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Glauberite Deposits of the Lerín Formation (Lower Miocene: Alcanadre Zone, La Rioja-Navarra)

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During the late lower Miocene the Alcanadre-Arrúbal area (La Rioja) received deposition of considerable amounts of glauberite within the Los Arcos unit of the Lerín Formation (see figures 13.1 and 13.4, this volume). In these sediments, the mineralogic paragenesis consists of gypsum-anhydrite, glauberite, polyhalite, halite, and magnesite, and the gypsum is always secondary. No indication of the presence of thenardite or mirabilite exists, as is usual in many other deposits of this type in ancient evaporite formations and many modern lakes.

Glauberitic deposits (or beds) are also known in some other continental evaporites of the Ebro Basin, both in Oligocene and Miocene sediments. In all these deposits the glauberite beds are always associated with the thickest gypsum horizons and are located in the paleogeographical centers of the basins. In general these sediments tend to crop out in unfavorable exposures (steep slopes with collapse structures) having little additional exposure in the third dimension. It is difficult to estimate their volumetric importance but based on borehole evidence they are ubiquitous in the subsurface.

The glauberite deposit of Alcanadre-Arrúbal has been known for a long time and has been discussed in the literature by numerous authors (Rios 1963; Riba 1964; Ortí et al. 1979; Ordoñez et al. 1982; Ortí et al. 1986b; Ortí and Salvany 1986b; Salvany and Ortí 1987, 1994; Salvany 1989). The glauberite is seen clearly in the cliffs along the Ebro river where the whole unit crops out (Los Arcos Unit) and is up to 200 m thick. It consists of a monotonous gypsiferous sequence, with argillaceous intercalations, in which several glauberite layers are particularly well-developed at the base of some of the thickest gypsum horizons. In this outcrop four main glauberite layers are noticeable ranging from 2 to 4 m in thickness. There are many other thinner beds as well. The principal layers were exploited in the past, although today the mines at this site are abandoned (figure 14.1). In 1983 and 1984, Unión Salinera de España S.A. drilled four boreholes with continuous coring: the Alcanadre-1 (118 m deep), Rioja-1 (112 m), Rioja-2 (85 m), and Rioja-3 (109.5 m). All the boreholes cut through several layers of glauberite, halite, and polyhalite in the Los Arcos Unit. These layers have been studied petrographically and are reported here.

Petrography

GLAUBERITE

Glauberite is mainly made up of nodular and/or enterolithic lithofacies in beds 10 to 30 cm thick (figure 14.2A and B). These beds are intercalated between the gypsum layers and may also occur in

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Fig. 14.1. Glauberite beds (white) intercalated within the laminated gypsum portion of the Los Arcos Unit (Lerín Formation). The Alcanadre deposit (La Rioja).

groups of beds, creating glauberite horizons meters thick. Much less commonly the glauberite lithofacies is banded and massive, with cm-thick tabular beds in which large crystals of glauberite are present (up to 1 cm). These contain variable amounts of clayey matrix with a reddish or gray tint. On the surface all these beds weather to a white powder of sodic sulfate composition. Usually, glauberite in the nodular, banded and massive lithofacies is coarsely crystalline (from less than 1 to 15 mm), with sub- to euhedral habits. Very fine-grained glauberite textures (30 to 500 microns) are also present.

Under the microscope the glauberite shows an unoriented fabric with typical rhombohedral sections (figure 14.3A), approximately interpenetrating, and some calcareous or clayey intercrystalline matrix. In some samples there is marked interpenetration, and the glauberite exhibits an almost anhedral, equigranular fabric (figure 14.3B). The petrographic study reveals the existence of three genetic varieties of glauberite:

1. *"Primary" (interstitial) glauberite.* In this variety the crystals apparently nucleated and grew directly from a brine within a soft host sediment of calcareous or clayey nature. Growth is displacive and may pass into nodular, enterolithic, and also banded lithofacies.
2. *Secondary glauberite.* This variety of glauberite forms by the interstitial brine reaction with a calcium-sulfate precursor mineral (anhydrite and/or gypsum) in a very early stage of diagenesis. Relic anhydrite inclusions are commonly present within the glauberite. However primary gypsum relics within these glauberite crystals have never been found.
3. *Poikilitic secondary glauberite.* In this variety, large anhedral glauberite crystals replaces polyhalite poikilitically (figure 14.3E). In the process polyhalite pseudomorphs (spherulites) are well preserved. This variety of glauberite develops in a relatively more advanced stage of the early diagenesis than type 2. This is because polyhalite is itself a secondary mineral, and comes from the early replacement of the earlier types 1 and 2 of the glauberite facies. This replacement sequence is relatively simple to recognize because pseudomorphs of both polyhalite and glauberite are noticeable when studying poikilitic glauberite under plane polarized light (figure 14.3F).

