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

F. ORTÍ*, L. ROSELL*, J. M. SALVANY** and M. INGLÈS *

*Departament de Geoquímica, Petrologia i Prospecció Geològica, Universitat de Barcelona, Barcelona.
**Departament d'Enginyeria del Terreny, Universitat Politècnica de Catalunya, Barcelona.

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: A. Ramos-Millán and M.A. Bustillo (Eds.), Siliceous rocks and cultures, Publ. Universidad de Granada (Spain), 1997.

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. Morever, 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:

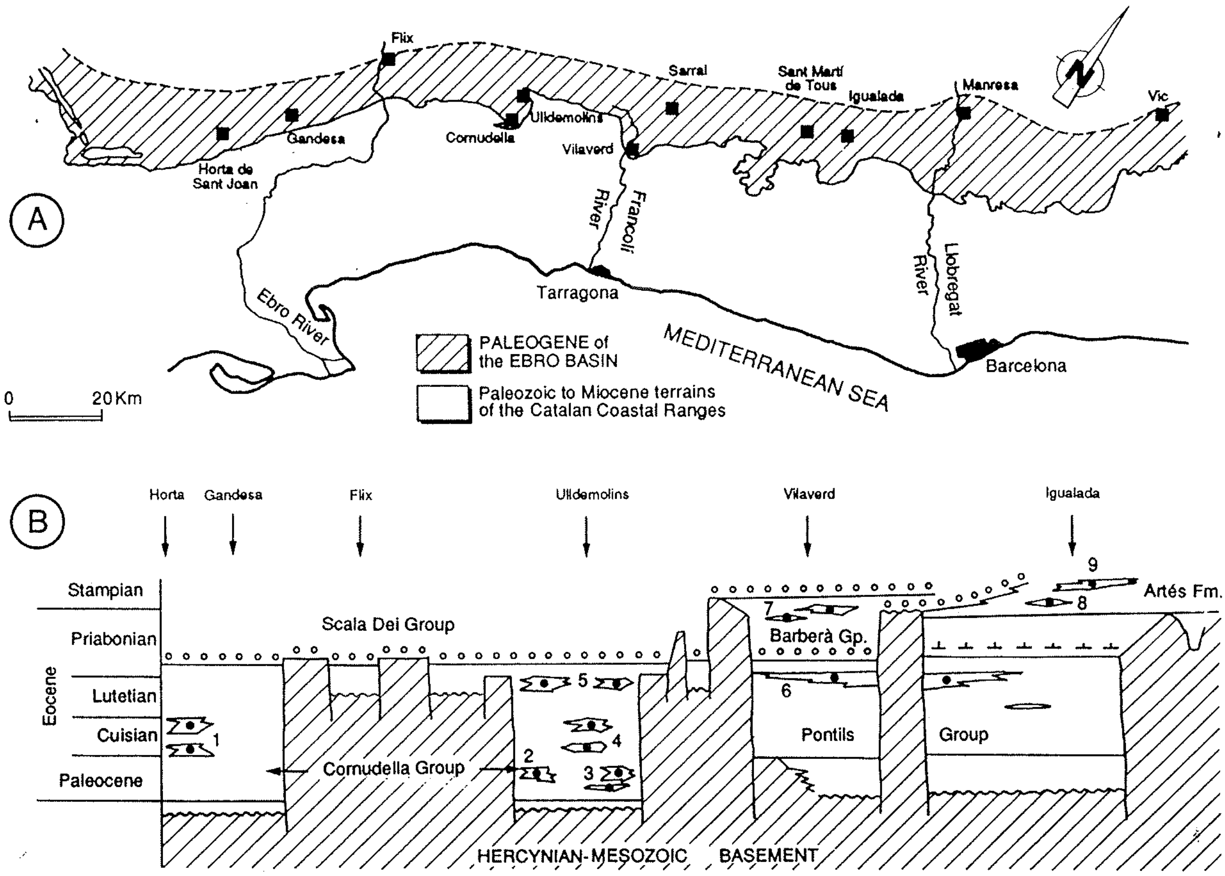

Figure 3.—A) Geographic position of the contact zone between the Paleogene sediments (striped) of the Ebro Basin and the Paleozoic-Mesozoic materials of the Catalan Range (in white); B) Distribution of the non-marine evaporitic units and associated chert in the Catalanide marginal evaporitic system. 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 Ortí 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

