

# Chert in Continental Evaporites of the Ebro and Calatayud Basins (Spain): Distribution and Significance

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## RESUMEN

*En las cuencas terciarias del Ebro y de Calatayud (NE de la Península Ibérica) existe un buen número de formaciones evaporíticas sedimentadas tanto en los centros de cuenca como a lo largo de los bordes meridionales de las mismas. Las formaciones centrales muestran facies y paragénesis minerales de alta salinidad, mientras que las marginales presentan sólo paragénesis de sulfato cálcico y características propias de baja salinidad. De un modo sistemático se observa que las formaciones marginales incluyen abundante sílex (cuarzo microcristalino), ya sea en forma de nódulos, cuerpos lenticulares, bioturbación silicificada o masas irregulares con morfología de costras. Los procesos de silicificación ocurrieron en diagénesis temprana principalmente como reemplazamiento del yeso, tanto a partir de las salmueras intersticiales ricas en sílice generadas en los lagos salinos, como de las aguas subterráneas drenando hacia ellos desde las zonas periféricas. El reemplazamiento silíceo ocurrió con anterioridad a cualquier transformación del sedimento yesífero en anhidrita, independientemente de que la anhidritización tuviera lugar ya en diagénesis temprana o en fase tardía.*

**PALABRAS CLAVE:** SILEX, EVAPORITAS CONTINENTALES, TERCIARIO.

## ABSTRACT

In the Ebro and Calatayud Tertiary basins (NE Iberian Peninsula) a number of non-marine evaporite formations exist in central basin positions as well as along the southern margins. The central formations have high-salinity facies and complex mineral paragenesis, while the marginal formations display only Ca-sulfate paragenesis and have relatively low-salinity features. Abundant occurrences of chert (microcrystalline quartz), such as silicified burrowing, nodules, lenses and irregular crust-like masses, are systematically related to the marginal units. Silicification processes happened in early diagenesis mainly through gypsum replacement from silica-rich interstitial brines generated in the saline lake, and from groundwaters flowing towards it. Silica replacement took place prior to any transformation of the primary gypsum sediment into anhydrite, whether this transformation happened during early or late diagenesis.

**KEYWORDS:** CHERT, CONTINENTAL EVAPORITES, TERTIARY.

## INTRODUCTION

The presence of silica in evaporitic formations is a common feature, although it generally occurs to an irrelevant extent from the point of view of sedimentology.

Idiomorphic quartz crystals in particular have been frequently mentioned with or without varieties of fibrous silica (length-slow chalcedony) replacing carbonates and Ca-sulfates or growing within clayey host rocks. Also significant is the occurrence of chert nodules and siliceous facies in evaporite formations. Nevertheless, a clear distinction is apparent between marine and continental environments.

In the sulfate facies of ancient marine evaporites the existence of chert nodules is scarce and mainly limited to the marine to non-marine transitional facies and episodes. In these transitions chert nodules are frequently pseudomorphs of precursor anhydrite nodules. Also, in ancient marine evaporites chert appears as replacement products of stromatolitic carbonates, as well as laminated facies (diatomite-rich facies) developed in pre-evaporitic stages.

In non-marine evaporites on the other hand, the existence of chert is more frequent, either as nodules or layers. Distribution is related in general to Ca-sulfate facies.

In the Iberian Peninsula, a great number of evaporite formations, both marine and non-marine, were deposited during the Alpine Cycle. These formations follow the aforementioned characteristics concerning chert. In the present contribution we will deal with some non-marine silica-rich evaporite formations that were deposited during the Tertiary in some lacustrine environments in the Ebro and Calatayud basins. In this contribution, the regional/paleogeographic distribution of chert in these basins will be emphasized as well as the timing of the diagenetic processes according to field observations. A brief discussion on chert origin and significance will be presented.

#### CONTINENTAL TERTIARY EVAPORITES AND CHERT OCCURRENCES IN NE SPAIN

The geographical situation in the NE quarter of the Iberian Peninsula of those major Tertiary basins with significant evaporite sedimentation is shown in fig. 1. The Ebro, Calatayud

