MIOCENE GLAUBERITE DEPOSITS OF ALCANADRE, EBRO BASIN, SPAIN: SEDIMENTARY AND DIAGENETIC PROCESSES

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ABSTRACT: The Alcanadre glauberite deposits are interbedded within the Lerín Gypsum Formation (Oligocene to Lower Miocene) in the western part of the Tertiary Ebro Basin of Spain. Glauberite forms several beds associated with other evaporitic minerals such as halite, polyhalite, gypsum, anhydrite, magnesite and dolomite. This association formed by sedimentary and early diagenetic processes in a playa-lake complex. The precipitation sequence was: carbonate, gypsum-anhydrite, glauberite, halite-polyhalite.

Gypsum occurs as a laminated facies precipitated as fine crystals on the floor of a shallow saline lake. Anhydrite formed at the lake margin and grew as interstitial nodules and enterolithic layers, or replaced pre-existing gypsum. Glauberite occurs both in nodular and enterolithic facies, commonly with convolution-like structures. Massive and banded facies are also present. Glauberite has textures ranging from fine-grained to euhedral macrocrystalline aggregates (up to 3 cm) that formed either from interstitial primary growth or from gypsum (or anhydrite) replacement. Polyhalite replaced all former sulfate phases (mainly gypsum and glauberite) and displays laminated facies and spherulitic microstructures. The polyhalite is associated with halite, which precipitated as primary crystals on the floor of the saline lake or as interstitial cement. The high Mg^{2+} content of the brines probably favored early transformation of all original $CaCO_3$ phases into dolomite or magnesite, both of which show micritic textures.

Because of dissolution by less concentrated (meteoric) brines, some retrodiagenetic processes have also been observed; polyhalite was replaced by glauberite, and polyhalite and glauberite by anhydrite. Burial led to further transformation of gypsum to anhydrite, and during exposure all pre-existing sulfates (anhydrite, glauberite, polyhalite) were transformed into secondary gypsum near the surface.

INTRODUCTION

The Tertiary Ebro Basin of Spain contains an important sequence of non-marine glauberite deposits of Oligocene to Miocene age (Fig. 1). Glauberite and its associated evaporite minerals are usually confined to the subsurface. Near the surface they have been extensively dissolved or transformed into secondary gypsum. The Alcanadre and Cerezo del Río Tirón deposits have been known for several years (Riba, 1955, 1964; Menduiña and others, 1984; Ordóñez and others, 1982). Several glauberite layers crop out, and were formerly mined (Alcanadre, Arrúbal); some deposits are still mined today (Cerezo, Belorado). More recently, glauberitic beds have been discovered in the subsurface evaporites, by new mining and oil boreholes (Fernández-Nieto and Galán, 1979; Mandado, 1987; Salvany, 1989a; García-Veigas and others, 1991). Overviews of the glauberite occurrences in the Ebro Basin are presented by Ortí and others (1989), and Ortí and Salvany (1991). However, their distribution and characteristics are still poorly known because of the paucity of subsurface data and drill core. Each deposit has its own specific mineral paragenesis, origin and differences.

In this paper we describe the main sedimentary and diagenetic features of the Alcanadre glauberite deposits. These are interbedded within the evaporites of the Lerín Gypsum Formation (Oligocene to Miocene boundary) in the western extremity of the Ebro Basin (Fig. 2). Besides glauberite, significant amounts of halite, polyhalite, magnesite and dolomite are also present, with gypsum and anhydrite forming the major part of the evaporitic host sediments. Preliminary results were given by Ortí and others (1986), Salvany and Ortí (1987), and Salvany (1989a).

REGIONAL SETTING

The Tertiary Ebro Basin is a foreland basin in the northeastern Iberian Peninsula. It is bounded by three Alpine chains that underwent uplift concurrently with the sedimentary filling of the basin: the Pyrenees to the north, the Iberian Ridge to the southwest, and the Catalonian Coastal Ranges to the southeast (Fig. 1). Basin evolution was controlled mainly by the Pyrenean uplift, which acted as a highly active margin, although significant structural roles were also played by the two other chains.

Two broad sedimentary cycles have been recognized in the basin (Riba and others, 1983): (1) from the early Tertiary until the upper Eocene the northern and eastern parts of the basin were the site of major siliciclastic, carbonate and evaporite marine sedimentation. To the south these sediments passed laterally into non-marine deposits; (2) since the late Eocene the basin has been the site of a thick sequence of non-marine sediments, both detrital and chemical. These include alluvial fan deposits that developed along the basin margins, and lacustrine carbonates and evaporites in the more central parts.

Tectonically, the Tertiary deposits of the Ebro Basin lie in two structural domains: (1) a northern domain, in which deformed sediments were incorporated into the South-Pyrenean nappes, and (2) a southern domain, where the sediments are in place and have been only affected by gentle folding related to emplacement of the nappes. The northern domain includes marine Paleocene and Eocene sediments, while most sediments in the southern domain are non-marine and Oligocene to Miocene in age (Fig. 1).

Glauberite deposits are found only within the large non-marine evaporite formations of the southern (autochthonous) domain. There, they are widespread and distributed along the western and central part of the basin. The evaporitic deposits were precipitated in playa-lake complexes. They indicate the former position of the basin depocenter, which shifted laterally during the Tertiary under the tectonic controls. Ortí and Salvany (1990) summarized these large evaporite sequences.

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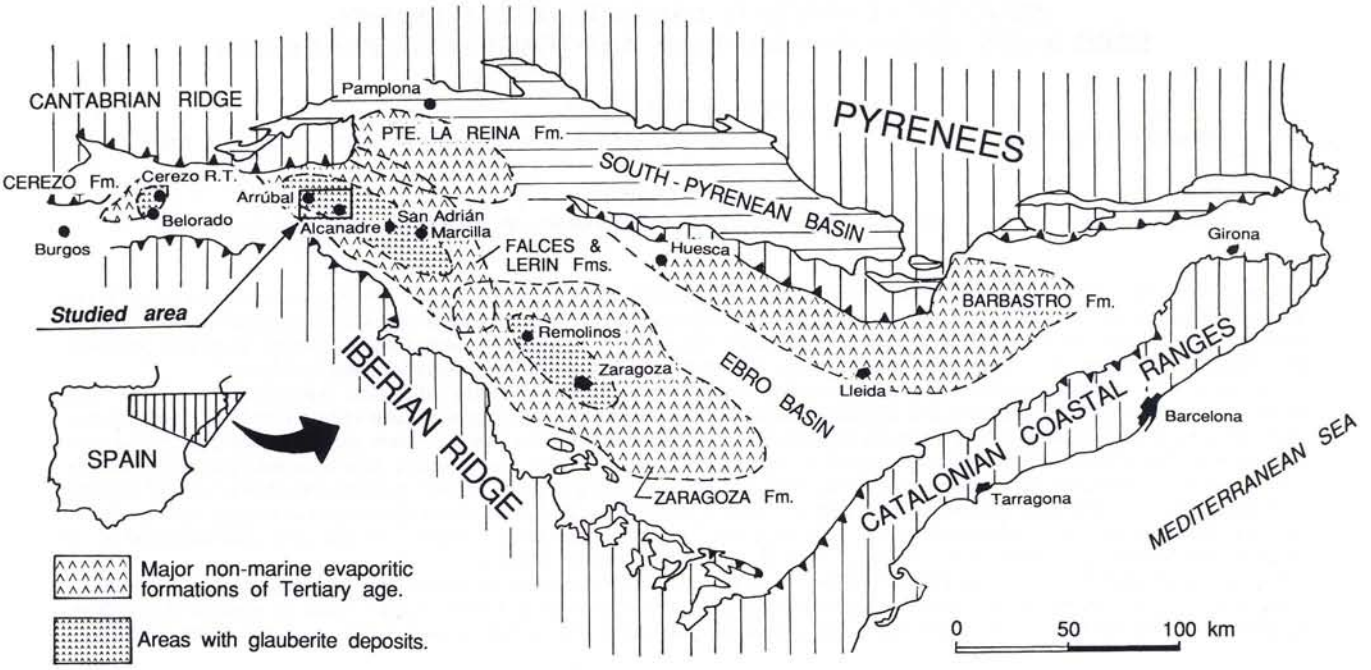

FIG. 1.—Geologic map of the Tertiary Ebro Basin showing distribution of major non-marine evaporitic formations and associated glauberite deposits.

