaxial calcite is formed originally from these fibres. Thus, this calcite is a crystalline aggregate formed by a mosaic of rhombohedrons that could originate either directly from the organic gel or through a small diagenetic arrangement of the rhombohedrons which constitute the fibres.

Thus, in our opinion, the cone in cone and the fibroradial aggregate are growths of calcite originated from a level of organic gel. When the gel deteriorates under superficial conditions, a network of septaria cracks is developed. If the degradation is very intense, it inhibits the growth of the fibres and the nodule undergoes a process of mineralization together with the micritic-microsparitic mosaic. If the degradation is milder, it takes the form of a network of cracks and fibrous growths. It is then frequent for the cathodoluminescence properties of crystals to mimic the network of cracks which have not mineralized as such (Photos 3 and 4).

In the majority of cases it is probable that the gel originates either from the segregation of microorganisms which degrade organic matter or from the metabolism of other sources of bacterial energy (sulphates, organic matter, volcanic glass, etc.).

All the nodules described are very young, among other reasons because of their feature of moving the fibres along the enveloping lutite and which following this should still have been in the consolidation process.

In model A, the relicts of anhydrite in the green sparitic nodule indicate that this was originally a nodule of calcium sulphate. Thus, the fibrous-septaria covering probably developed during the replacement process. From the geological context, we can deduce that, at that time, there were alternating oxidation-reduction conditions. During the oxidation period all the carbonates were mineralized as none of them has iron in its network. In this phase, the Fe, from which the hematites originated (which in turn give the red colouring to the external reniform covering) was oxidized.

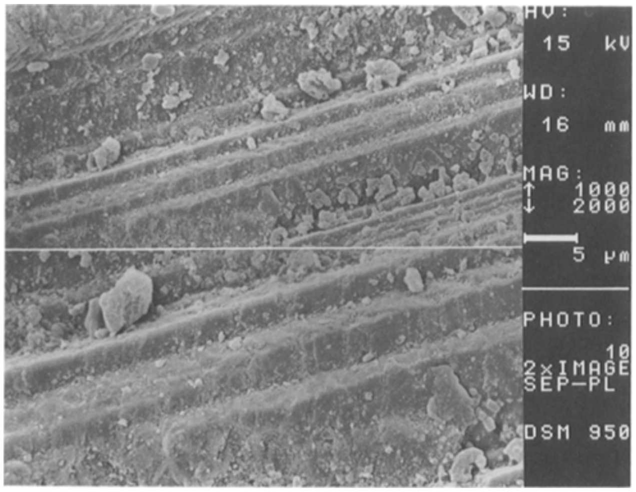

Photo 7. Ultramicroscopic aspect of type C nodule. Note how the fibres are formed by straightened rhombohedrons of 3–5 microns. This feature is similar in the fibres of all the nodules studied.

Photo 8. Aspect of straightened rhombohedron calcite fibres obtained experimentally with calcite growing in agar gel by addition of Na_2CO_3 and CaCl. One can see the macroscopical aspect of the aggregate obtained showing the "card house" network.

The nucleus of the nodule was always in a slightly higher state of reduction than its covering and as a result the iron was not firmly fixed to the clay, thus this zone was green in colour.

Therefore, it is very likely that the original sulphate nodule was "digested" by a colony of bacteria, possibly some of them from the family of the sulphate reductors. These microorganisms generated an important mass of organic gel which controlled the calcite replacement. Probably the ball-like gel is generated in the reductor stage and certainly the mineralization is produced in the oxidizing stage (absence of Fe in the calcite network).

The nodule mineralized at very early stages due to its moving feature and its oxidizing conditions.

The fibrous body of this nodule presents a remarkable morphological similarity with thė calcite spherulites that Dominguez Bella and Garcia Ruiz (1987) grew from silica gel in laboratory experiments. We do not believe this similarity to be a coincidence as this is one of the nodules with the highest proportion of chalcedony in its composition. We believe that, in this case there was a proportion of colloidal silica next to the organic gel and that it was this that caused the thinness of the fibres as well as regularity, as these are the morphological features which are similar to these obtained in the experiments with silica.

In model B: The nucleus was a superficial stromatolite. Taking advantage of this "exogenous" bacterial colony, it followed the activity of the microorganisms during the first stages of burial. The mineralization of the segregated gel took place in several stages; the internal stages occurred at an earlier age and the external ones later.

The fibres of the successive layers appear to have formed in alkaline conditions (calcite rich in Mg) with progressively more reducing conditions (increase of Fe in the network), however the small absolute quantity of Fe in the network indicates mild reducing conditions. It has been shown that the size of the fibres and their arrangement in cone in cone form increase the later they develop, probably as a result of the absence of microbial activity which would have destroyed the regular growth texture of the fibres.

The model type C: These are spherulitic nodules formed in reducing conditions as the ferrous composition of their calcite fibres proves; the important changes in alkalinity in the environment most probably controlled their crystalline growth. Conditions ranged from a pH of 7 (organic acids in the accumulation of organic matter) to extremely alkaline conditions which generated the autigenesis of ankerite in the surrounding lutite.

We do not yet know how important a role factors such as the gel composition (which can vary considerably, especially if we use mixtures of different types) or the action of different families of microorganisms which can alter the physical properties of the gel play. Nevertheless, from what we know about the Transition Unit we can draw the following conclusions.