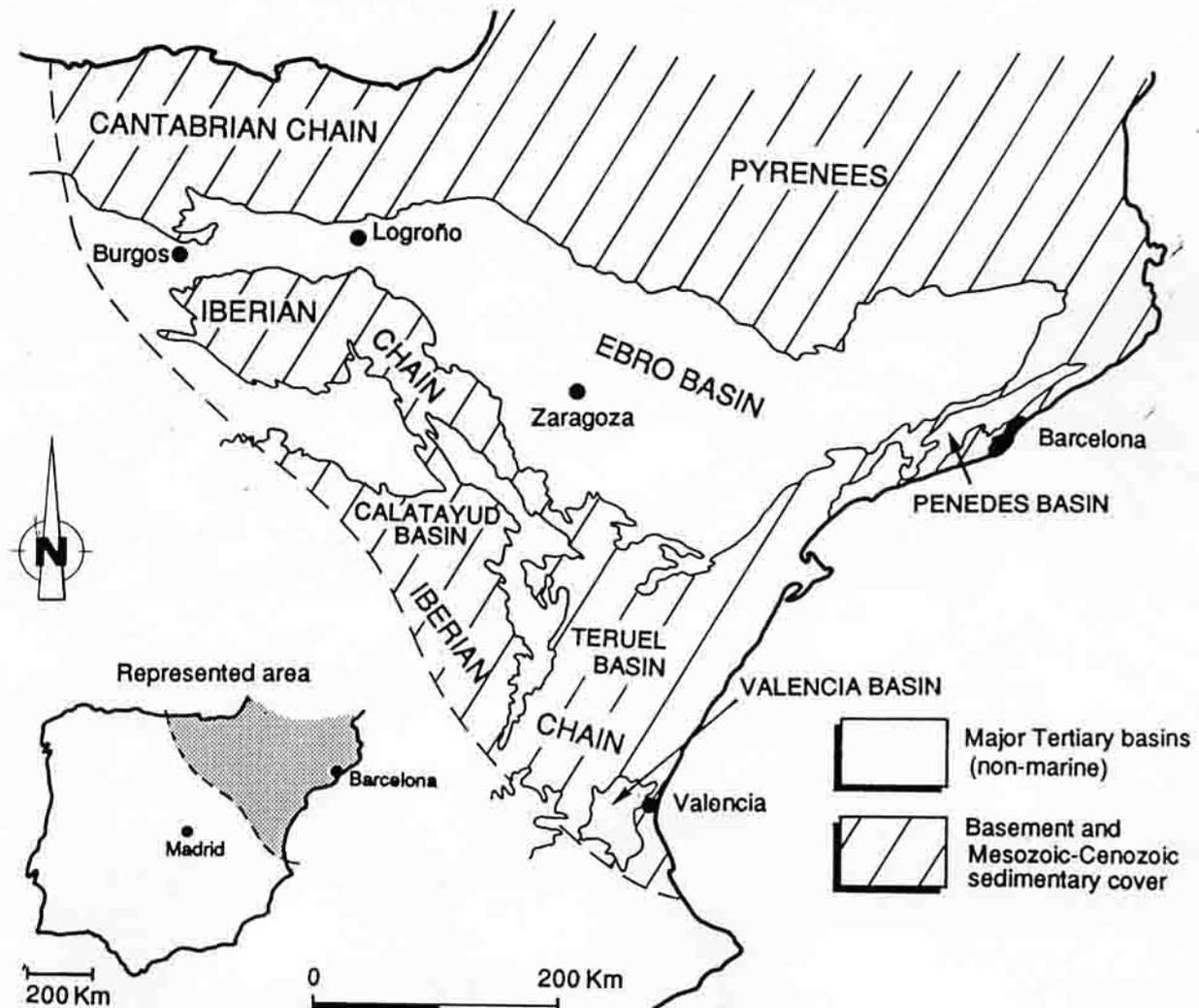


Figure 1.—Location map of major Tertiary basins bearing continental evaporites (Ebro, Calatayud and Teruel) in the northeastern part of the Iberian Peninsula.

and Teruel basins are the most important, though minor evaporite sedimentation is recorded in many others (Penedès, Valencia, Cabriel River, etc.). Both marine (of Eocene age) and non-marine (from Paleogene to Miocene) evaporites were deposited in the Ebro basin, while in the Calatayud and Teruel basins evaporite sedimentation remained non-marine and Miocene-aged.

Non-marine evaporite formations deposited in all these Tertiary basins can be classified according to: a) paleogeography, as occupying central or marginal positions in the basin, and b) salinity, as having low concentration (only carbonate and Ca-sulfates) or high concentration (paragenetic Na-sulfates and /or halite) facies. In the formations where high concentration paragenesis has not been found, the different calcium-sulfate lithofacies may also reflect differences in concentration.

All formations of the Ebro basin recording mineral paragenesis of high concentration were deposited in central basin positions. Moreover, Ca-sulfate facies in them have suffered intense diagenesis and their primary gypsum deposits have been almost completely lost. These formations may reach thicknesses up to several hundreds of meters.

In contrast, in the same basin all evaporite formations which have a mineral paragenesis of low concentration (only gypsum/anhydrite), occupy peripheral positions along the margins (in particular the southern margin). These formations reach thicknesses of less than one hundred meters and frequently have their primary gypsum facies preserved.

In the Calatayud basin a single Ca-sulfate evaporite formation occurs, that in its central part displays lithofacies similar to the central formations of the Ebro basin. Towards its margins, this single unit has Ca-sulfate facies equivalent to those of the peripheral formations (with low concentration paragenesis) of the Ebro basin.

In the Teruel basin exist several evaporite units of Miocene age that occupy central positions and display low-concentration facies formed by primary gypsum. These units in general were never affected by intense diagenesis.

For these continental evaporite basins, chert is most abundant in the Ebro and Calatayud basins. Moreover, in both basins chert is practically absent in the high-concentration formations but is extensively developed in the low-salinity formations.

## **EBRO BASIN**

### **Continental evaporitic sedimentation**

The distribution of major non-marine evaporite formations located in the autochthonous zone of the Ebro basin is shown in fig. 2. In the basin those evaporitic formations of high salinity that occupied central basinal positions during sedimentation have been numbered 1 to 4. They all display typical Ca-sulfate lithofacies composed of alternating laminated and nodular-banded facies formed in shallow lakes and during sabkha episodes respectively. These are made today of secondary gypsum in outcrop. In all these formations chert is practically absent and only the Zaragoza Gypsum Fm. (n. 3) presents a few occurrences of chert in its westernmost peripheral zone.

In contrast, all significant evaporite formations of low salinity are confined to the peripheral positions in the basin, thus forming a well-defined though discontinuous southern marginal belt along the contact with the Paleozoic-Mesozoic mountain ridges that border the basin. In this belt two major sectors may be distinguished:

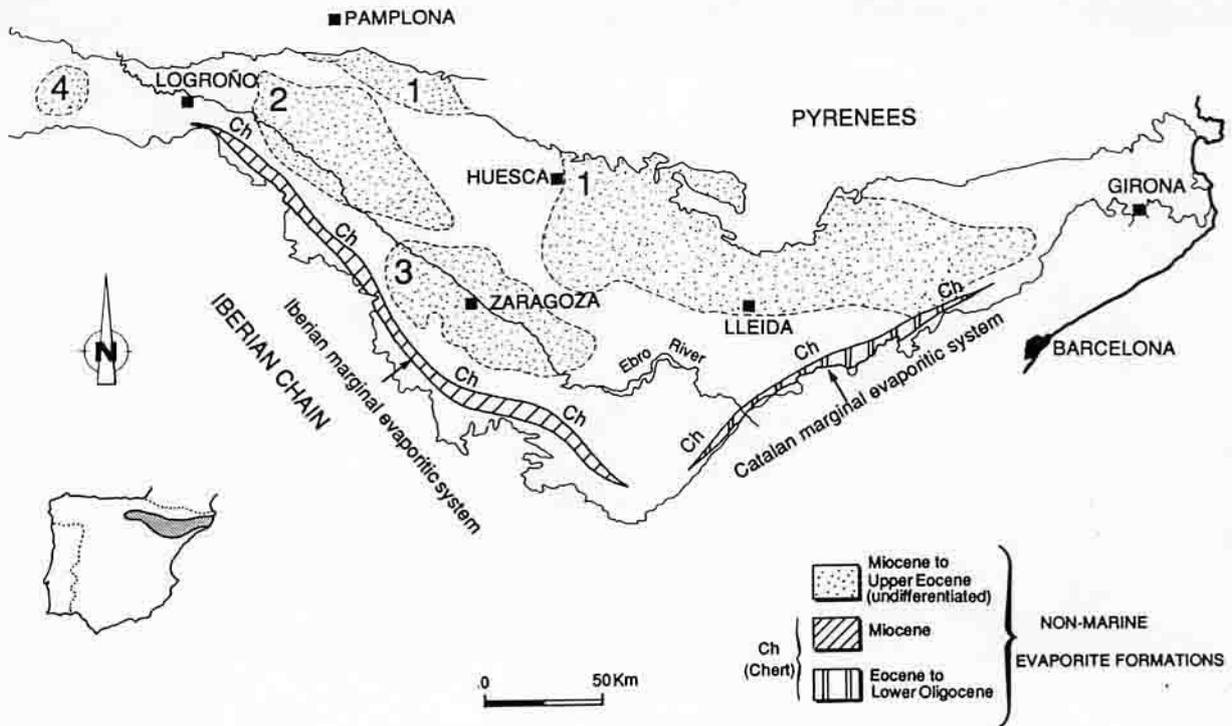


Figure 2.—Distribution map of non-marine evaporitic formations sedimented during the Tertiary in the autochthonous zone of the Ebro basin (in this figure all allochthonous terrains forming the northern part of the basin along the Pre-Pyrenean zone have been omitted). Numbers correspond to large formations of central position and high salinity: 1: Barbastro Gypsum Formation and Puente la Reina Gypsum Formation (Priabonian to basal Oligocene) (approximately the same distribution corresponds to the marine formations bearing potassic salts of Priabonian age). 2: Falces Gypsum Formation and Lerín Gypsum Formation (Oligocene to basal Miocene). 3: Zaragoza Gypsum Formation (Lower Miocene). 4: Cerezo Gypsum unit (Upper? Miocene) (simplified from Ortí *et alii* 1989b, fig. 2).

a) Catalan evaporitic lacustrine system, in the East (aged Eocene to Lower Oligocene), and

b) Iberian evaporitic lacustrine system, in the West (aged Lower-Middle Miocene).

A general overview of the evaporitic sedimentation in both systems and in the various large central formations has been described in previous works (Ortí *et alii* 1989a, Ortí *et alii* 1989b, Salvany 1989a, 1989c, Ortí and Salvany 1990).

### Chert distribution in the marginal systems

All the Paleogene evaporite units forming the Catalan marginal system (whose geographical and stratigraphical position is summarized in fig. 3) show Ca-sulfate facies that were deposited in shallow lakes and saline mudflats as microlenticular gypsum and as interstitial nodular anhydrite in peripheral saline mud flats. The existence of paleokarsts affecting these deposits is common. Associated carbonates in these Ca-sulfate deposits show abundant remains of Carophytes and more rarely Gastropods and Ostracods.

Some of these lakes evolved into sabkha environments during severe dry periods and