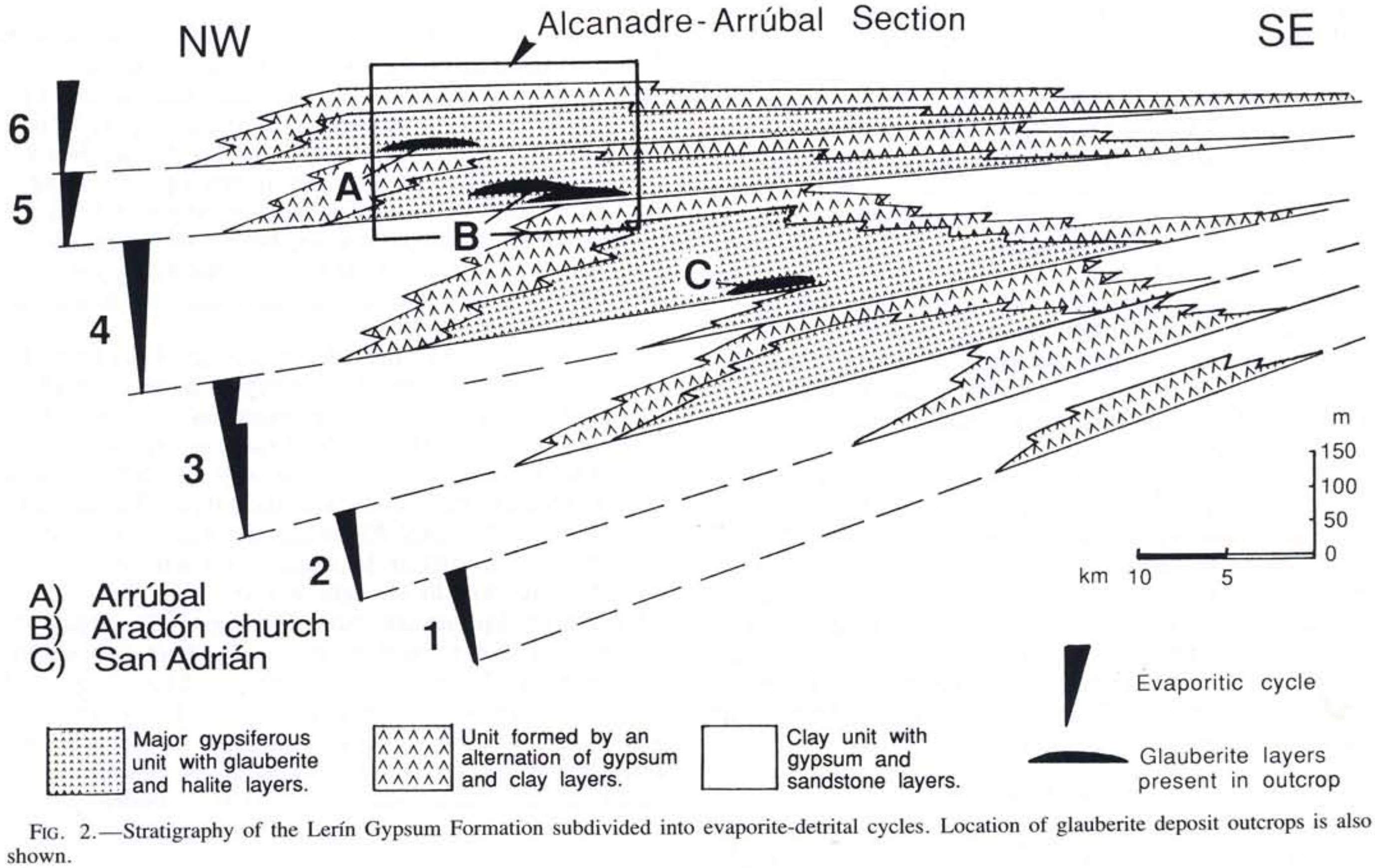

FIG. 2.—Stratigraphy of the Lerín Gypsum Formation subdivided into evaporite-detrital cycles. Location of glauberite deposit outcrops is also shown.

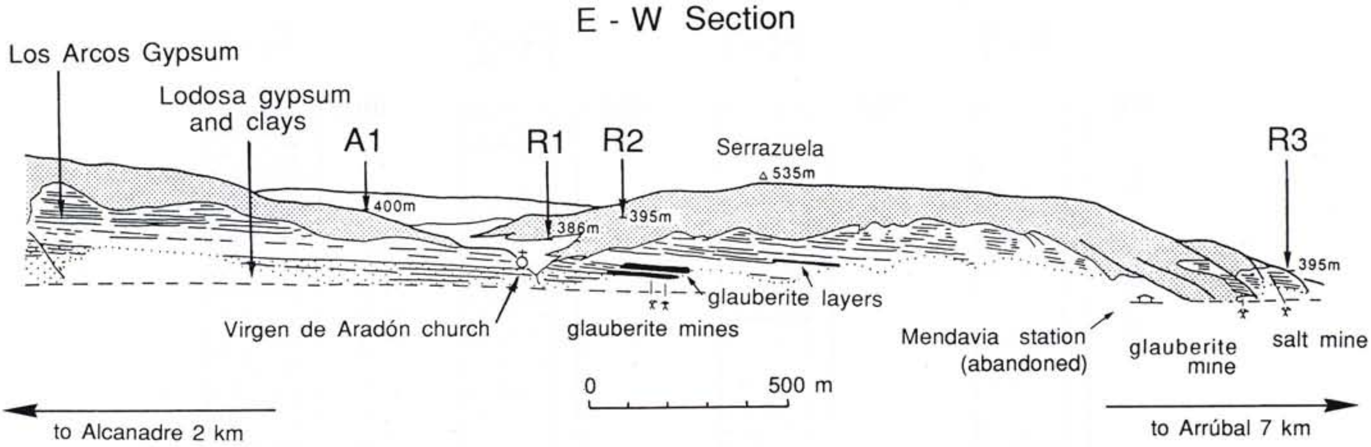

FIG. 3.—View of the Lerín Gypsum Formation at the Aradón church section near Alcanadre. Location of glauberite outcrops and boreholes is indicated (see Figure 4).

STRATIGRAPHIC SETTING AND EVAPORITE CYCLES

During Oligocene and Miocene time, non-marine sediments were deposited almost continuously in the western Ebro Basin, reaching 4 km in thickness. Three stratigraphic units with evaporites are recognized: the Puente La Reina Gypsum Formation (Lower Oligocene; 400 m thick), the Falces Gypsum Formation (Middle to Upper Oligocene; 800–1,000 m thick), and the Lerín Gypsum Formation (Oligocene to Lower Miocene; 400–600 m thick) (Castiella and others, 1978; Salvany, 1989a, b). These formations extend over an area about 100 km long by 30–40 km wide, and are separated by clastic units with subordinate evaporitic layers.

These three evaporitic formations are formed mainly by Ca-sulfates (gypsum, anhydrite) and halite. Anhydrite and halite are found in the subsurface, whereas gypsum occurs near the surface. In the Falces Formation and Lerín Formation, glauberite deposits are interbedded with Ca-sulfates. Glauberite deposits are unknown in the Puente La Reina Formation.

The Lerín Formation is composed of several evaporitic cycles about 100 m thick and more than 50 km in length (Fig. 2) (Salvany, 1989a, c). These cycles appear to have shifted progressively toward the northwest with time, with a concurrent shift of the basin depocenter. Maximum evaporite development occurs toward the top of the formation, the upper cycles becoming more gypsiferous than those below.

The cycles reflect the advance and retreat of the alluvial fan systems along the basin margins, which in turn affected the playa-lake complex in the central part of the basin. The base of an individual evaporite cycle represents the maximum expansion of lacustrine evaporitic conditions, while upward there is increasing influence of the progressive progradation of the alluvial fans. The tops of some cyclic units are formed by a thick (up to 10 m) layer of clays and fine-grained sandstones. This represents the maximum extension of the alluvial sediments that preceded the next cycle. The glauberite layers develop preferentially at the base of each cyclic unit and are confined toward the more central parts (Fig. 2).

THE GLAUBERITE DEPOSITS OF ALCANADRE

The uppermost two cycles that form the Lerín Formation are well exposed between the Alcanadre and Arrúbal (Fig. 3). Together these cycles form the most important evaporite level of the Lerín Formation, known as the "Los Arcos Gypsum" (Riba, 1964). In the eastern part of the Alcanadre-Arrúbal region the upper part of the fourth cycle of the Lerín Formation crops out and is composed of reddish detrital gypsiferous materials ("Lodosa Gypsum and Clay"; see Salvany, 1989a). Glauberite layers are found mainly at the base of the two evaporitic cycles that form the Los Arcos Gypsum. The lower one produces a steep escarpment near Aradón church. Two major glauberite layers, with thicknesses of 2 m and 4 m respectively, are exposed in the escarpment near sites of former mines. Near Aradón church the upper cycle has been eroded, but remains intact west of the old Mendavia railroad station. Overlying the upper cycle the clay and sandstones of the lower part of the Alfaro Formation crop out, representing the beginning of a new pattern of sedimentation, dominated by the fluvial environments.

