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# Silicification of plant remains in Messinian marine sediments in the Vera Basin (Almería, Spain)

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*Key words:* Silicification, Messinian, plant remains, Spain

## ABSTRACT

Silicified fragments of herbaceous plants and trees are common in the “Coscojar Section” in the Vera Basin, Almería (eastern sector of the Betic Cordilleras). These remains are incorporated in Messinian marly sediments deposited in a shallow, proximal marine environment. The plant fragments, which are terrestrial in origin, underwent early silicification with little or no burial. Petrification occurred in pore waters enriched in dissolved silica by the dissolution of amorphous silica skeletal debris and involved the impregnation and partial filling of the pores and voids in the plant structures with opal-CT. Subsequently, chalcedony spherulites and quartz grew in the cavities, without opal-CT as precursor mineral. Framboidal pyrite formed simultaneously in some cell lumina and other cavities. Finally, the opal-CT-quartz transformation took place selectively in some plant remains, probably in connection with hydrothermal fluids, which caused a later precipitation of iron oxides, metallic sulphides and/or gypsum in some plant remains. The plant remains of the “Coscojar Section” represent a good example of unusual silicification of plants in marine conditions and a rapid, atypical opal-CT-quartz transformation.

## RESUME

Dans la «série du Coscojar» du Bassin de Vera, Almería (secteur oriental des Cordillères Bétiques) on trouve fréquemment des fragments silicifiés de plantes herbacées et ligneuses. Ces restes sont inclus dans des sédiments marneux, d'âge Messinien, déposés dans un milieu marin pas très profond, près du continent. Les fragments végétaux, d'origine continentale, souffrirent une silicification précoce, avec peu ou pas du tout d'enfouissement. La silicification eut lieu par un enrichissement de la concentration de silice de l'eau des pores, venant de la dissolution de silice amorphe biogénique, et supposa l'imprégnation et le remplissage partiel par opale-CT des pores et creux des structures végétales. Postérieurement se produisit l'accroissement de quartz et de sphérulites de calcédoine à l'intérieur des cavités, sans opale-CT précurseur. Simultanément la formation de pyrite framboïdale dans quelques lumina cellulaires et dans d'autres creux a lieu. Finalement, la transformation opale-CT – quartz s'est produite de façon sélective sur certains restes végétaux, liée probablement à la présence de fluides hydrothermaux, qui donnèrent lieu à la précipitation d'oxydes de fer, de sulphures métalliques et/ou de gypses dans quelques restes végétaux. Les restes végétaux de la «série du Coscojar» constituent un bon exemple de la silicification inhabituelle de plantes terrestres dans un milieu marin, et d'une rapide transformation opale-CT – quartz.

## 1. Introduction

Silicification is the most common and best mechanism for preservation of plant structures. The fossil record presents silicified plant remains from the Devonian to the Holo-

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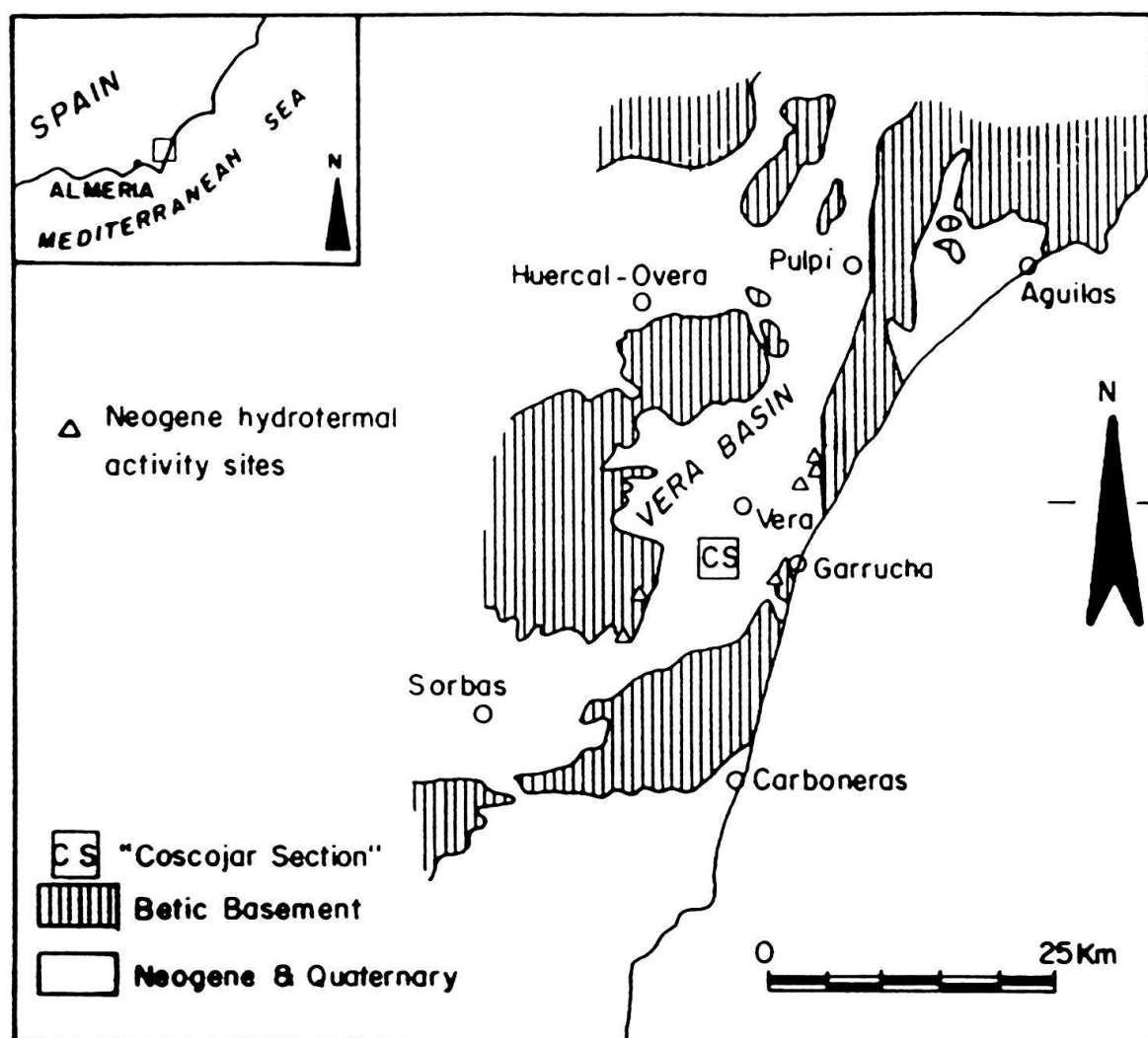


Fig. 1. Location of the sector studied.

cene (Buurman et al. 1973; Murata & Norman 1976; Leo & Barghoorn 1976). Silicified plants are mainly associated with continental sediments and the source of the silica is normally clearly inorganic. Silicification of plants in marine environments is an unusual process, information on it much scarcer and the diagenetic processes less well known.