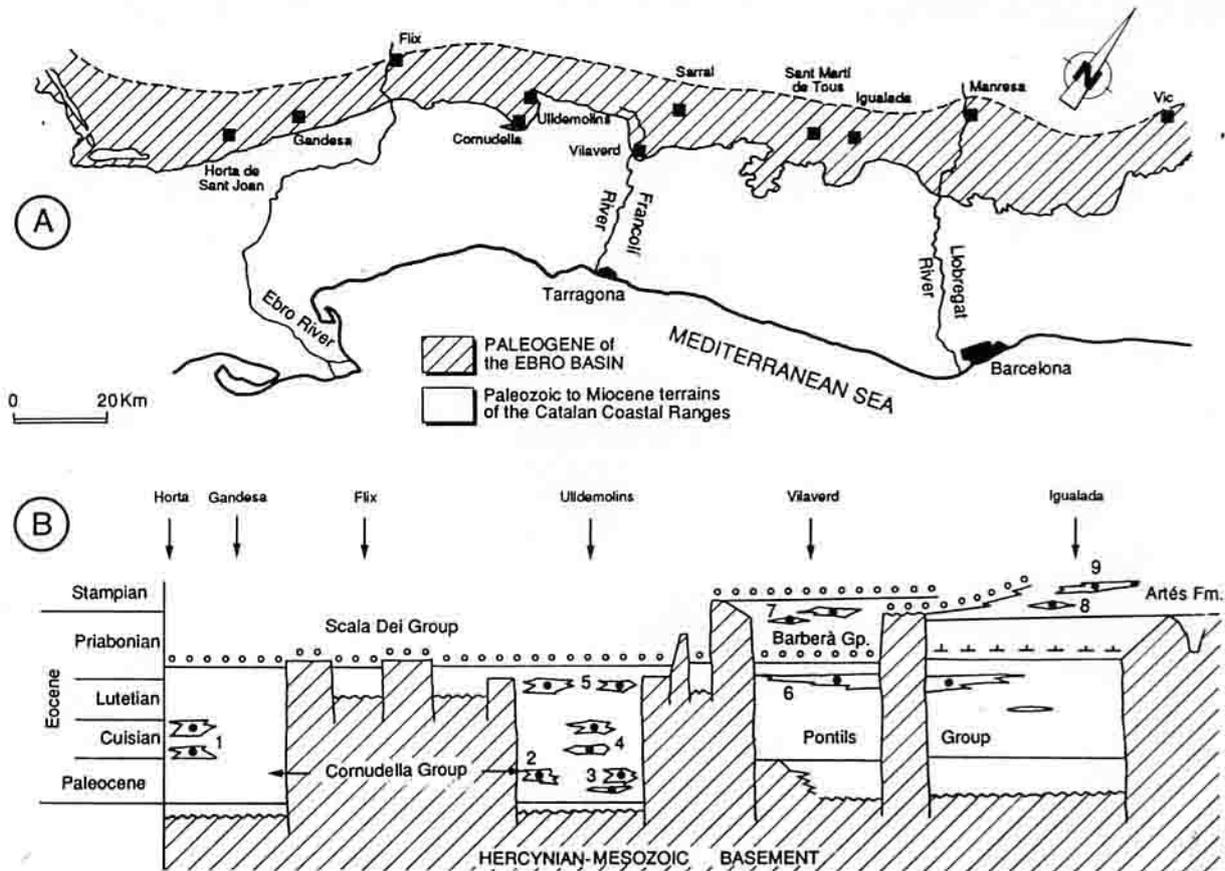


Figure 3.—A) Geographic position of the contact zone between the Paleogene sediments (striped) of the Ebro Basin and the Paleozoic-Mesozoic materials of the Catalan Range (in white); B) Distribution of the non-marine evaporitic units and associated chert in the Catalanide marginal evaporitic system. Note the discontinuous character of these units and the presence of chert within them. 1: Horta de Sant Joan Gypsum unit. 2: Santa Maria del Montsant Gypsum unit. 3: Cornudella Gypsum unit. 4: Ulldemolins Gypsum unit. 5: Vilaverd Gypsum unit. 6: Valldeperes Gypsum unit. 7: Pira and Sarral Gypsum units. 8: San Martí de Tous Gypsum unit. 9: Copons Gypsum unit. Scheme not to scale. Black points indicate occurrences of nodular chert in these gypsum units (simplified from Orti 1990a, fig. 1).

suffered anhydritization at different degrees in early diagenesis. Anhydritization was completed at depth by subsequent burial and these deposits are now found as secondary gypsum on the surface.

Almost all Ca-sulfate units that compose this system show significant silicification features as shown in fig. 3. An exception is unit 9 (Copons Gypsum) which corresponds to the margin of a large central evaporitic formation (Barbastro Gypsum Fm.; fig. 2, n. 1) belonging to the high-salinity group.

Sedimentary and diagenetic evaporite environments in the Iberian marginal system were the same as in the Catalan system. However, due to their younger age and limited burial, many units have been partly preserved as primary gypsum and only those parts which were transformed at the synsedimentary stage into anhydrite exist today as secondary gypsum in outcrop.

The stratigraphic and geographic position of the various Miocene evaporite units of the Iberian marginal system is shown in figs. 4 (western half of the system) and 5 (eastern half of

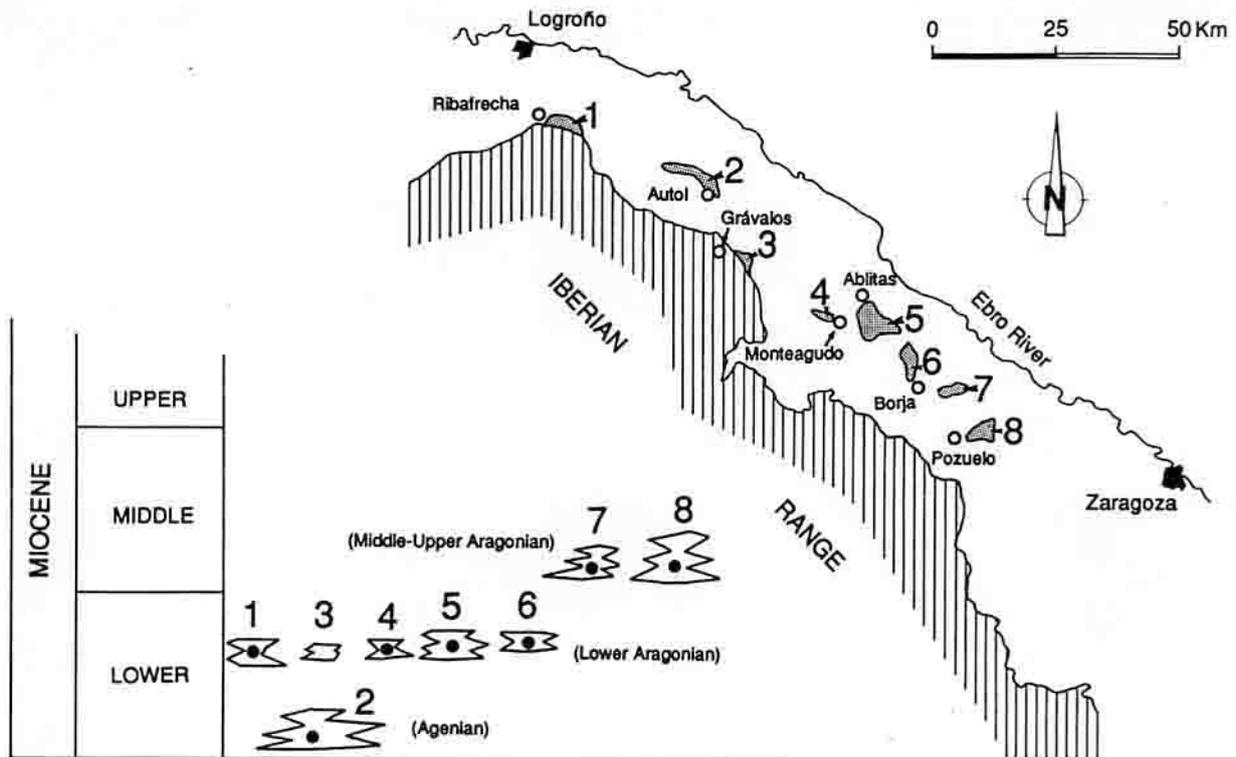


Figure 4.—A) Location map of the main Lower Miocene evaporitic units of the northwestern part of the Iberian marginal lacustrine system (the Tertiary Ebro basin). B) Stratigraphic scheme of these units and associated chert. Scheme not to scale. Black points indicate occurrences of nodular chert in these gypsum units.

the system). In the western part, many gypsum units occur, most of them bearing chert. Muñoz (1991) and more recently Salvany *et alii* (in prep.) have discussed in detail the sedimentological, structural and paleohydrological setting of these units. In the eastern part, the number of evaporite units is lower, but all contain chert (farther to the south-east of the area considered in fig. 5, the Calanda Gypsum unit marks the eastern end of the Iberian marginal system).

Another diagenetic feature displayed by many evaporitic units along both the Iberian and Catalan marginal systems is the presence of large anhydrite nodules displacing or replacing primary gypsum facies. Frequent interaction between these “meganodules” (diameter between 0.5 m and several meters) and chert nodules make them of interest from the point of view of silicification (see below).