The lower cycle was penetrated by the R1, R2 and A1 exploratory boreholes drilled by the Unión Salinera de España S. A. in 1983–84, near Aradón church (Figs. 3, 4). Glauberite layers that are thicker and more abundant than those exposed in the escarpment were cut by these boreholes. Borehole R3, located near Arrúbal, cut completely through the upper cycle. The glauberite layers are less common and less well developed than near Aradón church zone, but a thick halite bed is present, which was once exploited by a small mine near the top of the escarpment (Fig. 3).

EVAPORITE PETROGRAPHY

Petrographic analysis of the glauberite deposits has revealed extensive development of secondary minerals. These formed mainly during early diagenesis, but significant min-

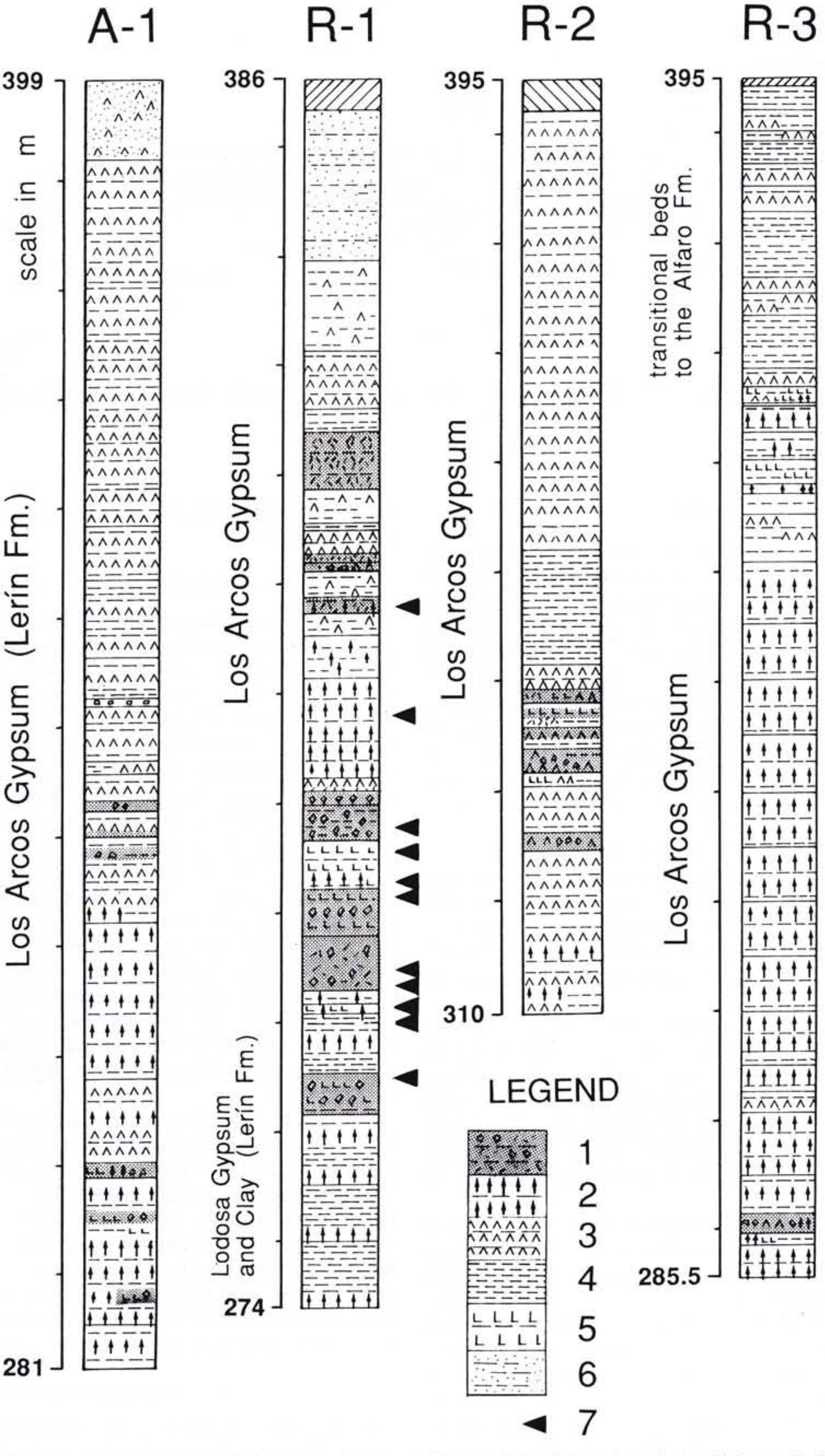

FIG. 4.—Simplified stratigraphy of boreholes drilled by Union Salinera de España, S.A., in the Alcanadre-Arrúbal zone for Na-sulfate exploration. (1) glauberite, (2) anhydrite, (3) secondary gypsum, (4) clay, (5) halite, (6) siltstone and sandstone, (7) interbeds of polyhalite.

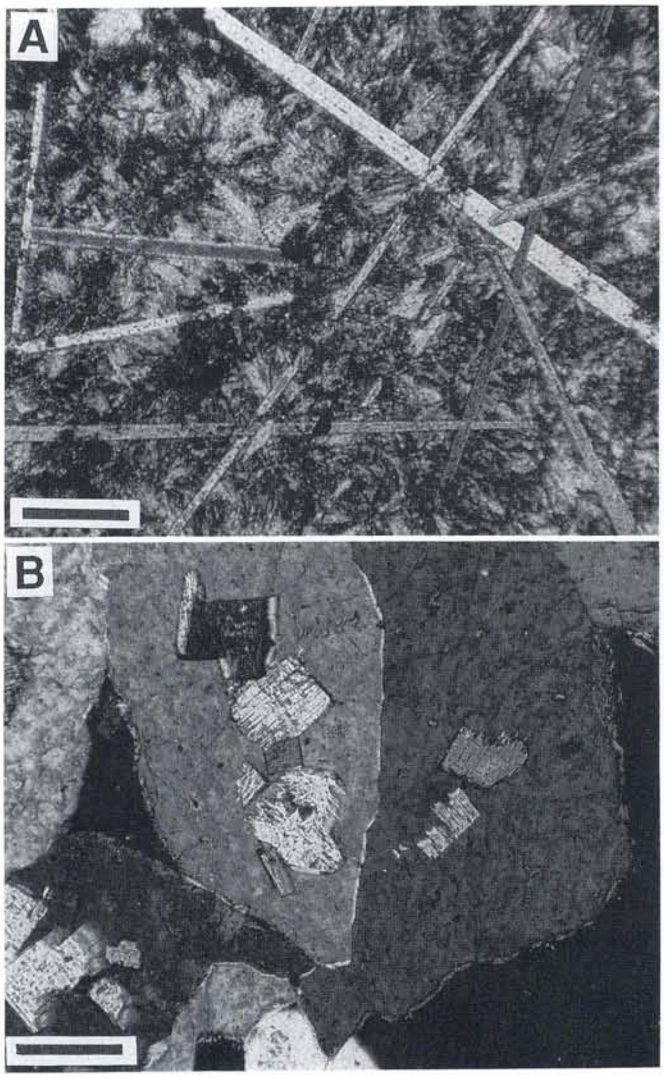

FIG. 5.—Anhydrite textural varieties: (A) elongated tabular crystals growing on (and replacing) polyhalite (scale bar= 300 μm), (B) equant to prismatic crystals growing on (and replacing) glauberite (scale bar= 300 μm).

eral changes also occurred during burial and final exposure (late diagenesis). Because of their long diagenetic history, primary evaporite minerals (i.e., any mineral precipitated and grown from brine, either in open water or interstitially) have only partly survived, but in places they can be identified as pseudomorphs, now composed of secondary minerals. Pseudomorphs may also have originated from secondary minerals, thus the final mineral may have had two or more precursor solid phases. The presence of partially replaced minerals and relict inclusions have allowed us to recognize the various mineralogical transformations that have taken place.