POLYHALITE

Polyhalite (figure 14.2C and D) frequently displays a laminated lithofacies inherited from primary gypsum, early diagenetic anhydrite, or glauberite

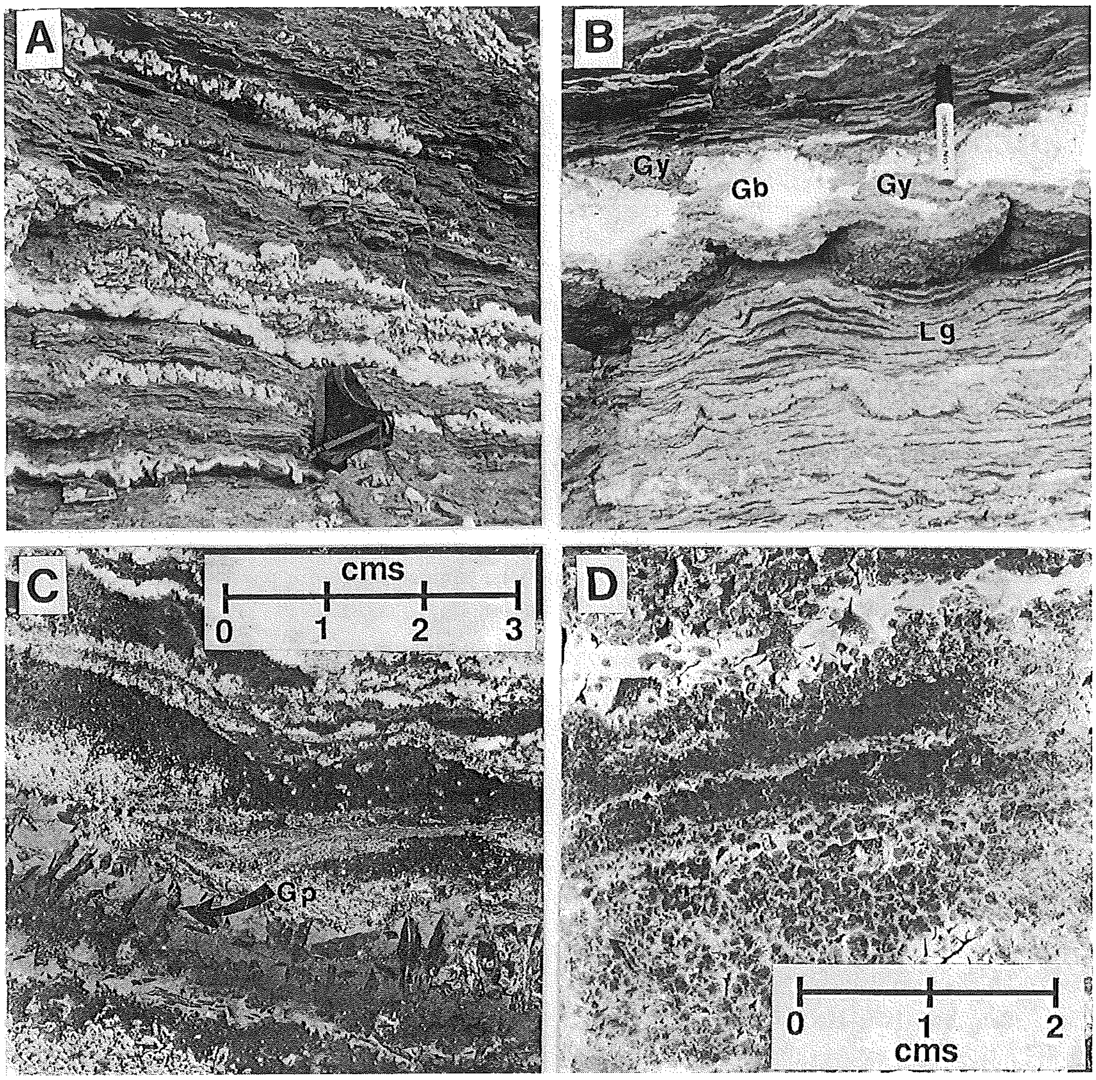

Fig. 14.2. Evaporative lithofacies of the Lerín Formation. A. Nodular and enterolithic layers of glauberite (white) alternating with laminated gypsum horizons (gray) in Los Arcos Unit. Alcanadre deposit. B. Detail of a nodular layer of glauberite (Gb) which has been partially replaced by secondary gypsum (Gy) from the borders towards the center of the layer. Original lithofacies has been strictly preserved. Lg = laminated gypsum layers. C. Detail (polished slab of a core sample) of pseudomorphs (Gp) of polyhalite after glauberite, in a level of laminated polyhalite. D. Detail of a spherulitic layer of polyhalite (polished slab of a core sample). Individual spherulites reach up to 1–2 mm and are distributed within an abundant calcareous (magnesite) matrix.

Fig. 14.3. Photomicrographs of microstructures found in the evaporites of the Alcandre deposits. A. Primary fabric in glauberite, composed of very characteristic rhombohedral sections of glauberite crystals, with abundant carbonate matrix (gray-black). B. Secondary crystals of glauberite bearing relic inclusions of anhydrite. C. Halite crystals displaying polyhalite replacement on their borders (see arrow). D. Spherulitic polyhalite. E. Polyhalite layer (Ph), partially replaced (retrodiagenetically) by tabular anhydrite crystals (Ah) and by anhedral poikilitic glauberite (Gb). F. Spherulitic polyhalite pseudomorphs after an idiomorphic glauberite precursor (central part of figure); at present all is secondary glauberite that replaced polyhalite in retrodiagenesis.