The "Coscojar Section" (Barragán 1986–87) is located in the Neogene Vera Basin, in Southeast Spain (Fig. 1). It is made up of a thick ensemble of marly sediments with various coarse detrital intercalations (Fig. 2). Silicified fragments of herbaceous plants and trees are common in the lower part of this Messinian marine section. The plants which grew in nearby continental areas were transported to the sea.

This paper is mainly concerned with the identification of the different silica phases present in the plant remains, and the relationships between the silica phases and other mineralizations found in the plants and sediments, in order to determine the silicification mechanism, the later diagenetic transformations of the plant remains and the conditions in which silica diagenesis took place.

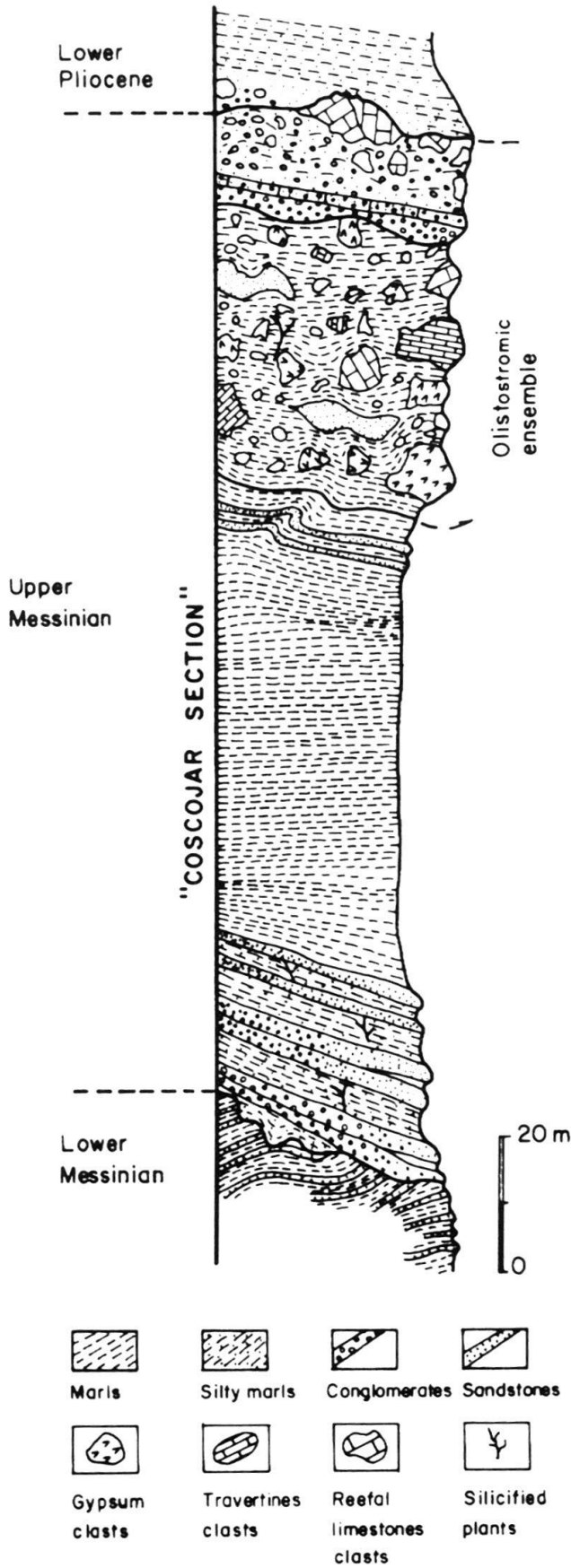


Fig. 2. Coscojar Section.

## 2. Geological setting

### 2.1 *The Vera Basin*

The Vera Basin, situated in the northeastern part of Almería province (Spain) (Fig. 1), is one of the intramontane Neogene depressions located in the eastern sector of the Betic Internal Zones. It contains mainly Burdigalian to Upper Pliocene marine sediments. The sediments of the basin are intercalated with abundant volcanic material, dated as Late Tortonian, and in some cases Messinian (Nobel et al. 1981; Bellón et al. 1983). Instances of hydrothermal activity during the Neogene have also been identified (Alvado 1986; Ott d'Estevou et al. 1990; López Gutiérrez et al. 1992; Martínez Frías et al. 1992; Barragán 1994).

### 2.2 *The Coscojar Section*

A group of sediments deposited mainly by massive gravitational processes (Barragán 1986–87) crop out in the vicinity of the Cerro del Coscojar, approximately 8 km SSW of Vera (Fig. 1). These deposits (Fig. 2) are clearly discordant on a sharp palaeotopography formed on turbiditic Lower Messinian marls and sandstones.

The “Coscojar Section” begins with whitish, at times laminated, silty marls with thick (2–3 m) intercalations of conglomerate beds, distributed in fan shapes with their apexes located on the aforementioned palaeotopography. The conglomerates are structureless and poorly-sorted with clasts ranging from 0.5 to 60 cm in diameter, originating from the underlying turbiditic sandstones and volcanic rocks. Abundant silicified plant remains were found in the silty marls. The lack of coarse detrital particles in the marls containing the silicified plant remains means that these remains could not have reached the basin as already silicified clasts. The bulk mineralogy of these marls (Sánchez-Bellón 1992) is: calcite (42%), dolomite (9%), phyllosilicates (26%), quartz (17%) and feldspar (5%). The major phyllosilicates are smectites and illite, which appear together with much less abundant chlorite, kaolinite and paragonite. According to Sánchez-Bellón (1992), these phyllosilicates are almost exclusively detrital, originating from nearby continental areas.