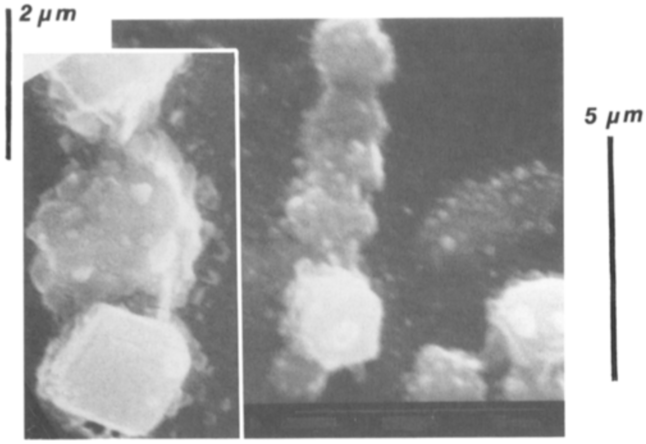

Photo 9. Aspects of straightened rhombohedron calcite fibres obtained experimentally with calcite growing in agar gel by addition of Na_2CO_3 and CaCl. One can see the straightened rhombohedrons of 1–2 microns of size in a ultramicroscopic detail of previous photography.

CONCLUSIONS

The nodules studied were formed in habitats rich in organic matter and sulphates. These habitats experienced important variations in alkalinity and short oxidation periods. In the habitats with longer oxidation periods the nodules have septaria cracks.

The fibres grow in organic gel but the moderated presence of silica colloids favours crystalline growth and probably causes some morphological features such as thinness and regularity of the fibres.

The mineralization of nodules always takes place at an early stage of diagenesis; the fibres are always thicker, have a better arrangement and are also longer the later the growth has occurred. All nodules have been formed at an early stage of diagenesis, but within it, type A is the first to develop and type C the last to do so.

ACKNOWLEDGMENTS

I want to thank the Chairman and workers of microscopical services of the Institute de Geologie (Université de Strasbourg, France) for their support and help and the Universidad Central de Barcelona. I would also like to thank my sister Macu who helped me with the English version of this paper.

GLOSSARY OF TERMS

[1] Beef: This term is used to describe a texture of parallel calcite fibres, generally displayed perpendicularly to the surface on which they rest. Almost identical to the term "parallel fibrous displacive calcite", but here we propose a wider meaning which also contains the addition of parallel fibres of calcite with interpenetrative arrangement.

[2] Feather-like cone in cone or arborescent or card house: E. Aso (1991) distinguishes three types of cone in cone depending on the arrangement of its fibres;

Feather-like: The fibers diverge from the axis of the cones as is the case with birds' feathers. There is no structural relation to the adjacent feather.

Arborescent: The cones have a greater bilateral symmetry than in the above mentioned and the different cones can have a more or less parallel axis, but there is no structural connection of individual fibres (i.e. from fibre to fibre).

Card House: The cones extend in bilateral symmetry, parallel axis and structural connection from fibre to fibre. This author's interpretation is that the first ones have an earlier genesis and the last ones a later genesis.

[3] **Flat or Planar Septaria:** Stratiform bed or transversal section of lutitic or marlous composition, along which runs a network of cracks with three types of cracks: parallel, transverse and curved (see Photo 4). For more details, see J. Gisbert and F. Gascon, 1985, and E. Aso, 1991.

REFERENCES

Aso, E., 1991, "Origen de Septarias y "Cone in Cone", Condiciones Geológicas y Reproducción Experimental. Tesis Doctoral Univ. de Zaragoza, Spain. 231 pp.

Dominguez Bella, S., and Garcia Ruiz, J. M., 1987, Banoing structure in induced morphology crystal aggregates of $CaCO_3$. Journal of Materials Science 22, pp. 3095–3102.

Franks, P. C., 1969, "Nature, origin and significance of cone in cone structures in the Kiowa formation (Early Cretaceous)". J. Sed. Petrology 39, 4, 1438–1454.

Gisbert, J., 1981, Estudio geológico petrológico de la Sierra del Cadí (Iérida, España). Diagénesis y sedimentología. Tesis Doctoral Univ. de Zaragoza.

Gisbert, J., and Gascon, F., 1985, "Several morphologies of septaria structure on Stephano-Permian continental series (Spanish pyrenees Catal.) Relationship with sedimentary environments. IAS 6th. Eur. Mtg. Lérida Abstracts, pp. 179–184.

Gisbert, J., Valero, B., and Albeniz, M. A., 1987, "Septarian and cone in cone genesis by activity of microorganisms producing organic gel". 8th IAS Europ. Meeting, Tunis Abstract book, pp. 206–207.

Lentsch, G., 1967, "Geochemie und Sulfidvererzung der Toneisenstein. Septarien aus den Lebacher Schichten des Saarlandischen Unterrotliegenden". Ann. Univ. Savariensis Math. Nat. Fak. Heft 5, 131–172.

McKenzie, Ws., 1972, "Fibrous calcite a Middle Devonian geological marker with stratigraphic significance. Canadian Journ. Earth Sc. 9, 1431–1440.

Valero, B., 1991, "Los Sistemas Lacustres Carbonatados del Stephaniense y Pérmico en el Pirineo Central y Occidental". Tesis Doctoral Univ. Zaragoza. 378 pp.

Manuscript received February 13, 1992
Manuscript accepted March 24, 1992