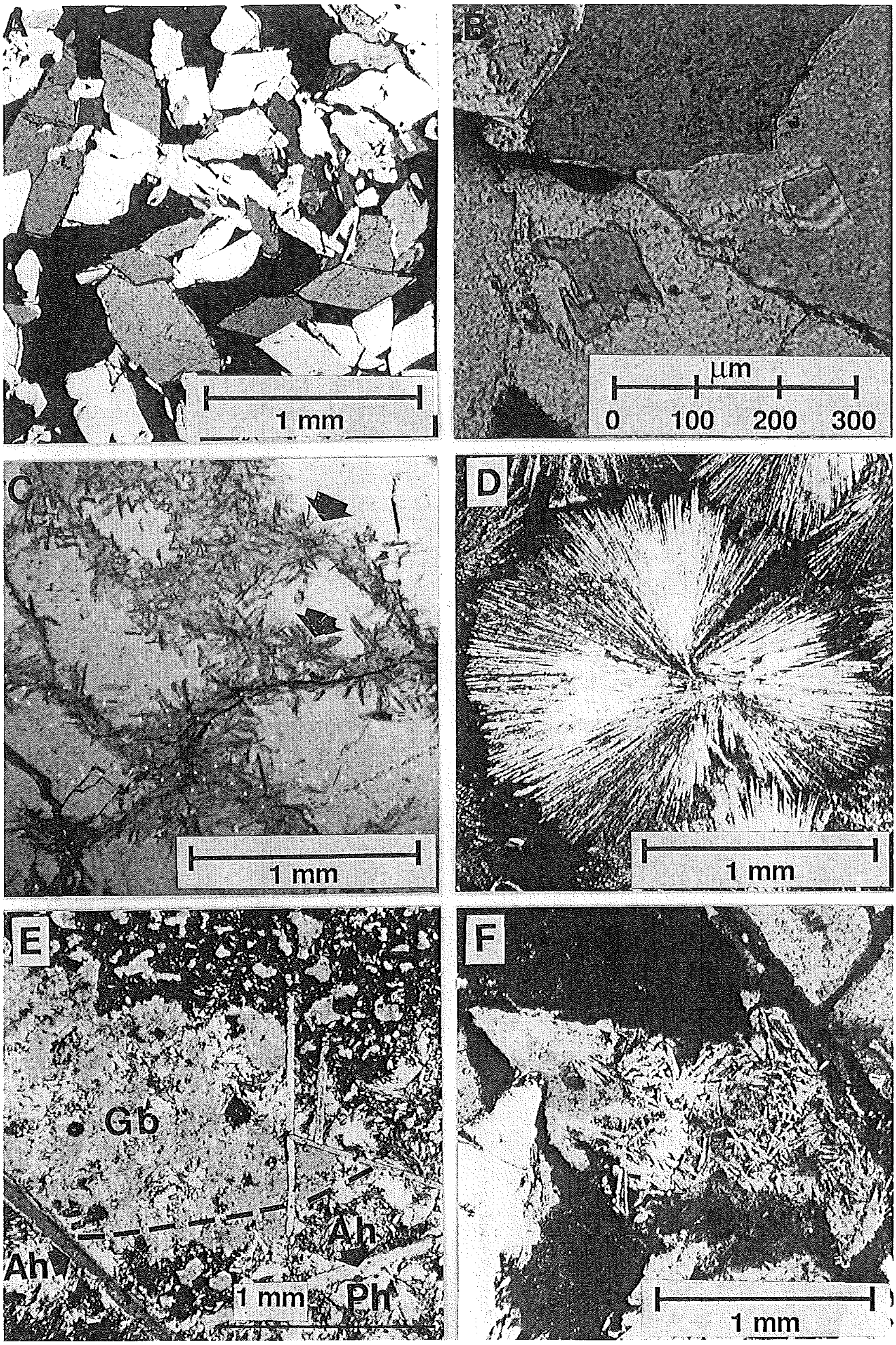

Fig. 14.3

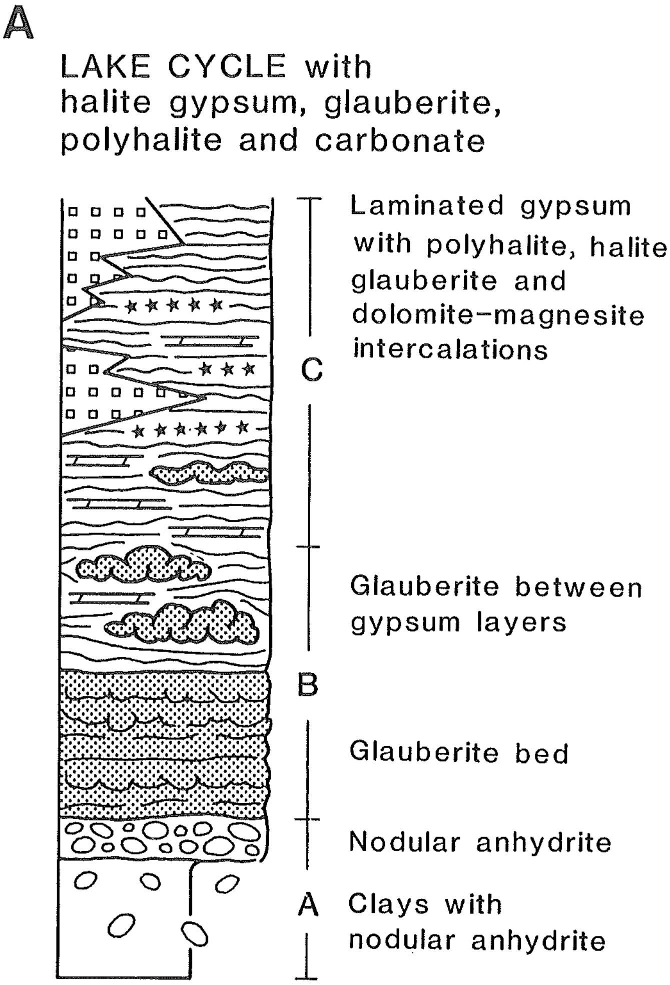

Fig. 14.4. A. Evaporitic cycle as recognized within the Alcanadre glauberite deposit of the Lerín Formation (from outcrop data). B. Interpretative playa lake environment during a single depositional stage, developed from the facies distribution in the Los Arcos Unit (Lerín Formation). Notice that the development of facies from the margin to the playa center parallels that of figure 13.10 (this volume) but is mineralogically different (Salvany and Ortí 1994).

lithofacies (types 1 and 2), and commonly all these minerals are preserved as pseudomorphs of polyhalite. The fabrics observed are fibrous and spherulitic, with sizes between 200 microns to 1 or 2 mm (figure 14.3C). In some instances the spherulites grow within a carbonate matrix without any apparent mineral precursor, or as a cement in cavities. The development of the polyhalite is mainly related to the halite precipitation. It is common to observe both minerals growing paragenetically within a single layer (figure 14.3D).

MAGNESITE

Magnesite is the carbonate mineral usually accompanying glauberite and polyhalite. It always displays a micritic texture.