Calcareous nannoplankton in these marls (Martín Pérez, personal communication) belong to the lowermost part of zone CN-10 (Okada & Bukry 1980) of the Upper Messinian. Siliceous sponge spicules are also found, together with frustule fragments of diatoms as well as the calcareous nannofossil *Braarudosphaera bigelowii* (Gran & Braarud) Deflandre, which is a species typical of coastal environments with low salinity (Bukry 1974; Siesser 1977).

Proximity of the deposits to the coast and shallow coastal water are suggested by the fan morphology of the conglomerate layers, whose apexes lie on the palaeotopography, and the nature of conglomerate pebbles from the closest reliefs.

The marls become gradually less silty towards the top, becoming uniformly massive with no silicified plant remains. The upper part of the marly unit includes several beds of turbiditic sandstones (up to 10 cm thick). Chaotically disposed material with a marly matrix similar to the preceding unit and containing olistoliths of widely varying size (1 cm<sup>3</sup> to over 50 m<sup>3</sup>) lies unconformably on the marls and sandstones. The clasts are predominantly made up of gypsum blocks, together with blocks of travertine, turbiditic sand-

stone, reefal limestone and also metamorphic and volcanic clasts. Silicified plant remains are also found in the marls making up the matrix of this chaotic unit, although the remains consist only of tree fragments and are much scarcer than in the marls of the lower part of the section (Fig. 2). This ensemble can be considered an olistostrome caused by one or more waves of massflow, the source area of which was located nearby.

Another olistostrome mainly made up of poorly-sorted conglomerates and calcarenites lies unconformably on this first one. Finally, a conglomerate ensemble from a littoral environment lies unconformably on top of the section, together with Lower Pliocene sands and silty-sandy marls.

### 3. Silicified plants

The silicified remains in the "Coscojar Section" belong to herbaceous plants and trees. The herbaceous plant remains consist of fragments of hollow stems with a cylindrical section less than 1 cm in diameter. The thickness of the wall material is less than 2 mm and their length is normally less than 5 cm. These remains were only found in the lowest part of the section. These hollow stems could not have had a detrital origin, as they would have been easily destroyed due to their fragile nature. The other remains belonged to trees and were found above and below the central uniform unit (Fig. 2). They appear either as amorphous fragments less than 10 cm long, or as trunk or branch-shaped fragments up to 50 × 35 cm in section and up to 20 cm long.

The degree of deformation by burial is commonly minimal or non-existent, which is evidence that lithification by silicification must have taken place rapidly before any significant compaction could have occurred by the weight of the overlying sediment. Some remains are fractured.

According to Koeniguer (personal communication), the microstructures of the trunks studied correspond to dicotyledon angiosperms reminiscent of African species of Moraceae and Meliaceae. The longitudinal striae, size, knot morphology and microstructures of the herbaceous stem fragments can be identified as belonging to Phragmites (Koeniguer 1972 and personal communication).

### 4. Mineralogical features

The plant remains studied are preserved mainly by opal-CT (following the terminology of Jones & Segnit 1971). Quartz is found in almost all the samples, although in a very small proportion. The herbaceous stems are partially or totally filled with chalcedony and quartz, occasionally together with quartzine and lussatite (following the terminology of Arbey 1980). Other non-siliceous minerals such as iron oxides and hydroxides, metallic sulphides and gypsum are also found in association with the plant remains. The most characteristic features of the different mineral phases present in the plant remains and the mineral relationships are briefly described below.

#### 4.1 *Opal-CT*

This is the common silica phase in the remains studied here. Opal-CT was identified by X-Ray diffraction, by a  $d(101)$  spacing from 4.12 to 4.09 Å. The opal-CT is distributed in