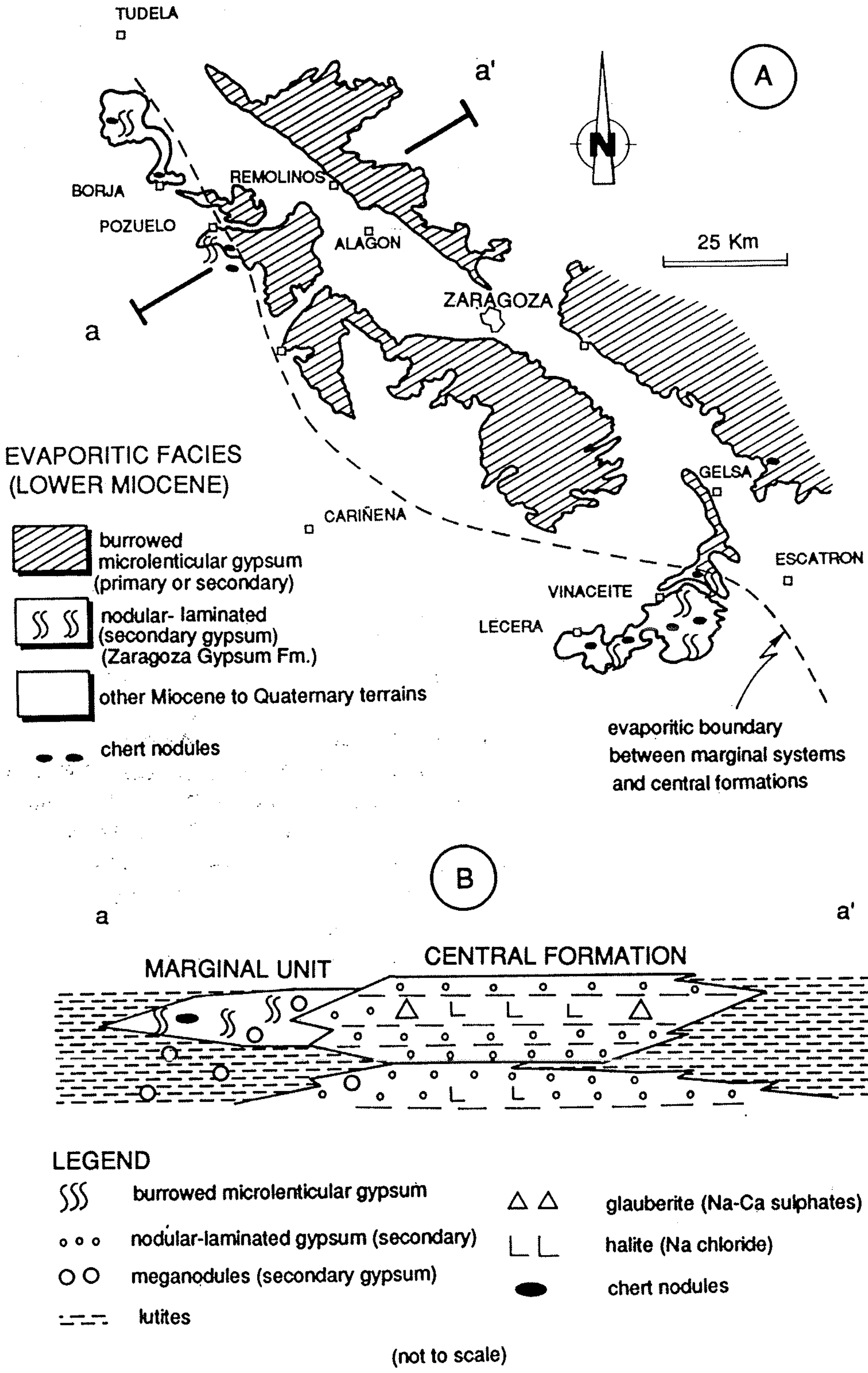

Figure 5.—A) Location map of the main Lower Miocene evaporite units of the southeastern part of the Iberian marginal lacustrine system; B) Scheme (not to scale) of the deduced facies relationships between the Lower Miocene evaporite marginal units and central formations (example of a section along Pozuelo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

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 untill 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,