Gypsum

All the gypsum ($CaSO_4 \cdot 2H_2O$) in these deposits is secondary, and displays the well-known alabastrine, porphyroblastic and megacrystalline petrographic varieties (Ortí, 1977). Gypsum formed during late diagenesis (exhumation) by rehydration of anhydrite. This secondary gypsum might also result from replacement of other sulfates, such as glauberite and polyhalite. Both in outcrop and in borehole samples, replacement by gypsum may be incomplete, then it is limited to the external boundaries of the precursor mineral facies, the inner part remaining unchanged. Where the precursor was glauberite or polyhalite, pseudomorphs are recognizable even after the total replacement, even though mineral relicts are generally not preserved in the secondary gypsum. In contrast, secondary gypsum after anhydrite commonly shows mineral relicts, especially in coarsely crystalline varieties.

Secondary gypsum displays lenticular, laminated or nodular-enterolithic facies. The lenticular facies is represented by individual crystal pseudomorphs (2 to 3 cm) or by rosette shaped aggregates of lenticular-tabular crystals of primary gypsum that grew within clay or carbonate. Gypsum laminae formed initially as fine crystals on the floor of the lake. Microbial structures (undulating and crenulated laminae; wave ripples superimposed on this lamination, etc.) and other sedimentary structures have been preserved. Both the laminated and lenticular facies were originally primary gypsum that transformed into anhydrite during early diagenesis or burial. In contrast, nodules, nodular banding and enterolithic layers that alternate with the laminated facies, represent anhydrite (or glauberite) that formed during very early diagenesis. Salvany (1989a) gave a detailed description of the various gypsum facies of the Lerín Formation.

Anhydrite

Anhydrite ($CaSO_4$), which occurs only to depths of a few tens of meters (Fig. 4), displays the same facies described for secondary gypsum. The anhydrite is white or blue, fine-grained (30–150 μm), and petrographically usually displays a granular or unoriented prismatic fabric, in which a bimodal trend may be apparent.

Anhydrite formed mainly during early diagenesis as interstitial nodules or by replacement of laminated gypsum. Displacive nodular anhydrite formed both in lake marginal sediments and as nodular-enterolithic bands in the central playa during periods of desiccation. In both settings, anhydrite caused deformation of the host sediment. Laminated gypsum was replaced without disruption of the facies, concurrently with growth of the enterolithic structures.

Commonly, anhydrite partly replaces all other evaporite minerals (polyhalite, glauberite, halite) during early diagenesis. In polyhalite fabrics (see below) it occurs as tabular crystals up to several mm long, preferentially in the purest polyhalite zones (Fig. 5A). These narrow elongate laths are randomly oriented and have poikilotopically trapped the host impurities (carbonate micrite and clay) in the original polyhalite fabric. In some cases, laths are bent and fractured, probably due to compaction. Anhydrite crystals replacing glauberite and halite are smaller, about 100 μm, and resemble isolated and disoriented porphyroblasts (Fig. 5B). Glauberite replacement by anhydrite is well known from other Tertiary glauberite deposits of the Ebro Basin,

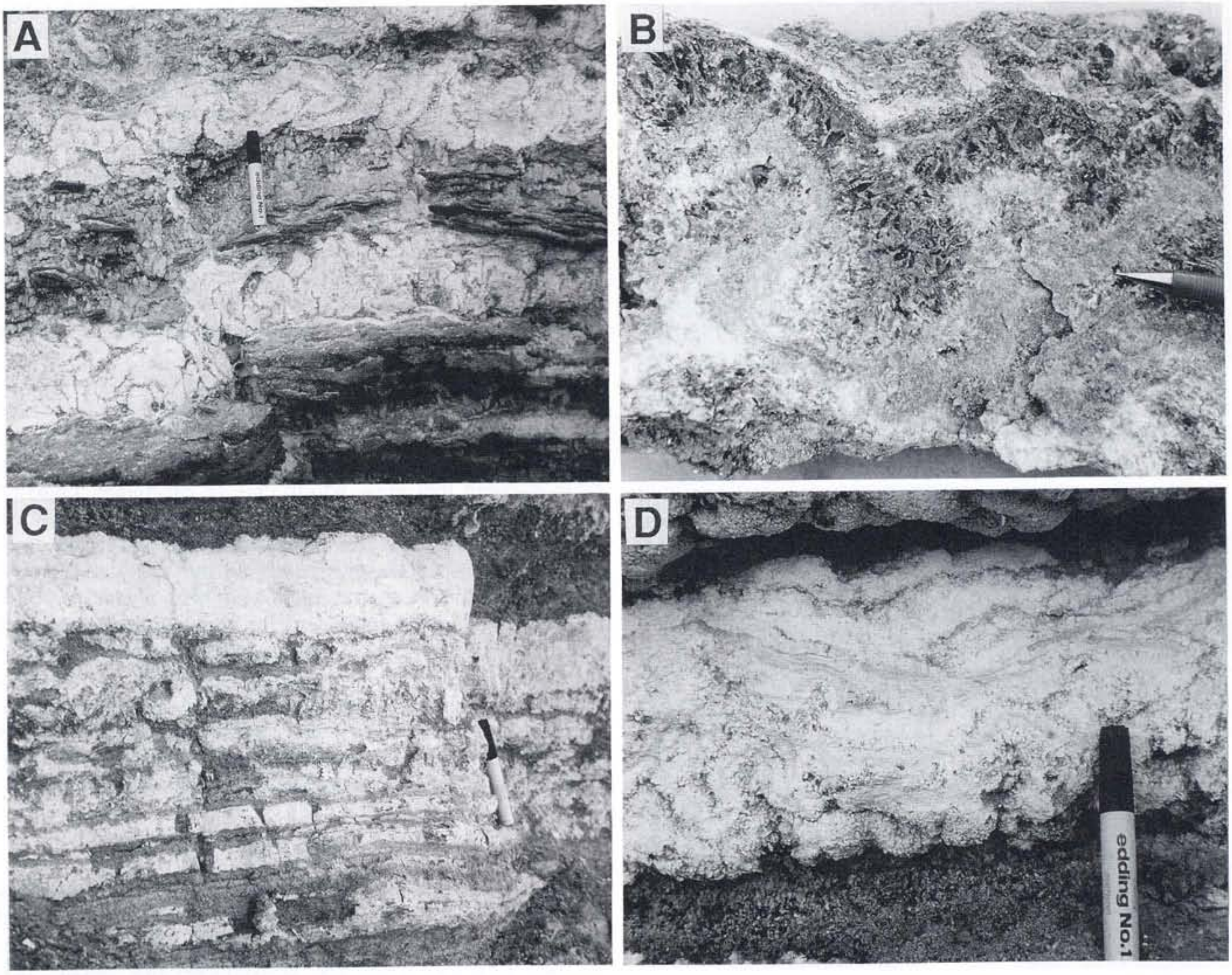

FIG. 6.—Glauberite facies: (A) enterolithic glauberite layers, (B) close up of an enterolithic structure in which crystal size increases from the core toward the margin, (C) banded (even tabular) facies of glauberite, and (D) nodular glauberite layer displaying fine-grained fluid-like laminate in the upper half and coarse-grained enterolithic level in the lower half.

notably in the Zaragoza Formation (Miocene), where large (up to 5 cm) pseudomorphs of anhydrite after glauberite are found in borehole samples obtained from the Remolinos mine (García-Veigas and others, 1991).

Glauberite

Glauberite ($Na_2Ca(SO_4)_2$) is easily identified at the surface because of the white efflorescence of sodium sulfate that covers the rocks. In borehole samples it may be mistaken for gypsum, especially where it is fine-grained. Glauberite forms: (1) thin (20–30 cm thick) nodular-enterolithic horizons interbedded with laminated gypsum (Figs. 6A, B), and (2) thick (1 to 4 m) layers with well-defined internal banding, in which massive, banded and nodular facies alternate (Figs. 6C, 6D, 7).

The glauberite nodules form continuous bands interbedded with the massive and banded facies. They commonly display an internal lamination toward the upper half of the band in which deformation and fluid-like structures modify the laminae (Fig. 6D). In the lower half, the nodules are better defined and contain large crystals, some resembling the enterolithic levels described previously. In the nodular-enterolithic levels, which usually displace the host gypsum laminae, the glauberite is very pure and compact, with fine to medium crystals. Crystal size commonly increases from the core to the edges of the nodules (Fig. 6B), such that the outermost glauberite crystals are large (1 to 2 cm) and arranged perpendicular to the nodule surface, projecting into the host sediment (Fig. 8A). Petrographically, glauberite nodules have a dense, fine-grained (<500 μm) crystalline core with a subhedral granular mosaic, and with large euhedral crystals toward the periphery.