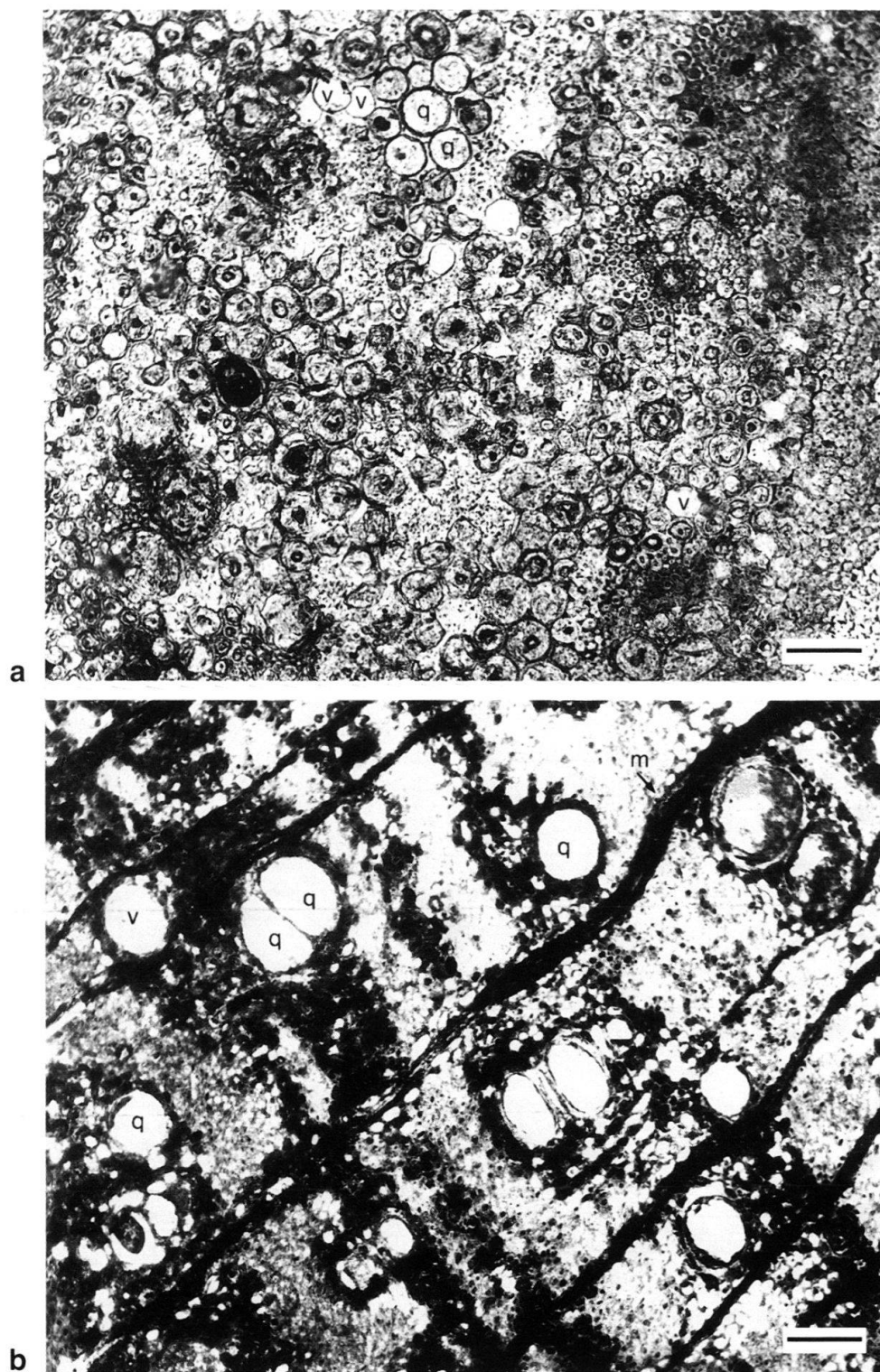


Fig. 3. (a) Cross-section of herbaceous stem. Opal-CT. q: quartz-filled cell lumina, v: empty cell lumina, (CCM-4). Polarized light. (b) Cross-section of stem. Opal-CT. q: quartz-filled cell lumina, v: empty cell lumina, m: massive Fe oxides (CCM-6). Polarized light. Scale bars = 100  $\mu$ m.

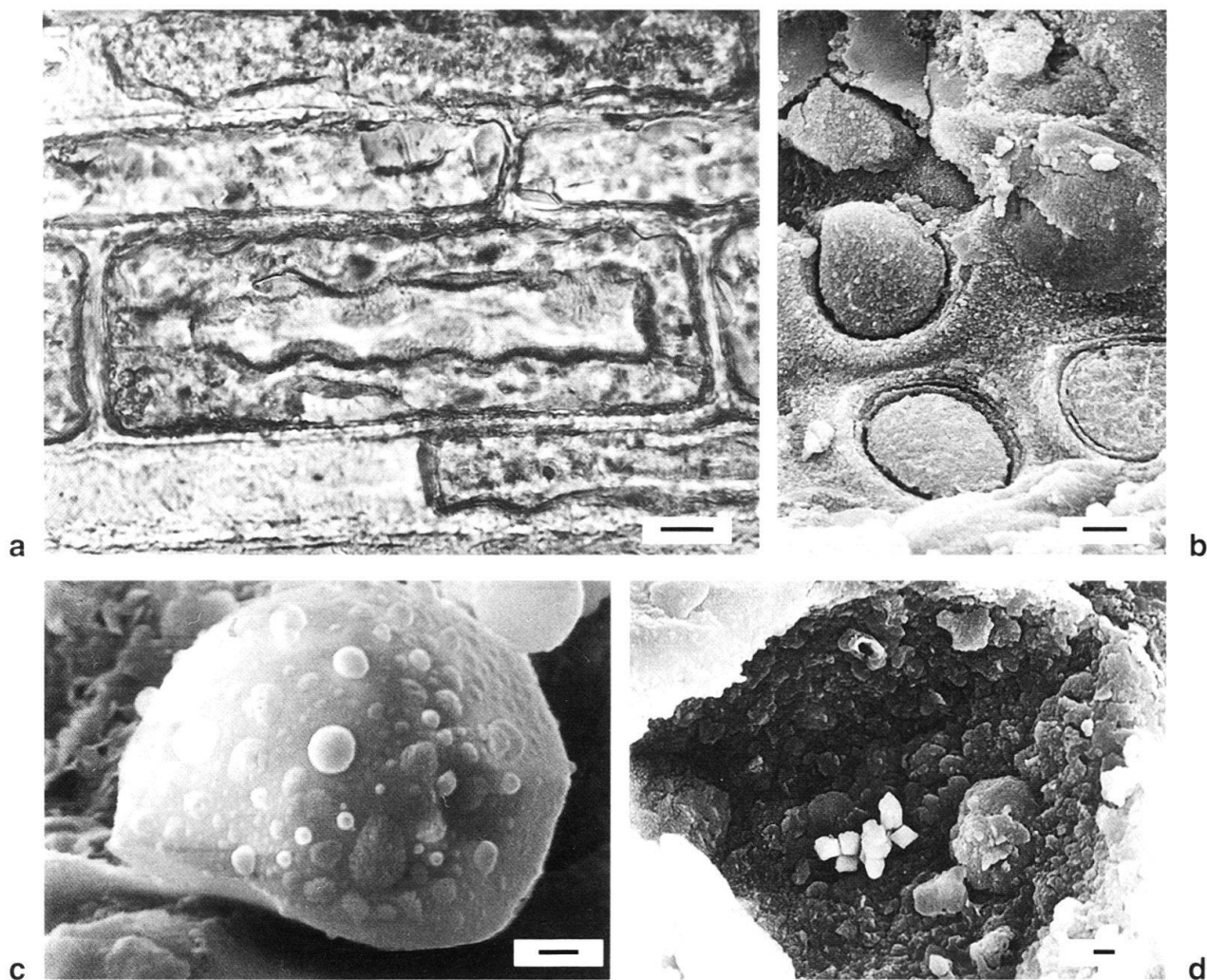


Fig. 4. (a) Longitudinal section of herbaceous stem. Opal-CT in cell walls and partially filling cell lumen, (CCM-4). Polarized light. (b) Bordered pits filled with opal-CT, (CCM-100). SEM. (c) Globular opal-CT in cell lumen, (CCM-105). SEM. (d) Partially empty cell lumen, with globular opal-CT on cell walls enclosing quartz crystals, (CCM-105). SEM. Scale bars: a = 10  $\mu$ m; b = 5  $\mu$ m; c and d = 1  $\mu$ m.

the internal plant structure in a similar fashion to that described by Buurman (1972) and Scurfield & Segnit (1984), i.e. the cell walls are distinct and well preserved (Figs. 3a, b and 4a) and are occasionally slightly thickened. The cell lumina are hardly ever completely filled and at times are empty or partially occupied by globular (Fig. 4c) or spherulitic opal-CT. The intercellular areas in the wood remains are poorly cemented, and therefore disintegrate easily with loss of individual cells.