Genesis of the Glauberite Deposits

To explain the origin of the glauberite deposits two different processes which have operated simultaneously must be take into account:

SEDIMENTARY PROCESSES

Glauberite layers are always related to the main gypsiferous horizons in the various units of the Lerín as well as in the Los Arcos Formation. Usually such layers developed towards the base of thick, laminated gypsum horizons, and the following idealized sequence apparently developed (from several meters to several tens of meters thick). From base to top the sequence is made up of the following components (figure 14.4A):

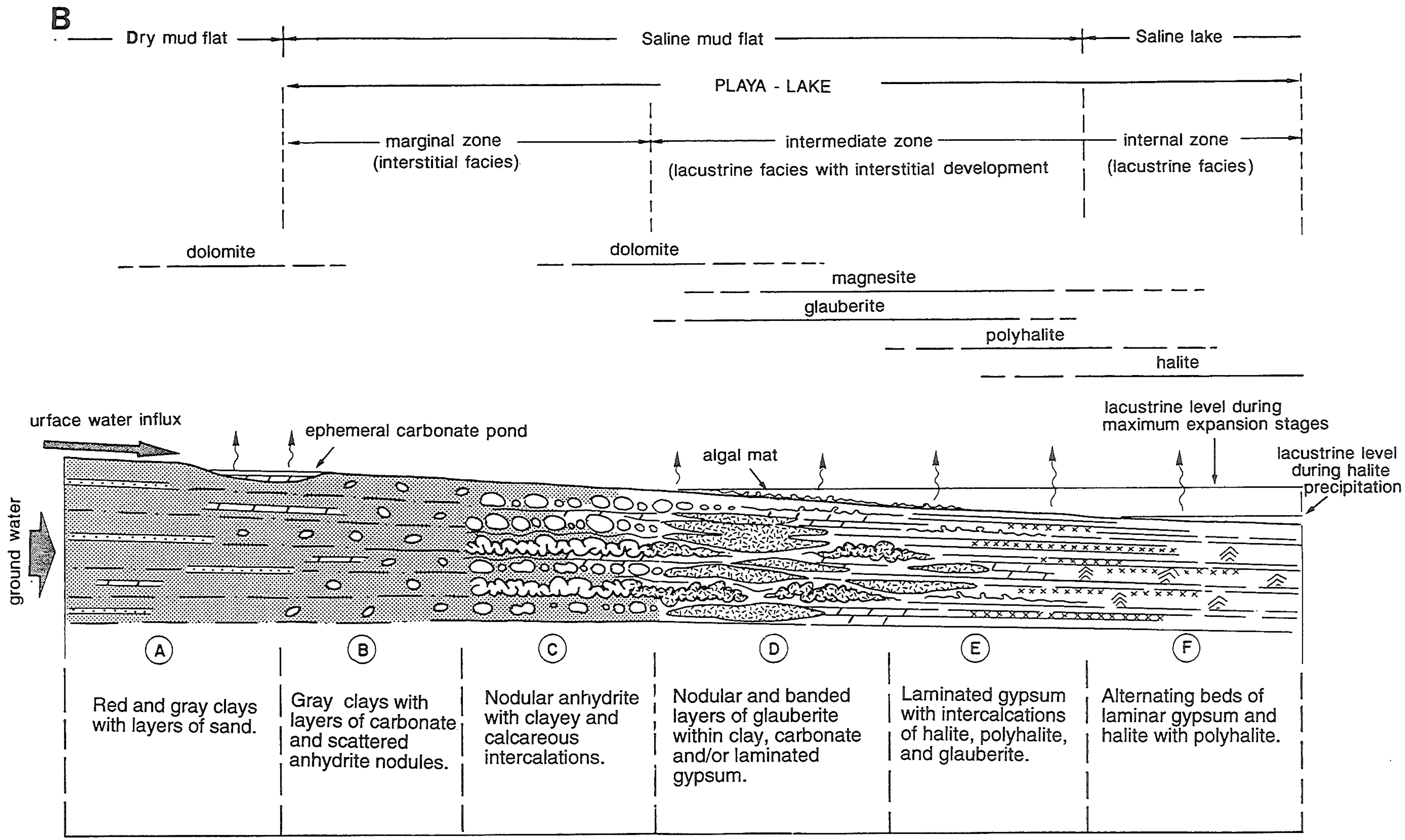
B
Dry mud flat
Saline mud flat
Saline lake
PLAYA - LAKE
marginal zone
(interstitial facies)
intermediate zone
(lacustrine facies with interstitial development
internal zone
(lacustrine facies)
dolomite
dolomite
magnesite
glauberite
polyhalite
halite
urface water influx
ephemeral carbonate pond
algal mat
lacustrine level during maximum expansion stages
lacustrine level during halite precipitation
ground water
A
Red and gray clays with layers of sand.
B
Gray clays with layers of carbonate and scattered anhydrite nodules.
C
Nodular anhydrite with clayey and calcareous intercalations.
D
Nodular and banded layers of glauberite within clay, carbonate and/or laminated gypsum.
E
Laminated gypsum with intercalcations of halite, polyhalite, and glauberite.
F
Alternating beds of laminar gypsum and halite with polyhalite.