The massive and banded glauberite of the thick layers is porous and fragile. In these facies, glauberite displays randomly oriented, variably sized aggregates, ranging from 100

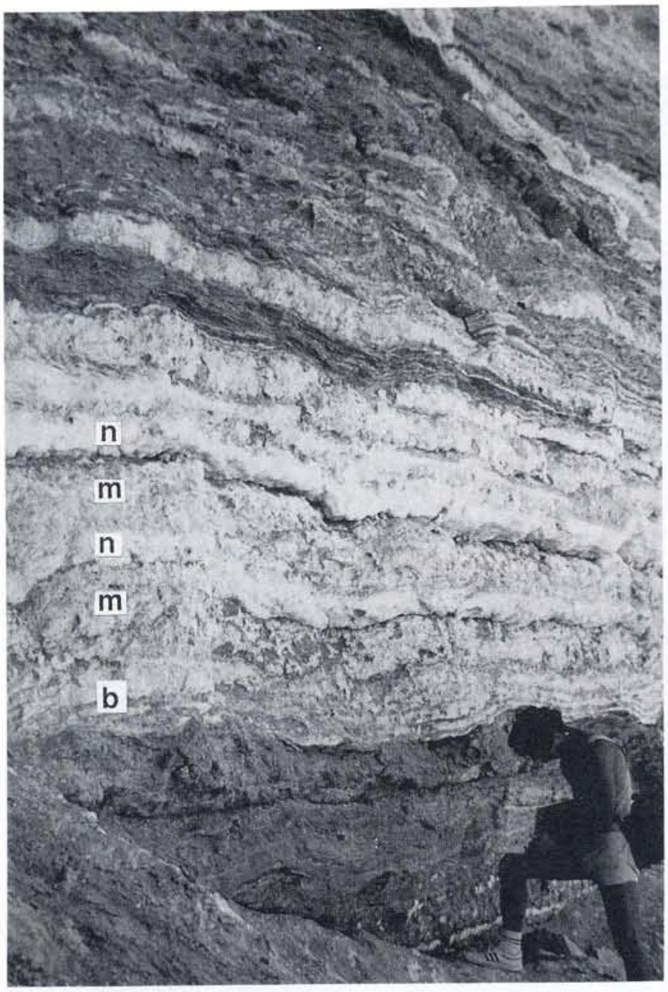

FIG. 7.—View of major glauberite unit near the Aradón church outcrop. The following facies may be distinguished: (m) massive, (n) nodular, and (b) banded.

μm to 3 cm, with a clay or marl matrix. Crystals are usually prismatic and rhombohedral, especially where host matrix is abundant (Fig. 8B). The crystals are commonly interpenetrant with a sub- to euhedral fabric (Fig. 8C). Bimodal textures are also present, in which fine (<500 μm) crystals form the matrix of larger crystals (several cm long). In all cases, the crystals are clean, lacking other sulfate mineral inclusions, but very commonly they display a zonal growth pattern shown by the presence of matrix (i.e., non-evaporitic) inclusions. Thus, we infer that these are interstitial textures with crystals displacing or partly trapping the host sediment, but becoming progressively deformed during crystal growth. Locally, euhedral crystals are also seen within the gypsum laminated facies, either isolated or grouped in partings parallel to the laminae.

Poikilotopic glauberite is a textural variety only seen under the microscope (Fig. 8D). It is formed by millimeter-sized crystals that mainly replace polyhalite, trapping and preserving matrix (i.e., host-sediment) inclusions. Such glauberite crystals are usually anhedral with undulatory extinction, although euhedral forms have also been observed. In these textures not only polyhalite but also glauberite and gypsum pseudomorphs have been well preserved.

The various glauberite facies formed from interstitial brines at the margins of the lake. The glauberite crystals grew during early diagenesis by displacement of the host sediment (mud, sulfate or carbonate). The preservation of anhydrite inclusions in some glauberite crystals, notably in the nodular and enterolithic facies, suggests that they may also in part be replacive, although this is difficult to confirm petrographically. The transformation of glauberite to anhydrite is more common than the reverse.

Polyhalite

Polyhalite ($K_2MgCa_2(SO_4)_2 \cdot 2H_2O$) is associated with gypsum, carbonate, glauberite and halite. It occurs mainly as a banded or laminated facies. Laminae (mm) and bands (cm) usually display dark colors and undulatory structures (Fig. 9A). These facies were formed by replacement of fine-grained primary gypsum, containing carbonate and glauberite. Thus, pseudomorphs of gypsum and/or glauberite are common (Fig. 9B), especially where carbonate matrix is abundant. As an early diagenetic mineral, polyhalite grew as laminae or bands interstitially within the microcrystalline carbonate that is commonly interlaminated with gypsum. Polyhalite also occurs with halite, especially along halite crystal boundaries (Figs. 10A, B).

The polyhalite always occurs as acicular to fibrous crystals arranged in spherulites (Figs. 10C, D). In size, the spherulites vary from 200 μm to 2 mm, the largest of which are visible to the naked-eye (Fig. 9C). Where polyhalite is microcrystalline, massive and very pure, it is difficult to distinguish from the fine-grained secondary varieties of gypsum.

Halite

Halite (NaCl) forms beds centimeters to decimeters thick interbedded with laminated gypsum. No major salt layers (i.e., tens of meters thick) are known in the Lerín Formation. This differs from other non-marine evaporite formations precipitated in the Tertiary Ebro Basin, such as the Falces Formation (Salvany, 1989a) or the Zaragoza Formation (Ortí and Pueyo, 1977), where thick halite beds are well developed.

The halite texture is made up of millimeter to centimeter-size subhedral crystals. Hopper fabrics, with zoned growth patterns marked by small fluid inclusions, are frequently observed. As mentioned, inclusions of anhydrite and polyhalite crystals are common.

Magnesite and Dolomite

Magnesite ($MgCO_3$) and dolomite ($CaMg(CO_3)_2$) occur as homogeneous micritic host-sediments for the sulfate minerals, but also form massive or laminated beds, a few centimeters thick. We have found only magnesite associated with glauberite or polyhalite, whereas dolomite may accompany any sulfate mineral.