#### 4.2 *Lussatite*

This fibrous, length-fast form of opal-CT, with low refringence and straight extinction (Arbey 1980) is not present in the plant structures, but is found covering empty spaces and enclosing the chalcedony spherulites inside some hollow stems (Fig. 5c).

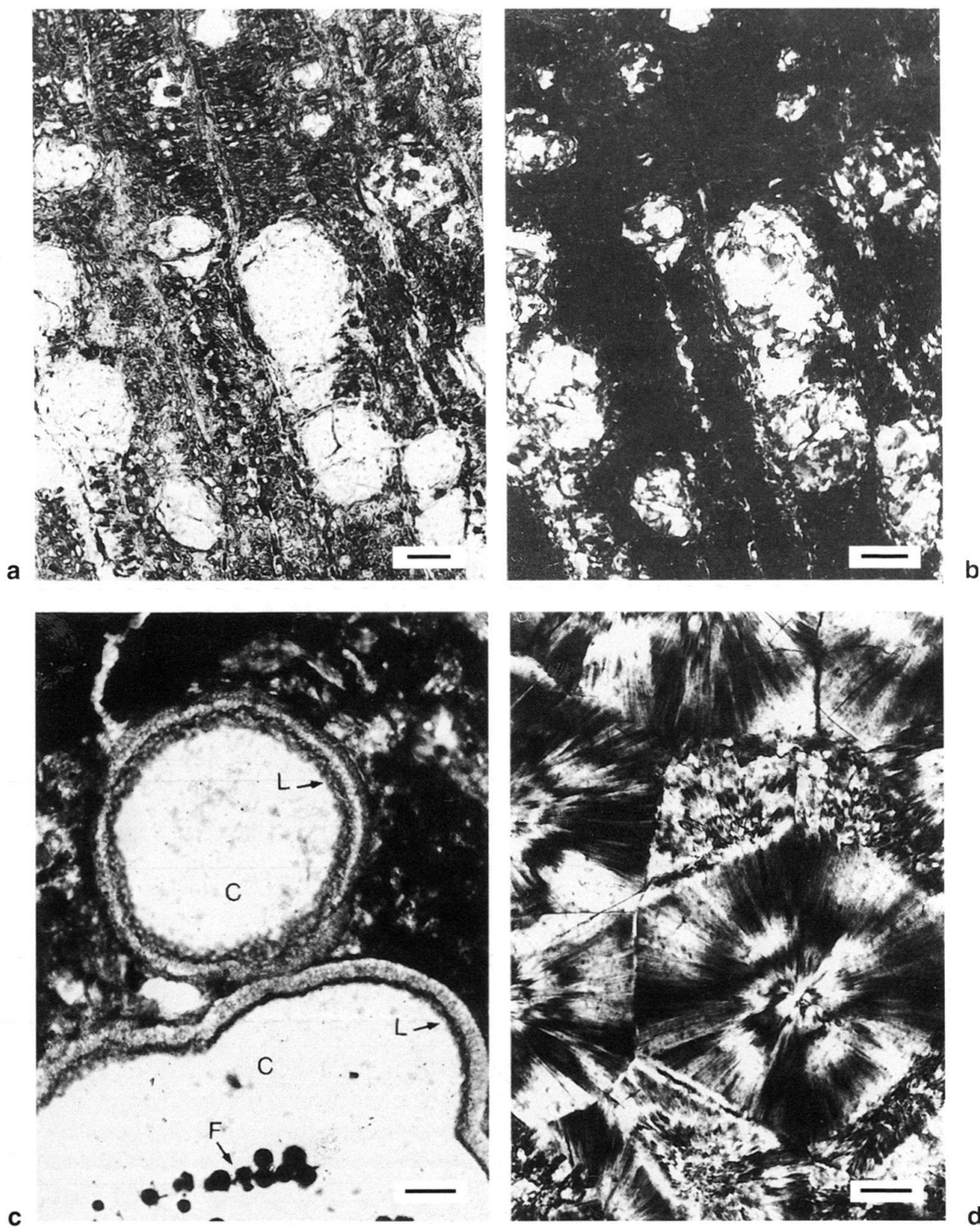


Fig. 5. (a) Cross-section of stem. Polarized light. (b) Crossed Nicols. Opal-CT, polyblastic and oligoblastic quartz (CCM-O-2). (c) Inner cavity of a herbaceous stem. Lussatite (L) surrounding chalcedony spherulites, (C) framboidal pyrite (F), (CCM-4). Polarized light. (d) Chalcedony spherulites filling inner cavity of a herbaceous stem, (CCM-2). Crossed Nicols. Scale bars: 100  $\mu\text{m}$ .

### 4.3 Quartz

Quartz is in most cases very scarce, except in some samples. According to the terminology by Storz (1933) (in Buurman 1972 and Jefferson 1987) for the types of quartz crystallization in silicified plants, the major form in our samples is polyblastic quartz, i.e. many small crystals (microquartz,  $< 20 \mu\text{m}$ , or macroquartz,  $> 20 \mu\text{m}$ ) in the space of one cell or in a vessel lumen (Fig. 5a, b). In the samples where quartz is more abundant, it occurs as polyblastic quartz or hyperblastic megaquartz. The latter quartz type is characterised by crystals filling several cells and growing through the cell walls with the same optical orientation. Oligoblastic quartz (a single crystal filling a single cell) was also recognised in some samples. Quartz also appears in the plant structures: a) as microquartz or megaquartz grains inside partially empty lumina (Fig. 4d, b) associated with opal-CT filling cell lumina and c) partially or totally permineralizing the cell walls (Fig. 5b). In some remains the plant structure has been obliterated by mosaic growth of macroquartz crystals, occasionally together with microquartz. The small cracks in the plant remains are filled by palisadic quartz, *sensu* Arbey (1980), often together with chalcedony. The cracks are more often found to be empty or filled with iron oxides.