All these evaporitic units pass laterally into red lutites and siliciclastic deposits towards the basin margin. Towards the center, however, they may grade into clayey units (mud flats), lacustrine carbonates or the above mentioned high-salinity evaporitic formations. As an example of the latter case, fig. 5B shows a gradual transition between the Pozuelo Gypsum unit and the Zaragoza Gypsum Formation.

### Chert petrography

The close relationship observed between chert and the previously mentioned Ca-sulfate units has prompted these authors to distinguish the existence of a “chert belt” coincidental

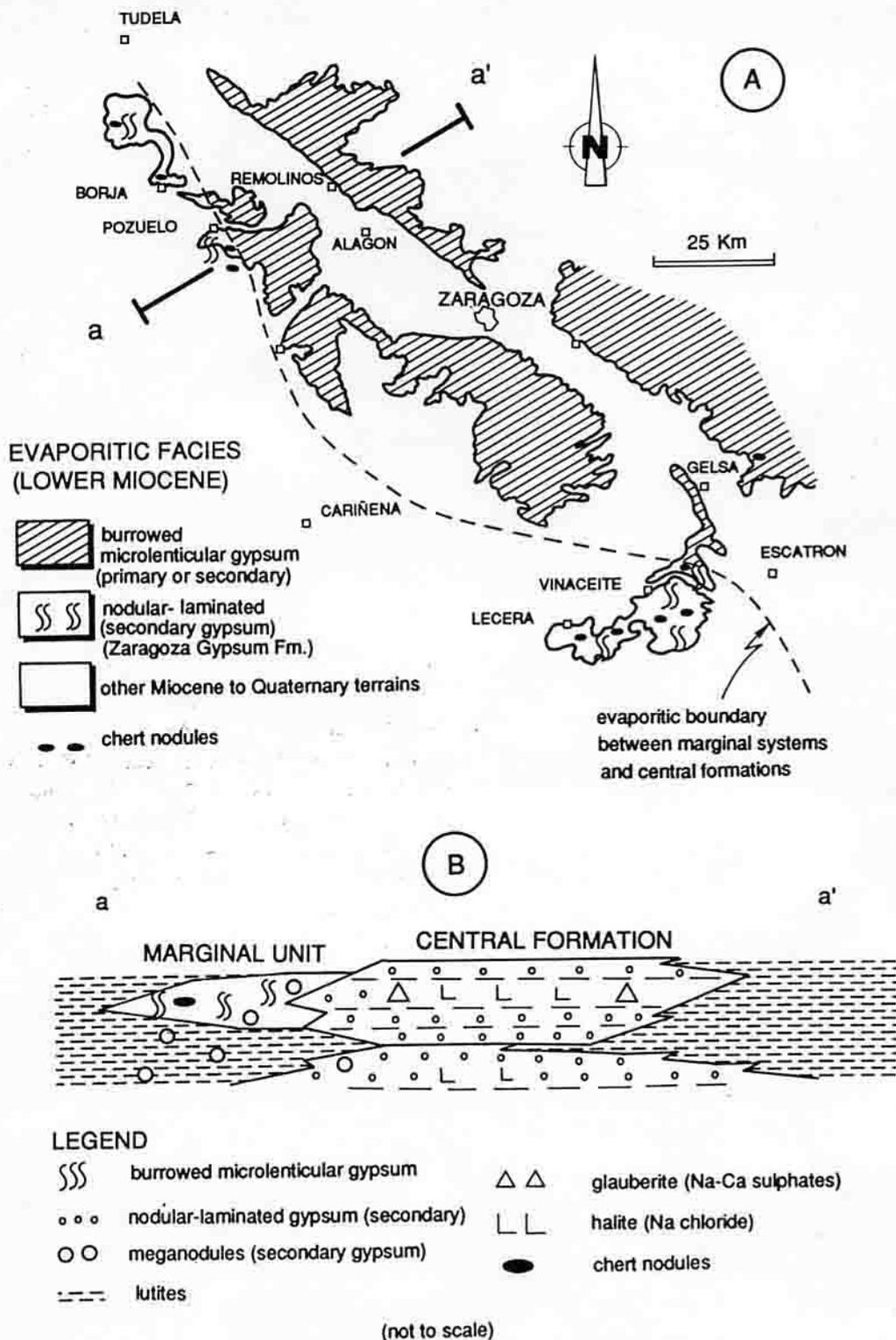


Figure 5.—A) Location map of the main Lower Miocene evaporite units of the southeastern part of the Iberian marginal lacustrine system; B) Scheme (not to scale) of the deduced facies relationships between the Lower Miocene evaporite marginal units and central formations (example of a section along Pozuelo de Aragón and Remolinos villages) (simplified from Ortí 1990b, figs. 1 and 2).

with the marginal lacustrine systems of the Tertiary Ebro basin (Ortí *et alii* 1989a, Ortí *et alii* 1989b).

In this belt authigenic silica is mainly developed as: 1) bioturbation structures either as isolated burrows or as densely-packed burrowed masses giving way to irregular or nodular-like lithofacies; 2) nodules (1 to more than 100 cm in length) either isolated in the host gypsum rock or grouped defining a weak layering; 3) lenticular bodies more or less adapted to layering (tens of centimeters to a few meters in length); and, 4) irregular horizons resembling crusts.

Nodules is by far the most abundant lithofacies. In general, all chert occurrences display dark-brown tonalities, being locally gray or almost black.

About 30 representative samples taken along this chert belt belonging to both Iberian and Catalan systems were studied in thin section and by XR diffraction. Quartz is the only important silica phase, opal C-T being locally present. However, it seems likely that another SiO<sub>2</sub> phase, moganite (fibrous microstructure and positive elongation character; Flörke *et alii* 1984) occurs in most samples.

Petrographically this chert is composed mainly of a microcrystalline quartz (10 to 50 µm) mosaic fabric, but other components exist, some of them being typical of evaporite replacement (Bustillo 1976, Arbey 1980):

- a) fibrous textures of length-slow chalcedonic aggregates (mainly lutecite and in minor proportion quartzine; also moganite?) and spherulites;
- b) some chalcedonic films and opaline (isotropic) areas;
- c) rosettes of wedge-shaped megaquartz crystals;
- d) blocky mosaic fabric of cementing quartz (several hundreds of µm) as cavity-filling and exceptionally in geodic cavities.