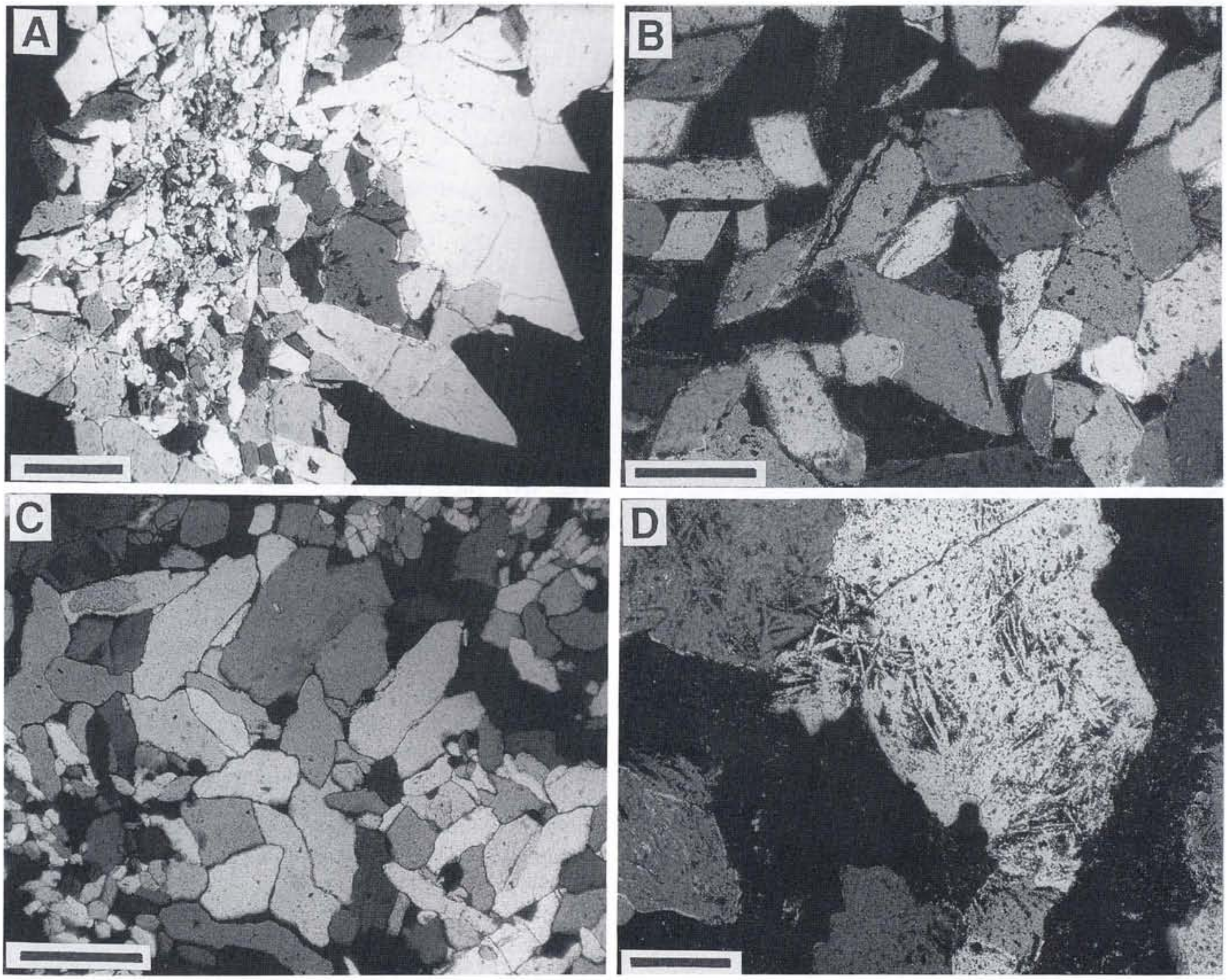

FIG. 8.—Textural varieties of glauberite: (A) nodular glauberite displaying crystalline fabric composed of a fine-grained core and a coarse-grained external rim with crystals arranged perpendicular to the margin (scale bar= 1 mm), (B) euhedral zoned glauberite crystals grown within abundant clayey matrix (dark) (scale bar= 500 μm), (C) sub- to anhedral glauberite fabric displaying interpenetrant crystal contacts (scale bar= 500 μm), and (D) poikilotopic (anhedral) glauberite crystals preserving pseudomorphs of precursor polyhalite texture (scale bar= 300 μm).

Clays

In the Lerín Formation, the detrital sediments of each evaporite cycle are commonly reddish, while muds associated with the chemical sediments are generally gray. Detailed analysis of the clays has not yet been undertaken, although existing data (mainly by X-ray diffraction) suggest a rather homogeneous mineralogy. The clays are mostly illite and chlorite with subordinate kaolinite. Dolomite is the ubiquitous carbonate accompanying these clays.

GENESIS OF THE EVAPORITE DEPOSITS

Sedimentary and Early Diagenetic Processes

In the sedimentary environment, mineral phases formed in two distinct settings: (1) as chemical precipitates in the lake and (2) by intrasedimentary growth from phreatic or vadose water, either around the lake margins or in the central part of the lake during periods of desiccation (Fig. 11). In the first setting, carbonates, gypsum and halite were precipitated. In the second setting, a wide range of primary and secondary diagenetic minerals formed, whose origins are related directly to the chemical evolution of the interstitial brines, and to the reaction of these brines with some of the previously formed minerals.

The distribution and the origin of the evaporites can be best explained by an ephemeral saline lake or playa-lake model (Fig. 12). We distinguish three zones that grade laterally into each other: (1) an inner or central zone, normally covered by lake brine; (2) an intermediate lacustrine zone that periodically desiccates; and (3) a marginal zone or sa-

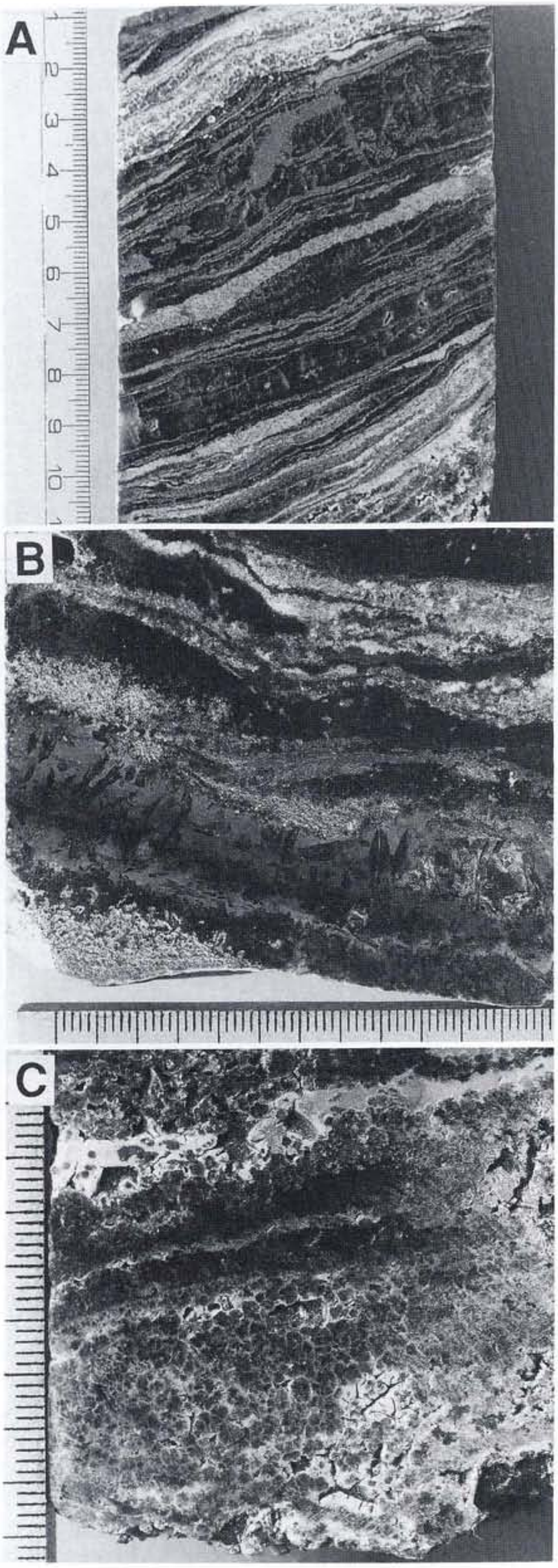

FIG. 9.—Polyhalite facies: (A) laminated polyhalite (scale in cm), (B) polyhalite pseudomorphs after glauberite in laminated polyhalite facies (scale in mm), and (C) spherulites of polyhalite with carbonate matrix (scale in mm).

line mudflat with phreatic saline groundwater, that is only occasionally flooded by the lake.

Fundamental to this model is the presence of a gradient in groundwater salinity, increasing from the lake margins toward the basin center. The same trend is shown by the subaqueous precipitates, although they reflect the alternate dilution (lake expansion) and evaporative concentration (lake retraction) of the lake brine. The sequence of precipitation would be: carbonate → gypsum (+ anhydrite) → glauberite → halite (+ polyhalite).

During phases of lake expansion and less saline water, the less soluble minerals (carbonates, primary gypsum) precipitated together with some diagenetic anhydrite. During periods of lake retraction or desiccation when the brine was highly saline, the most soluble minerals formed (primary halite; diagenetic glauberite and polyhalite). Alternating lacustrine and interstitial (phreatic) evaporite facies reflects the ephemeral nature of the saline lake. The fluctuations in lake level were a response to intermittent surface recharge, while the groundwater flow might have been almost constant.

Our petrographic study of the sulfates shows that some mineral sequences developed contrary to those expected by progressive evaporation. These can be termed retrodiagenetic, even though they may also have occurred during early diagenesis. Thus, polyhalite may be replaced by glauberite and/or anhydrite (Figs. 5A, 10A) and glauberite may be replaced by anhydrite (Fig. 5B). Such replacements are normally incomplete. They may result from brine dilution and associated reactions with pre-existing sulfate minerals, eventually producing new phases of lower solubility. This could occur, for example, when brines are diluted by surficial runoff flowing into the lake.

Late Diagenetic Processes

The Lerín Gypsum Formation was buried to more than 500-m depth, resulting in the transformation to anhydrite of all gypsum that had survived early diagenesis. For the primary gypsum, this late diagenetic process was conservative and their original facies were preserved. Mineral phases other than gypsum lack evidence of any significant mineralogic transformation due to burial.

Exhumation of the Lerín Gypsum Formation produced important changes in the sulfate minerals both at the surface, and in near-surface zones affected by groundwater. Anhydrite, glauberite and polyhalite were altered to secondary gypsum. This process also appears to have been conservative (i.e., isovolumetric) because all precursor facies, both sedimentary (microbial laminations, wave ripples, etc.) and early diagenetic (enterolithic layers, etc.) have been perfectly preserved. The evidence from the cores shows that the hydration zone extends a depth of several tens of meters (but less than 100 m), below which all sulfates remain unaltered.