### 4.4 Fibrous forms of quartz

The inner cavities of the herbaceous stems, especially the peripheral zones, are partially or completely filled by granular mosaic quartz and by fibrous spherulite and bundle forms in the central areas. The spherulites are mainly length-fast chalcedony (chalcedonite) (Fig. 5d), zebraic chalcedony, and, more rarely, length-slow chalcedony (quartzine). Cavities and major cracks in trunk fragments are also filled by chalcedony spherulites and granular mosaic quartz.

The spherulites are normally large (up to 1 mm in diameter) and well formed, with frequent pseudo-hexagonal forms and concentric spheroid growths, indicative of different stages of development with sufficient space and little interference. Mosaic quartz grains are common between the spherulites. The chalcedony spherulites and bundles are sometimes covered by lussatite (Fig. 5c). Small cracks are occasionally observed beginning inside the stems and penetrating the cellular network occupied by opal-CT. These cracks are filled with spherulite chalcedony and mosaic quartz as a distinct continuation of the inner filling.

### 4.5 Non-siliceous minerals

Apart from the silica phases described above, other mineral forms were recognised in the plant remains: hematite, goethite, pyrite, galena, sphalerite, celestite and gypsum. These minerals were produced in at least two stages. The first stage is represented by partially altered framboidal pyrite (now hematite and goethite) that partially fills some cell lumina and together with chalcedony and quartz fills the internal cavities of the herbaceous stems (Fig. 5c). The second stage is represented by massive and low crystallinity iron oxides and hydroxides (hematite, goethite), which in some samples impregnate wide areas of the plant tissues and fill some cracks. These iron compounds, together with galena and/or sphalerite and occasionally celestite, cover some plant remains forming coatings

up to 1–2 cm thick. Abundant crystalline gypsum can also appear in these coatings, in which case the gypsum almost totally replaced the plant fragment. Only the outer morphology of the plant remains is preserved, whereas only small parts of the organic structures are preserved in remains where the opal-CT has not been completely lost.

#### 4.6 Mineral relationships

In all the remains studied we observed more than one silica phase, although one phase tends to clearly predominate. Assemblages and interrelations among the phases and other minerals are:

- a) Remains mainly made up of opal-CT occupying the cell walls and partially or totally filling the cell lumina and other voids in the plant structure. Some cell lumina (< 5%) filled with quartz and others filled with framboidal pyrite and/or iron oxides, many empty cell lumina (Fig. 3a, 4a).
- b) Majority of opal-CT in cell walls, partially or totally filling the lumina and other tissular voids, associated with quartz (> 5%) found on cell walls together with opal-CT and iron oxides and partially or totally filling cell lumina where it can be found alone, with opal-CT, or with iron compounds (Fig. 3b).
- c) Remains in which the opal-CT is still majority, but where the quartz (10–15%) in section shows a distribution in “patches” 200–300 µm in size, with irregular, unclear edges and containing groups of 10–20 cells. The quartz “patches” tend to be more abundant towards the periphery of the plant fragments, where the quartz occupies the walls and cell lumina.
- d) Remains in which quartz is majority and occupies most of the plant structure (Fig. 5b) whose features are rather well preserved. A certain amount of opal-CT (15–30%) is still present, iron oxides and other metallic minerals tend to be abundant, particularly on the periphery of the fragments and filling cracks.
- e) Specimens mainly made up of mosaic megaquartz together with microquartz and chalcedony, the plant structure has been partially or totally obliterated.
- f) Remains similar to those described above (a, b and c) in which only small portions of the tissular structure are preserved by opal-CT, quartz or iron oxides, and also by the framboidal pyrites occupying the cell lumina; most of the fragments is occupied by gypsum and only the external morphology of the plant is conserved.

The mineral assemblages described above are those that petrified the plant remains. Length-fast chalcedony, quartz, and occasionally lussatite and length-slow chalcedony are also found totally or partially filling cavities and cracks. These fillings have clear boundaries and do not encroach on the permineralized plant zones. On the other hand, framboidal pyrite is very abundant in the cavity fillings (Fig. 5c), and iron oxides and hydroxides, other metallic minerals and gypsum are mainly found filling cracks and fractures and/or covering the plant remains.

## 6. Silicification processes

The silicification of plants includes the same transformational sequence as oceanic biosiliceous sediments, i.e., opal-A – opal-CT – quartz (Buurman 1972; Stein 1982), in a process

of dissolution and reprecipitation. This process in plants is not replacement but permineralization (Buurman 1972; Leo & Barghoorn 1976; Sigleo 1978; Scurfield & Segnit 1984), i.e., the penetration of silica through the pores and voids of the plant structure, which are subsequently impregnated and filled.

The plant remains in the "Coscojar Section" originated in nearby emerged areas. During the Messinian, in the Vera Basin, extensive areas emerged where erosive and/or continental sedimentation processes took place (Barragán & Martín-Penela 1994). The plant remains of the "Coscojar Section", which are terrestrial in origin, must have been transported to the sea by fluvial streams originated in these nearby emerged areas, as were most of the lutitic sediments of this series (Sánchez-Bellón 1992). The source area could not have been very distant, as these accumulations of terrestrial plant remains on the sea floor were mainly deposited in areas relatively close to the coast (Hedges & Parker 1976). At present, on the northwestern margin of the Mediterranean, continental plant remains are concentrated near the mouths of some rivers and never more than 5 kms from the coastline (Hernández-Molina 1993). Once the plant remains were immersed in water, they would have swollen and sunk to the bottom, where their partial decay would have continued.