Only rarely do positive and negative chalcedonic generations alternate in some spherulites. Lutecite pseudomorphs after microlenticular gypsum crystals is usual and displays several types of fabric arrangements. Mixed fabrics built up by microcrystalline quartz and irregular lutecite aggregates are very frequent. Although opal was not found as a major component (massive opal occurs only rarely), it could have been an original silica phase because: 1) some peloidal-like textures constituted by very fine microcrystalline quartz (opal ageing to quartz?) are noticeable, and 2) an almost cryptocrystalline quartz matrix surrounds the lutecite pseudomorphs in some thin sections. The importance of opal as a precursor phase of the microquartz textures is difficult to determine petrographically.

Any particular relationship between these crystalline fabrics and the various chert lithofacies mentioned above has not been found. The existence of lenticular gypsum pseudomorphs in chert is very common and they can even be distinguished by the naked eye in many samples (several millimeters in size). Additional petrographic and mineralogic observations of chert belonging to the Iberian marginal system (mainly in the Ablitas-Monteagudo area, fig. 4) have been undertaken in articles by Mandado (1987), Mandado and Tena (1989) and Salvany (1989a, b). For the Catalan marginal system, mainly in the Cornudella-Ulldemolins area (fig. 3), the work by Estop (1974) is cited.

#### CALATAYUD BASIN

In the Calatayud basin (fig. 1) evaporite deposits are mainly limited to the Calatayud Gypsum unit, which is a Lower Miocene-aged formation occupying the central part of the basin. This formation displays all sedimentary and diagenetic Ca-sulfate facies typical of the

high-salinity central evaporite formations of the Ebro basin, although the presence of Na-sulfates or Na-chloride in the formation has not been reported until now. It is formed by secondary gypsum in outcrop.

Towards the South this large formation changes laterally to a unit which has features typical of low-salinity conditions: microlenticular primary gypsum affected by burrowing, local development of anhydrite meganodules, and chert (Rosell and Ortí 1992).

The transition from the central laminated-nodular gypsum facies (the Calatayud Gypsum unit in the Maluenda-Morata area) to the marginal facies (the Fuentes Gypsum unit between the towns of Fuentes and Villafeliche) is shown in fig. 6.

Chert has both lithofacies and petrographic characteristics similar to those in the chert belt of the southern margin of the Ebro basin: burrowing, isolated nodules, nodular horizons,

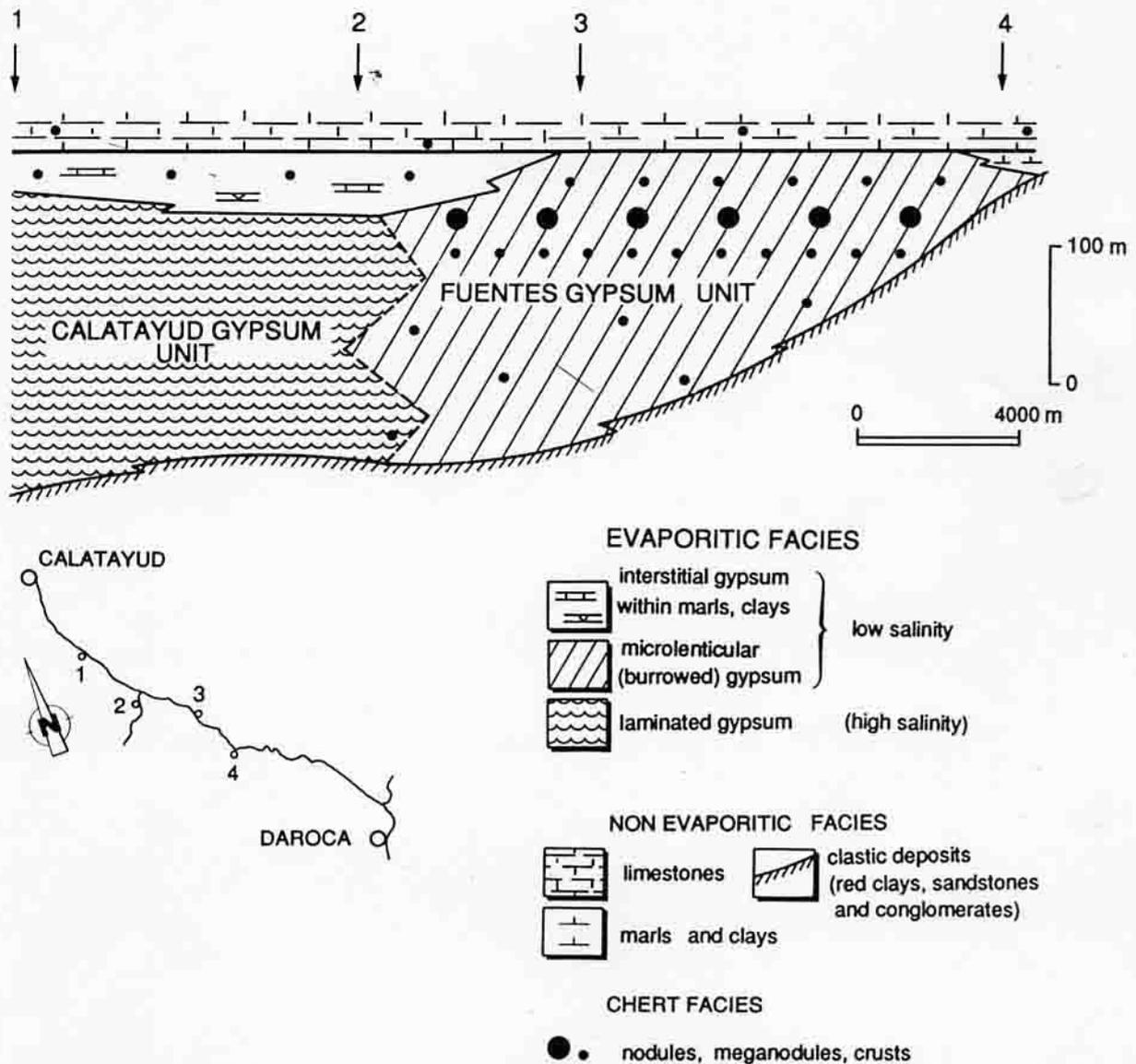


Figure 6.—Scheme of chert occurrences in the Lower Miocene evaporite facies of the southern part of the Calatayud Basin (simplified from Rosell and Ortí 1992, fig. 1).

lenticular bodies and irregular crust-like horizons. It is also of interest to notice that chert progressively decreases from the margin (Villafeliche zone) to the contact zone with the central facies (Morata zone) where it completely disappears.