DISCUSSION

The mineralogic assemblage in the Lerín Gypsum Formation suggests that the lake water was dominated by Ca^{2+},

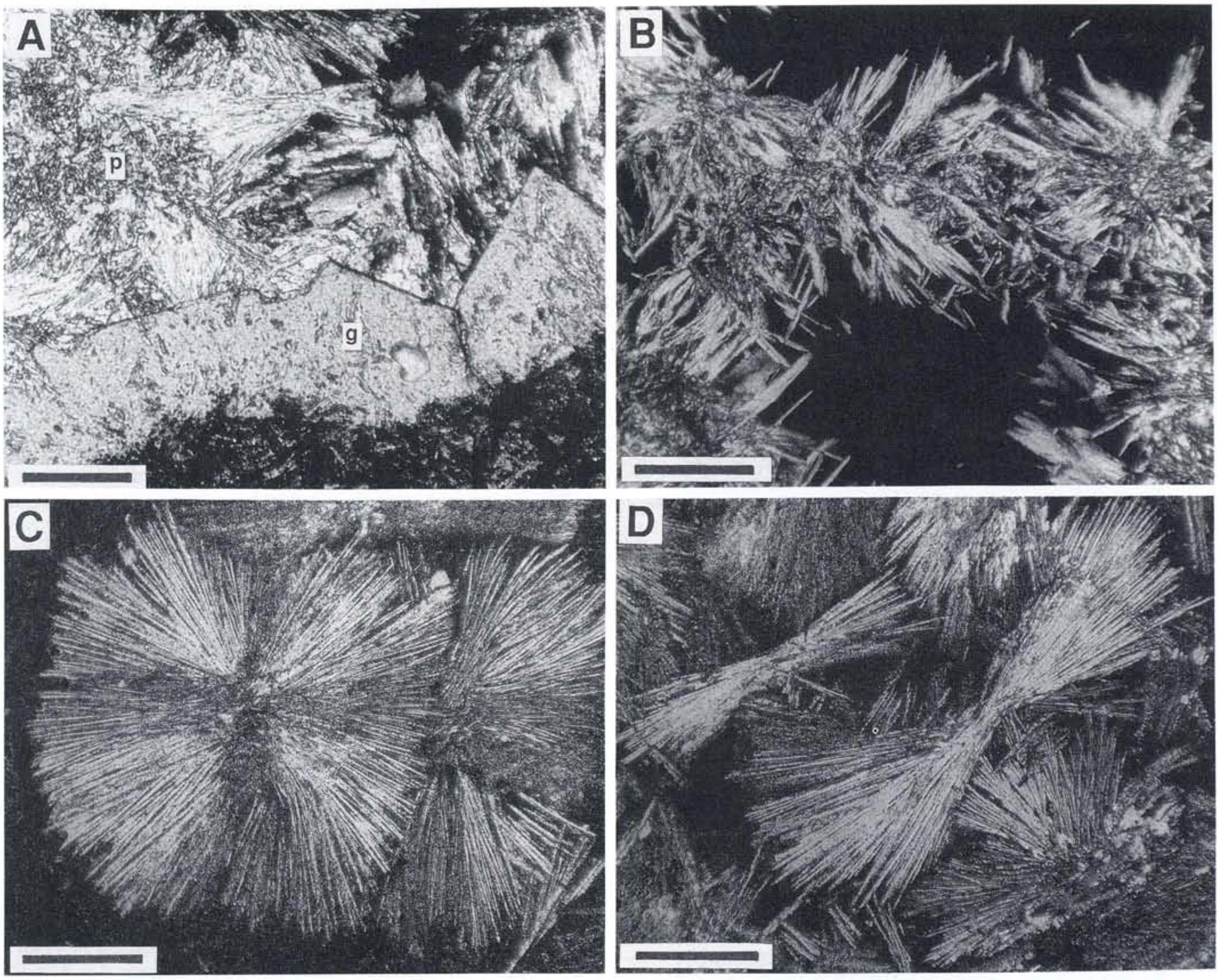

FIG. 10.—Polyhalite textural varieties: (A) glauberite crystals (g) partly replacing a polyhalite fabric (p) (scale bar= 200 μm), (B) polyhalite prisms growing along crystal boundaries of halite (dark) (scale bar= 500 μm), (C) spherulitic aggregates of polyhalite (scale bar= 500 μm), and (D) sheaf-shaped aggregates of polyhalite (scale bar= 500 μm).

Na^+, SO_4^{2-}, and Cl^-. Sulfate was the dominant anion, since sulfate minerals precipitated from the earliest stages of evaporation (gypsum, anhydrite) until the final most concentrated brine (glauberite and polyhalite paragenetic with halite). Carbonates are subordinate to sulfate, suggesting that HCO_3^- and CO_3^{2-} were less important that the other anions in the lake waters. Small amounts of Mg^{2+} and K^+ were also present, as shown by the occurrence of dolomite, magnesite and polyhalite.

After the initial precipitation of carbonate minerals (calcite or aragonite?), early evaporative concentration led to major precipitation of gypsum and anhydrite, causing significant loss of Ca^{2+} and SO_4^{2-} from the waters. Further brine evolution resulted in precipitation of glauberite and possibly Na-sulfates (thenardite, mirabilite) that were not preserved. In the final stages of evaporation halite precipitated, with small amounts of polyhalite. This partly depleted the residual brine in K^+ and Mg^{2+}, and completely removed remaining Ca^{2+}.

The increasing Mg^{2+} content of the brine changed all carbonate precursors into dolomite and magnesite. However, interstitial growth of magnesite in highly concentrated brines is also possible (Pueyo and Inglés, 1987). Although pure Na-sulfates (mainly thenardite) have not been found in the Alcanadre deposits, thenardite is present in other formations of the Ebro Basin (e.g., Zaragoza Formation: Mandado, 1987) and the Tajo Basin (Ortí and others, 1979). Although Ca^{2+} in polyhalite could be supplied mainly from the diagenetic replacement of former Ca-sulfates, the presence of beds of spherulitic polyhalite lacking pseudomorphs suggests direct precipitation from brines that retained some Ca^{2+}.

Thus, from the mineral paragenesis and diagenetic alteration observed in these deposits, the inferred hydrochem-

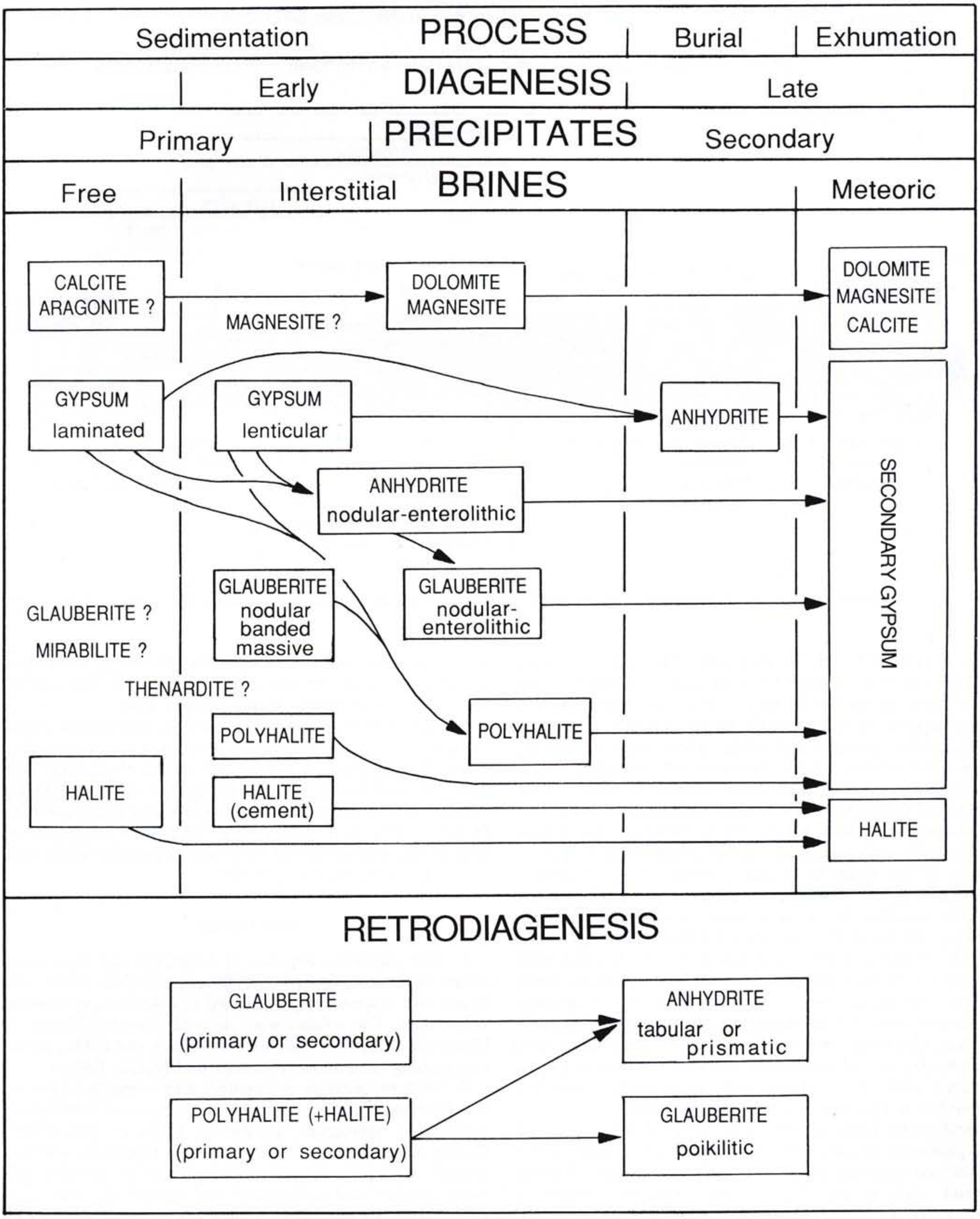

FIG. 11.—Summary of the diagenetic evolution of the glauberite deposits of Alcanadre.