Decomposition of at least part of the organic components of the plants is necessary for silicification to take place (Leo & Barghoorn 1976; Carson 1991). Partial decay, together with the swelling caused by water, increases the diameter of voids and micropores and, consequently, the permeability of the plant, which depends on the type of plant and its internal structure (Scurfield & Segnit 1984). The components of the cellular walls of the plants (cellulose and lignin) have different degrees of resistance to decay. The cellulose breaks down first, whereas lignin can be preserved for long periods, particularly in anoxic environments (Hedges & Parker 1976; Leo & Barghoorn 1970; Sigleo 1978). Even though lignin is still much more resistant to decay than cellulose, which breaks down much faster in aerobic conditions (Leo & Barghoorn 1970; Gardner & Menzel 1974). Rapid decay of plants thus does not occur in anoxic conditions leaving time for silicification to occur.

Many of the samples collected from the "Coscojar Section" present very low or no deformation by burial. This is especially the case of the hollow herbaceous plants, which often have preserved a practically intact original morphology. We can therefore deduce that at least the initial stage of silicification must have taken place rapidly after deposition under a low sediment load, since relatively low burial pressure would have been enough to completely crush this type of stem. Although the sedimentary conditions are very different, Karowe & Jefferson (1987) described the short time (a few thousand years) necessary for silicification of plants remains to take place at Mount St. Helens. In general, preservation of soft-tissue structures by silica takes place in a short period and before significant burial (Carson 1991).

Concerning the silica source, most documented silicified plant remains were found in continental sediments. Although in the literature different silica sources have been considered in different cases, the most common were the alteration of volcanic ash and glass and the transformation of some silicates by weathering and/or diagenesis (Murata 1940; Schopf 1971; Buurman et al. 1973; Stein 1982; Elorza & Arriortua 1985; Karowe & Jefferson 1987; Jefferson 1987). The "Coscojar Section" plant remains however were found in marine sediments containing the partially dissolved remains of siliceous sponge spicules

and diatom frustules. These organic remains are the likely silica source for silicification of the plant remains. Almost all the silica accumulated in Phanerozoic marine sediments were derived from organisms with a siliceous test or skeleton, such as radiolaria, diatoms, siliceous sponges and silicoflagellates (Siever 1957; Calvert 1968; DeMaster 1981). Diatoms were mainly responsible for biosiliceous sedimentation from the beginning of the Cenozoic on (Hein & Obradovic 1988). Ocean water becomes enriched in silica by dissolution of the skeletal remains of these organisms and, in general, the concentration of dissolved silica increases with depth in the water column. The dissolved silica concentration is much higher in the pore water of the first few centimetres of sediment (DeMaster 1981; Hein & Obradovic 1988; Hesse 1988).

According to experimental work by Leo & Barghoorn (1976), the perimineralization of plants by silica takes place by monomeric silicic acid in solution, forming hydrogen bonds with the hydroxyl groups in the molecular components of the partially decayed vascular tissues of the plants (cellulose and lignin). Silicification continues with polymerization of the silicic acid monomers, forming siloxane bonds and subsequent water loss (Leo & Barghoorn 1976). A thin film of silica forms on the cell walls taking the form of the tissue structure. The progressive polymerization and dehydration of this opaline silica involves transformation to the more stable phases opal-CT and quartz. The final stage in the process is the filling of the cell lumina by silica (Leo & Barghoorn 1976; Jefferson 1987). According to Scurfield & Segnit (1984), the silica penetrating the cell walls can be either silica in solution and/or a fine colloid, and the filling of the cell lumina and intercellular voids can be simultaneous with the permineralization of the cell walls. In the "Coscojar Section" plants, the silica derived from the dissolution of biogenic opal-A would have penetrated the cell walls according to the process described above, impregnating the walls and partially filling the lumina and intercellular voids with opal-CT. The poor cementing of the intercellular voids by the silica observed in several tree specimens makes them friable and easily broken down. These features suggest that the first stage and most significant feature of the silicification of these plants was the permineralization of the cell walls.

The cell lumina and intercellular voids in the plant remains studied here can be: partially or totally filled by opal-CT (Fig. 3a, b, 4a, b), empty, partially or totally filled by quartz (Fig. 3a, b, 5a, b, 4d) or partially occupied by framboidal aggregates of pyrite/hematite (10–100 µm in diameter), or massive iron oxides and hydroxides (Fig. 3b). Lumina filled with more than one mineral phase (opal-CT and quartz; opal-CT, quartz and iron compounds; quartz and iron compounds) are also abundant. These differences in the degree and type of filling in the cell lumina and intercellular voids indicate several stages of filling and different stages of diagenesis.

The spaces between the knots of the herbaceous stems are occasionally filled with marly sediment, but more often filled with length-fast chalcedony and quartz (Fig. 5d), together with a much lower proportion of length-slow chalcedony and occasionally lussatite (Fig. 5c). The chalcedony spherulites and quartz filling the inner cavity of these stems, small cracks and some cell lumina are surrounded by the opal-CT that had previously permineralized the plant structure. Likewise, in the trunk fragments in which quartz is more abundant, there are also spaces filled with chalcedony and mosaic quartz. The chalcedony and quartz do not seem to have had an opal-CT precursor and must have formed from unsaturated solutions with respect to opal-A and opal-CT that allowed primary precipita-

tion of quartz (Mackenzie & Gees 1971; Kastner et al. 1977; Williams & Crerar 1985; Williams et al. 1985). Precipitation of quartz and/or chalcedony without an opal-CT precursor has been described by several authors (Lancelot 1973; Oehler 1976; Kastner et al. 1977; Hein et al. 1978). In the plants studied here this precipitation took place under conditions that did not promote the opal-CT – quartz transformation, since the opal-CT surrounding the chalcedony and quartz shows no signs of transformation. Quartz and chalcedony precipitation might have occurred during a fall in the silica concentration in the environment, which permitted growth of chalcedony and quartz in the inner cavities of the stems, in some cell lumina, and other voids not previously occupied by opal-CT, framboidal pyrite, or sediment. After development of the chalcedony and quartz spherulites, the introduction of solutions with a higher silica concentration might have led to lusatite growth, which filled the remaining voids between the chalcedony spherulites (Fig. 5c).