Noteworthy is that while chert is totally absent in the laminated-nodular facies, it is abundant in the marginal primary gypsum facies.

#### TIMING OF SILICIFICATION

One of the most outstanding aspects of all these evaporite-related occurrences of silica in both the Ebro and Calatayud basins from the Paleocene to Miocene times is their early diagenetic origin. In order to document this correctly, we need first to refer to the evolution of the Ca-sulfate deposits themselves (Salvany 1989b, Ortí 1992).

In the marginal lacustrine systems the simplified succession of sedimentary and early-diagenetic events that can be generalized for many Ca-sulfate units is as follows:

1) precipitation of fine-grained primary gypsum in very shallow saline lakes and interstitially in some saline mudflats; intense burrowing of these deposits by animals, giving way to the typical "bioturbated microlenticular" gypsum lithofacies with massive layering; in it, burrows are dominantly infilled by the same gypsum crystals and by gypsum cement, and also locally by carbonate and lutites (NaCl concentration in these sediments and interstitial waters had to be extremely low); in some saline mud-flats a primary interstitial growth of anhydrite could have occurred;

2) episodic evolution of these shallow lakes to subaerial environments due to falls in water level during major desiccation periods; as a result, bioturbated microlenticular facies are partly or totally replaced by nodular-mosaic anhydrite;

3) local development of anhydrite meganodules that: 1) replace the primary gypsum facies; 2) displace the host sediment, or 3) displace any former diagenetic facies. This "meganodular anhydritization" apparently took place at the beginning of the burial stage (Salvany 1989b, from a few meters to about some tens of meters depth?), or even synchronously with stage 2 (Ortí 1992).

With regard to this diagenetic sequence, chert development in the marginal evaporitic units took place after sedimentary stage 1, but prior to any anhydritization of stages 2 or 3.

Silicification processes may follow one or more of these pathways:

a) delicate replacement of the gypsiferous (or carbonate) burrows in which the original microlenticular crystals may be preserved as pseudomorphs; this case was first documented by Bustillo and Díaz (1980) in the Tajo basin;

b) development of chert nodules and lenticular bodies in the shallow lakes either replacing the microlenticular gypsum or displacing it by interstitial growth; all transitions between this and the former case may be found; locally such nodules give way to small enterolithic-like structures which suggest a soft (uncemented) character of the gypsum deposit; in those saline mud flat areas bordering the lake in which direct nodular anhydrite occurred, chert nodules do not show any burrowing structures;

c) extensive replacement of the host sediment (usually gypsum but locally carbonate) by large irregular chert masses, giving way to crust-like horizons up to one or two meters thick; such masses may destroy (but locally preserve as pseudomorphs) the preexisting gypsum crystal generations.

Due to the interaction of both Ca-sulfate diagenetic evolution and the silicification process,

any nodulization of a primary gypsum deposit by its transformation into anhydrite (stage 2) did not affect those bioturbated masses that had been previously silicified. Thus burrowing was preserved as a pseudomorphic structure more or less isolated within a host rock made up of a nodular-mosaic anhydritic fabric.

Regarding the growth of anhydrite nodules (stage 3), other direct results of the sequence are the following:

- 1) nodules of chert (silicification pathway b) may have acted as nucleation points for meganodules (they frequently include smaller chert nodules in their cores);

- 2) chert nodules may be fractured or mechanically displaced by progressive growth of anhydrite meganodules (Ortí 1992).

Additional observations on timing of chert precipitation may be made in the case of the low-salinity gypsiferous unit of the Calatayud basin, particularly at some stratigraphic levels that were never affected by the anhydritization process. There, diagenetic growth of gypsum within lutitic or marly layers occurs as: a) nodules—ranging from a few cm to several tens of cm in diameter—formed by microcrystalline “primary” gypsum, and b) macrolenticular crystals—between 1 and more than 100 cm—(Rosell and Ortí 1992). Although to a lesser extent, at these particular levels chert has also developed, in such a way that:

- 1) gypsum nodules grew around silicified burrows and small chert nodules to include them;

- 2) gypsum macrolenticules cut through and pushed away the silicified structures (burrows and nodules).

This example taken from the Calatayud basin confirms that silicification is an early process that acted prior not only to any sabkha anhydritization of the shallow lakes, but also to the growth of some gypsum generations considered as very early diagenetic (macrolenticules).

## SILICIFICATION PROCESSES

### Sedimentary environment

Occurrences and petrologic characteristics displayed by chert in the marginal lacustrine systems of the Ebro and Calatayud basins are rather similar, of most relevance being the only association with low-salinity facies and the growth in very early diagenesis, prior to any evolution of primary gypsum precipitates into anhydrite during sabkhatization episodes.

This would imply that silicification preferentially occurred either: 1) during the saline lake stage (relative high water level) as a continuous interstitial replacement or direct growth, and 2) during periods of alteration of the lake hydrochemistry (enrichment in silica) and water level fluctuation; nevertheless, such fluctuations did not cause the evolution to sabkha.

Locally, chert lithofacies display a roughly layered arrangement and the possibility of a paleosol may be interpreted. In the host gypsum rock, however, no evidence is found for linking such occurrences neither to well-defined sedimentary hiatuses and weathered surfaces nor to any type of cyclicity. Therefore a purely edaphic origin for silicification seems unlikely.

Typical cementing replacement textures described in silcretes are difficult to recognize petrographically in the predominantly chert lithofacies (nodules) that are constituted by a dense microquartz mosaic. Furthermore, this chert is not connected laterally with calcretes or other duricrusts. Nevertheless, some thick crust-like horizons suggest extensive replacement related to stable groundwater level position.