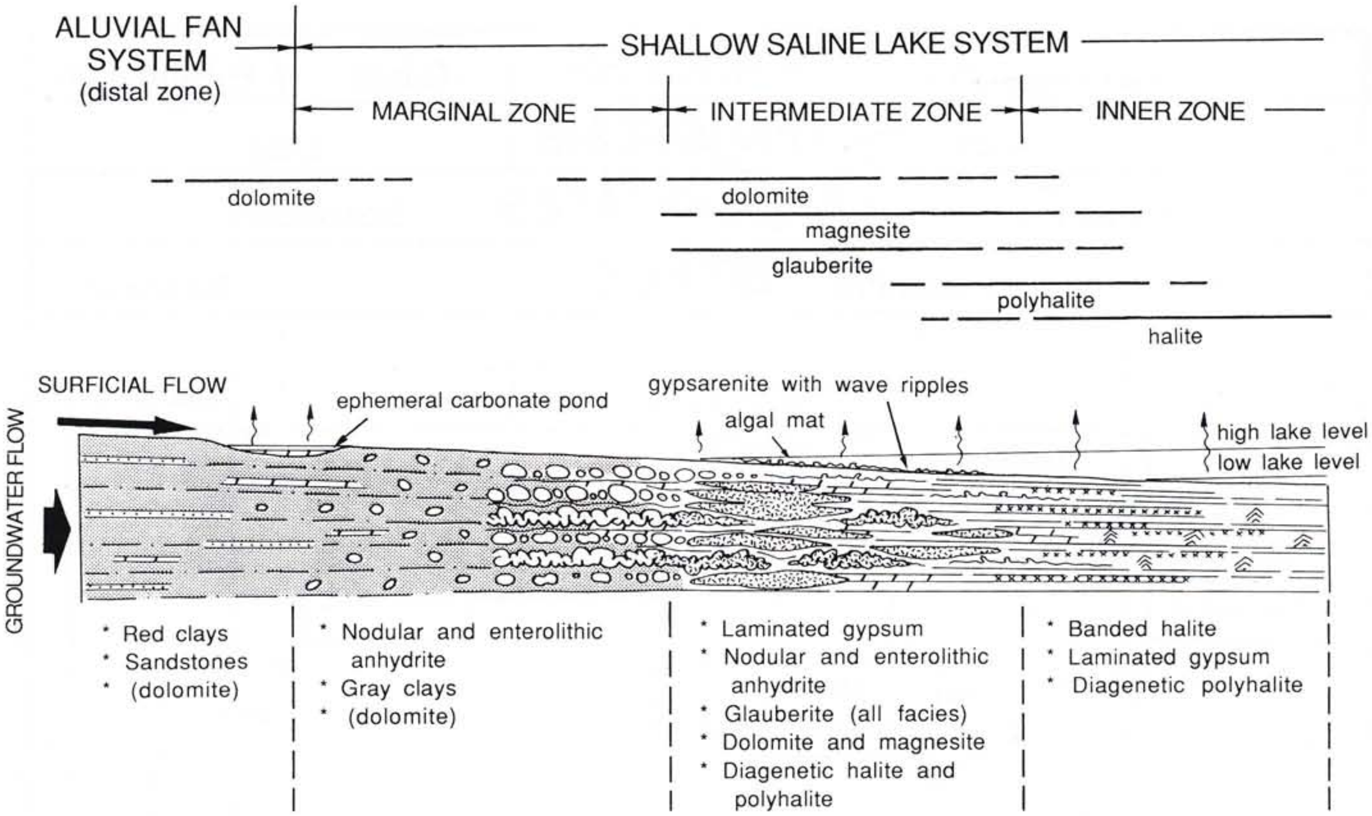

FIG. 12.—Sedimentological model for deposition of the Alcanadre glauberite deposits showing facies arrangement and evaporitic environments.

istry is in accord with the expected composition of major solutes that were drained from the marginal ridges of the Ebro Basin during the Tertiary. Significant Mesozoic evaporite deposits are present in the former source areas, mainly as anhydrite, gypsum and halite, which may explain the ionic trend of lake waters. This chemical recycling mechanism is also supported by stable isotopic evidence (Birnbaum and Coleman, 1979; Utrilla and others, 1991).

Glauberite has been reported from Holocene non-marine saline lakes with brines of similar composition to that inferred in this study in several countries (e.g., Australia, China, U. S. A., Canada, etc.). However, detailed petrographic descriptions of the mineral occurrence are usually lacking. Of particular relevance are the studies by Hardie (1968) of Saline Valley (California, U. S. A.) and more recently by Arakel and Cohen (1991) on the Karinga Creek playas (Amadeus Basin, Australia). In both examples, glauberite forms a significant part of the evaporite deposits of these playa-lake systems, having grown interstitially from the phreatic or vadose brine at the lake margins and is associated with other sulfates such as gypsum, thenardite, mirabilite or epsomite, as well as with halite.

Arakel and Cohen (1991) gave detailed descriptions of the glauberite textures in the Karinga Creek system, which developed either as primary or secondary phases. Primary crystals grow in the phreatic zone displacing the detrital host sediment, producing nodular aggregates and lenticular beds of glauberite. In the vadose zone, glauberite crystals grow in the same manner, but some are of secondary origin and display rim and poikilotopic textures on gypsum crystals that have been partially or totally replaced. The salinity of the interstitial brines attains 300 g/l TDS.

Polyhalite is less frequently cited in non-marine saline lakes than in ancient formations or recent coastal evaporitic lakes. Nevertheless, it is common in the continental Tertiary basins of Spain, where it always has the same textural features and a diagenetic origin (Ortí and Pueyo, 1980). Holser (1966) described similar diagenetic polyhalite in coastal Baja California that grew from interstitial brines with a salinity of almost 400 g/l TDS.

CONCLUSIONS

1. The glauberite deposits of Alcanadre and their associated minerals (gypsum, anhydrite, polyhalite, halite, dolomite and magnesite) precipitated in a shallow, ephemeral saline lake. The solutes were derived from dissolution of Mesozoic evaporites, mainly Ca-sulfates and halite, in the surrounding mountains (Pyrenees and Iberian Ridge).

2. With progressive evaporative concentration of the saline lake brine, the precipitation sequence was: carbonates, gypsum (+ anhydrite), glauberite, halite (+ polyhalite). During stages of low salinity and lake expansion, the less soluble minerals precipitated on the floor of the lake (primary gypsum and carbonates) and around the lake (diagenetic nodular anhydrite). During more saline stages with lake contraction or desiccation, the most soluble minerals grew mainly in saline mudflats surrounding the lake (dia-

genetic glauberite and polyhalite). Thin halite beds formed in the lake before desiccation.

3. The petrographic study shows that in many cases anhydrite, glauberite and polyhalite are secondary minerals. The alteration occurred during early diagenesis. Brines reacted with solid precursor phases by two main methods: (1) reaction of concentrated brines with solid phases precipitated during stages of low salinity (e.g., anhydrite altered to glauberite; glauberite altered to polyhalite) and (2) reaction of dilute brines with solid phases precipitated in stages of higher salinity (e.g., glauberite altered to anhydrite; polyhalite altered to glauberite or anhydrite).

4. Burial and exhumation produced further mineral transformations. With burial, gypsum altered to anhydrite. With exhumation, anhydrite, glauberite and polyhalite altered to secondary gypsum.

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