In the remains studied, the pyrite must have begun to form during early diagenesis when the opal-CT was precipitated in marine sediments. Formation would have continued contemporaneously with precipitation of the chalcedony and quartz that fill the longer cavities, as this is where the framboidal pyrite is most abundant. In non-euxinic marine environments, pyrite formation occurs in anoxic pore water conditions, a few centimetres below the water-sediment interface, where decaying organic matter is present (Berner 1970; 1984). Framboidal pyrite frequently fills organic cavities in marine sediments (Lougheed & Mancuso 1973; Hudson 1982; Allison 1988). Its genesis is related to the anaerobic decay of organic matter by sulphate-reducing bacteria in the presence of detrital iron minerals (Berner 1970; 1984).

## 7. Later diagenesis and hydrothermalism

The increase of temperature and length of time seem to have been the main factors controlling the opal-A – opal-CT – quartz transformations in biosiliceous marine sediments. Other factors such as the chemical characteristics of interstitial water, the composition of the host rock and the surface area of the particles can have an important influence on the development of the diagenetic sequence (Kastner et al. 1977; Hein et al. 1978; Isaacs 1982; Williams & Crerar 1985; Williams et al. 1985). In the plant remains studied here, time and temperature increases caused by burial do not seem to have greatly affected the silica diagenesis. The  $d(101)$  spacing of the opal-CT in the samples studied varies from 4.12 to 4.09 Å. According to Murata & Nakata (1974), Murata et al. (1977), Isaacs (1982) and Keller & Isaacs (1989) this spacing corresponds to low grade diagenesis in biosiliceous sediments, with little burial and low temperature. The opal-CT – quartz transformation does not, therefore, seem likely in these circumstances. However, in the remains studied, this transformation is clearly observed. It can be observed in samples in which the opal-CT constitutes over 90% of the permineralized volume, as well as in samples in which the opal-CT is still majority, but is associated with abundant polyblastic, oligoblastic or hyperblastic quartz, which occupy the cell lumina and grow through the cell walls, and finally samples in which the opal-CT – quartz transformation is complete. This is indicative of a rapid, atypical diagenetic change, if we consider that the opal-CT – quartz transformation in the plant remains is affected by the same factors as in the case of biosiliceous sediments.

The partial or total opal-CT – quartz transformation was clearly selective, occurring mainly in samples with abundant iron oxides and hydroxides that had clearly penetrated the plant structures, filling intercellular voids, cracks and some cell lumina. It therefore seems that these oxides encouraged the opal-CT – quartz transformation. The action of some metallic cations ( $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$ ,  $\text{Mg}^{2+}$  and  $\text{Mn}^{2+}$ ) as accelerators of diagenetic processes causing quartz formation was described by Harder (1965) and Harder & Flehmig (1970). Moreover, Kastner et al. (1977) indicated that the hydroxides of these same elements also increase the degree of the opal-A – opal-CT reaction. In the “Coscojar Section», the iron oxides that partially impregnate the plant remains and the accompanying mineralizations of sphalerite and/or galena and celestite in the surface coatings of some specimens would likely have derived from submarine hydrothermal fluids such as were present in nearby areas (Fig. 1). Several Tortonian-Messinian submarine hydrothermal mineralizations have been recognised in these areas, that contain Fe and Mn oxides, metallic sulphides, barite, gypsum, native silver, jasperoids, etc. (Alvado 1986; Ott d’Estevou et al. 1990; López-Gutiérrez et al. 1992; Martínez-Frías et al. 1992; Barragán 1994). In the “Coscojar Section” hydrothermal mineralization only occurs in association with specific silicified plant fragments, which must have acted as preferential sites for the precipitation of certain minerals from the hydrothermal fluids. Similarly, the gypsum which, together with the metallic minerals mentioned above, covers and fills some of the plant remains, and, in other cases, fills small fractures in the marls of the lower part of the “Coscojar Section” might also have been associated with these hydrothermal flows, although a possible diagenetic origin can not be discounted. Concerning the hydrothermal fluids, an increase in the alkalinity of the pore waters might also have been associated with the hydrothermal fluid along with a greater activity of sulphide, as indicated by the formation of sulphide minerals (Martínez-Frías, personal communication). The increase in alkalinity might have encouraged dissolution of opal-CT in some silicified remains, where the voids created by the dissolution would have been occupied by gypsum crystals, as observed in some samples.

## 8. Conclusions

Analysis of the silicified plant remains from the “Coscojar Section” suggests that an initial precipitation of silica, derived from biosiliceous organisms, took place in a marine environment as a result of the tendency of silicic acid to form hydrogen bonds with the organic molecules of the plants. At least this first precipitation of silica occurred rapidly, during early burial of the plant fragments.

After deposition, the plant remains underwent several transformations in successive stages, which can be summarized as follows:

### A – Early diagenesis:

- Penetration of the plant fragments by silica solution and impregnation and filling of pores in the cell walls by opal-CT.
- Partial or total filling by opal-CT of some cell lumina and intercellular voids.
- Growth of chalcedony and quartz in large (centimetre sized) cavities and small cracks, and probably in some cell lumina, without opal-CT as precursor. Simultaneous

development of framboidal aggregates of pyrite/hematite in some cell lumina and larger cavities.

#### B – Later diagenesis:

- The initial opaline phases underwent an early opal-CT – quartz transformation, apparently due to the chemical characteristics of the interstitial water, rather than pressure by burial or temperature. This transformation led to growth of mainly polyblastic quartz in some cell lumina and intercellular voids, as well as in small cracks or even complete opal-CT – quartz transformation, with obliteration of the plant structures.

#### C – Hydrothermal stage

Other processes occurred later in relation with submarine hydrothermal flows during the Late Messinian:

- Precipitation of massive Fe oxides, which filled empty cell lumina, intercellular voids and cracks. Some plant fragments show development of surface coatings of sulphides and iron oxides and hydroxides, at times together with gypsum.
- Finally, in only a few samples, part of the opal-CT conserving the plant structures was dissolved, and the subsequent voids were occupied by gypsum.

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