### Particularities of the evaporite-related chert belts

Although a detailed study of chert in the various evaporite units is beyond the scope of this study, all observations regarding lithofacies show that silica growth took place under conditions ranging from an extremely delicate replacement/cementing mechanism in burrows (perfect burrowing pseudomorphism), to a replacive/interstitial precipitation in nodules, until a massive replacive (sometimes destructive) mechanism in crust-like horizons.

Locally, lateral changes in thickness and abundance of chert structures have been observed in a perpendicular direction through the marginal system, either increasing or decreasing towards the external zone. Nevertheless, the linear shapes of outcrops in general do not agree with this observation. Some indicators suggest that in fact facies evolution may occur across these chert belts presumably due to the existence of either original silica gradients in water or to slightly different hydrologic conditions from the outer to the inner zone of the belt.

On the other hand, these particular belts cannot be taken as isolated occurrences of silica in basins. It has been already mentioned that some Tertiary basins rich in non-marine evaporite formations contain chert (Ebro, Calatayud) while others do not (Teruel), and this is also true for other Tertiary basins of the Iberian Peninsula with similar conditions. Unfortunately, a satisfactory explanation for this phenomenon is not as yet available.

Nevertheless, it should be emphasized that in those basins whose evaporite formations display chert (Ebro, Calatayud; also Tajo basin), such occurrences can be extended to other chemical sediments also. This is particularly true for lacustrine carbonate formations in stratigraphic vicinity to chert-bearing evaporitic ones, as well as for many others widely distributed in intermediate or central position in the basins.

All these facts suggest that chert in the evaporite formations under discussion is only part of a generalized phenomenon operating on a broad basinal scale. At the same time, however, they clearly document the manner in which evaporite environments control chert deposition. Thus, as well as one basinal factor conditioning the presence or absence of chert in each case (of difficult prediction, as commented), a second factor (salinity?) seems to govern chert distribution between the major groups of evaporite formations.

### Silica provenance and precipitation mechanism

Chert distribution along some margins of the Ebro and Calatayud basins suggests that silica reached the basins dissolved in groundwaters and in stream waters being drained off the surrounding mountain reliefs. In the case of the today's Ebro Valley depression, waters discharged by springs and from deep aquifers by regional flow along the southwestern (Iberian) margin are highly mineralized and contain a total amount of solutes up to 1000-3000 mg/l, due to recycling of old (Triassic and Lower Liassic) evaporite formations (Sánchez *et alii* 1989: 3-8, Martínez *et alii* 1988: 57-80). Locally, silica content in these waters is high (10-40 mg/l) and also temperatures are elevated (22 to 25°C, up to 40-45°C). All these aspects are discussed in detail in the paper by Salvany *et alii* (in prep).

The same recycling mechanism operated during Tertiary times as demonstrated by the isotopic composition of sulfates (Utrilla *et alii* 1991: 353-360). Probably both paleogeography and paleohydrology along the basin margins combined in such a manner that silica reached these marginal evaporitic systems and preferentially precipitated there, these environments acting as effective chemical barriers for further penetration towards the inner part of the basin.

The provenance of silica is difficult to establish accurately and may have been varied. The existence of paleosols in the surrounding mountain reliefs (Iberian and Catalan ranges) during the Mesozoic-Paleogene is known. Obviously, weathering processes were able to leach important silica amounts from igneous rocks and siliciclastic sedimentary materials as well.

But other (autochthonous) possibilities should be considered, as the generation of silica in the sedimentary environment itself, either by corrosion/dissolution of detrital quartz and feldspar or by clay reactions. For this second point, articles by Inglès *et alii* (1991: 170-173) and Inglès and Anadón (1991) on the evaporite units of the Catalan marginal system show that significant mineral transformations of clays took place (palygorskite and Mg-rich trioctahedral smectites). This suggests that silica concentration was high in the interstitial waters of these sedimentary environments during the Eocene-Lower Oligocene.

Of great interest is the proposal by Bustillo *et alii* (1991) for some marginal basins (Sepúlveda-Ayllón, Fuentidueña-Sacramenia) of the Duero Tertiary basin. These authors suggest that extensive calcrete formation on lutitic and marly host sediment during the Miocene leached silica in significant amounts so as to produce enrichment in groundwaters. Flow of these shallow aquifers towards the center of the basin would have facilitated silcrete formation, locally replacing gypsum sediments.

The precise physico-chemical mechanism for silica precipitation remains unknown. Changes of pH values caused either by rapid dilution of dense alkaline brines or by intermittent photosynthetic activity, is a major mechanism widely accepted in the literature on sedimentary chert as responsible for the precipitation of unusually high amounts of amorphous silica from lake waters.

In our study, however, there is no clear evidence as to the way this could have operated. No diatomites or other sediments that suggest elevated silica contents in open waters have been found in the stratigraphic record of these shallow lakes. A second mechanism, evaporite concentration, is considered in the literature as very efficient in precipitating silica in evaporite-related lacustrine environments (Jones *et alii* 1967). Such a mechanism was considered also by Bustillo *et alii* (*op. cit.*) to explain the formation of opaline silcretes and nodular chert in some Miocene marginal basins of the Tertiary Duero basin. These authors attributed silcrete formation on gypsiferous host-rock to a stage after gypsum precipitation in playa lakes, due to a continued drop of water level to an underground position. In this situation, silicification would have resulted from evaporative pumping of siliceous groundwaters moving under the mud flat towards the lake.

Comparing this example to that studied in this paper, it should be remembered that in the Ebro and Calatayud basins a further evolution of the saline lakes to sabkha stage has frequently occurred. Thus, silicification apparently occurred at an intermediate water concentration between the primary gypsum stage and the generalized anhydrite stage. Nevertheless, any well-defined cyclicity involving these three stages (gypsum precipitation, its interstitial replacement by chert, and final transformation/disorganization by sabkha anhydrite) has not been found. So, sabkhatization probably happened as an independent mechanism from chert generation.

One final comment that needs to be emphasized in the case we are dealing with is that chert preserves the original structures and behaves as a lithologic testimony of previous sedimentary conditions now completely destroyed by intense evaporitic diagenesis.

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