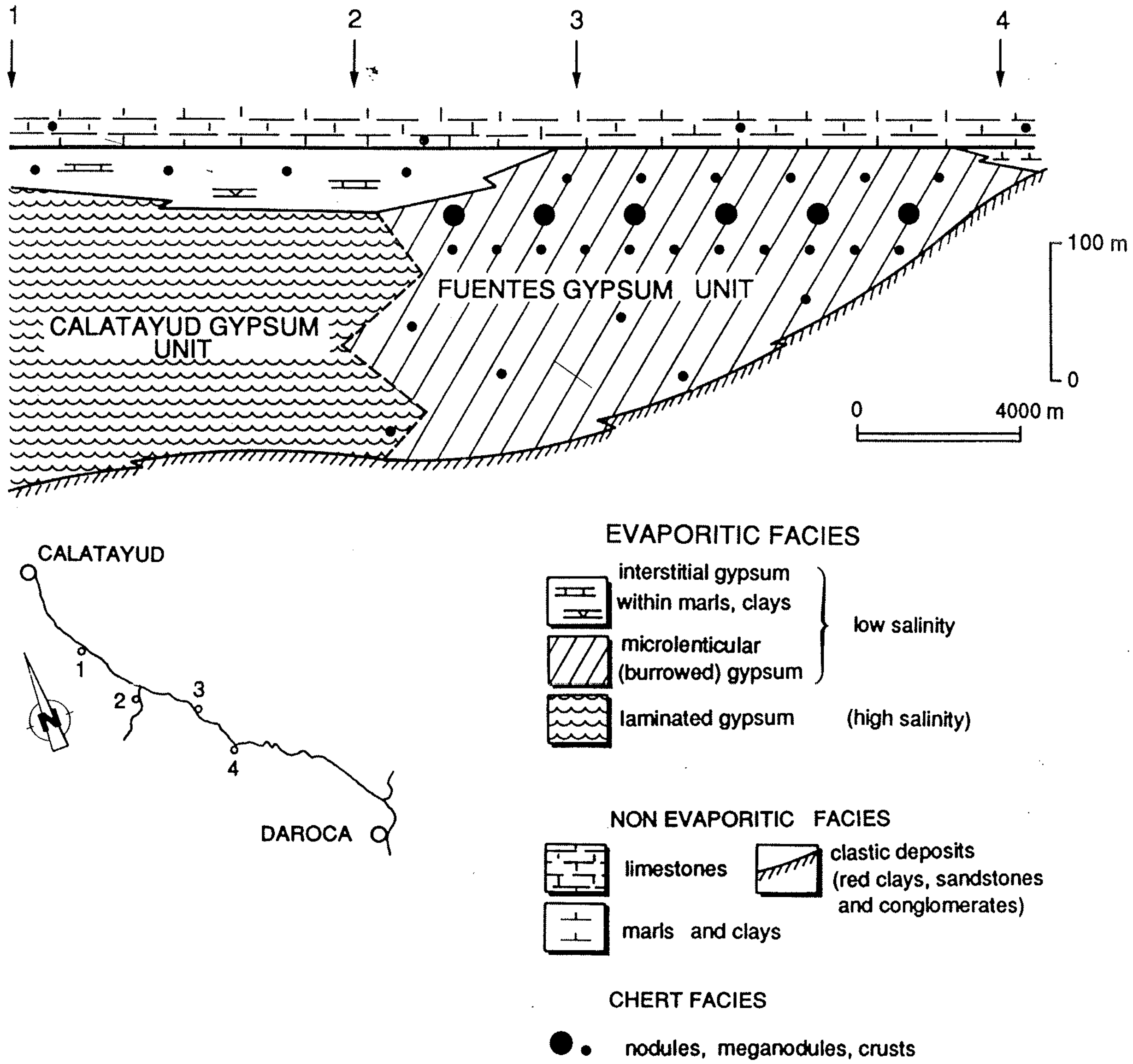

Figure 6.—Scheme of chert occurrences in the Lower Miocene evaporite facies of the southern part of the Calatayud Basin (simplified from Rosell and Ortí 1992, fig. 1).

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 paleosoil 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.

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 (autochtonous) 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.

Work supported by DGICYT Project PB90-0485

Salvany, J. M. (1989c). Los sistemas lacustres evaporíticos del sector navarro-riojano de la Cuenca del Ebro durante el Oligoceno y Mioceno inferior. *Acta Geológica Hispánica* 24 (3-4), 231-241.

Salvany, J. M., Muñoz, A., and Pérez, A. (in prep.). Non-marine evaporitic sedimentation and associated diagenetic processes of the SW margin of the Ebro Basin (Lower Miocene, Spain).

Sánchez, J. A., de Miguel, J. L. and Martínez Gil, F. J. (1987). El drenaje subterráneo de la Cordillera Ibérica en la Depresión terciaria del Ebro y procesos geológicos asociados. *II Congreso de Geoquímica de España, Libro de Resúmenes* (Soria, 1987), 3-8.

Utrilla, R., Ortí, F., Pierre, C. and Pueyo, J. J. (1991). Composición isotópica de las evaporitas terciarias continentales de la Cuenca del Ebro: relación con los ambientes deposicionales. *Revista de la Sociedad Geológica de España* 4 (3-4), 353-360.