FIG. 14.4B

(A) *argillaceous lower horizon* containing thin sandstone beds at the base and gypsum nodules at the top. Some carbonate beds can also be intercalated within the argillites.

(B) *glauberite intermediate horizon* is a glauberitic horizon up to a few meters thick, in which several glauberitic lithofacies may alternate. Usually, however, a banded lithofacies is developed within the lower part just above the argillite, and layers of nodular and enterolithic glauberite occupy the central and upper part of the horizon.

(C) *gypsiferous-chloride upper horizon* displays both laminated and laminated-nodular gypsum lithofacies. Individual layers of nodular or enterolithic glauberite and banded halite are intercalated within the laminated gypsum. Some carbonate laminae may alternate with the gypsiferous ones. Individual crystals of glauberite, arranged in single layers, may also be present within the gypsum laminae. It is mainly in such zones that polyhalite is developed, replacing both the laminated gypsum and the nodular glauberite, and halite as well. This C horizon is the thickest one, reaching 10 to 40 m or more.

This sedimentary cycle, composed of the A, B, and C lithofacies, constitutes a very restricted stage of evaporitic development. Facies distribution in this highly concentrated playa lake is composed of concentric depositional belts similar to that in the evaporitic lake setting. The detailed relationship of the various facies belts that are to be found in one of these glauberitic lakes is illustrated in figure 14.4B.

DIAGENETIC PROCESSES

Brine evolution has played a fundamental role in the development of these saline lakes. Mineral phases originated either as primary precipitates from the brines or as secondary minerals, the latter being a reaction product between the interstitial brine and a mineral precursor. In the first case the precipitation would be a free growth on the lake floor, commonly the case for gypsum and halite. Intrasedimentary crystallization is the case for all the other sulfates, but only in part for gypsum and halite.

Under progressive evaporation conditions, with increasing ionic concentration the mineral sequence of precipitation commonly follows this pattern: (1) carbonates → (2) gypsum (+ anhydrite) → (3) glauberite (+ gypsum/anhydrite) → (4) halite (+ glauberite, + anhydrite, + polyhalite).

1. *Carbonate* precipitates from slightly concentrated brines, probably as calcite or aragonite. The reaction of these phases with the interstitial brines would cause progressive alteration to dolomite and magnesite.
2. *Gypsum* precipitates within shallow lakes as small crystals (gypsiltites or gypsarenites), forming laminar lithofacies. In the border zones of the basins, coarse crystals of gypsum precipitate interstitially within previously existing sediments, within a clayey or calcareous host matrix. A part of this gypsum may be converted into anhydrite in very early diagenesis, giving way to nodular and enterolithic layers that alternate with the less altered laminar lithofacies.
3. *Glauberite* precipitates interstitially as variably sized idiomorphic crystals, either as a direct product or replacing both gypsum and anhydrite. It mainly displays nodular and enterolithic lithofacies. No certain evidence has been found to support a primary origin for the glauberite as a free-growth precipitate on a lake floor (such as competitive upward-directed crystalline fabrics formed in open water).
4. *Halite* precipitates during the highest brine concentration, either as a primary product or as a cement filling porosity in the sediments. In association with halite, sulfates such as glauberite also may precipitate. The sulfate polyhalite characterizes the chloride stage of these lakes, replacing any of the earlier minerals (gypsum, anhydrite, glauberite) and depleting the interstitial brines of potassium and magnesium.

Some retrodiagenetic processes take place when the brine of these lakes becomes diluted by rain or periods of flooding. Polyhalite is apparently replaced by poikilitic glauberite, as well as by anhydrite in phases of reduced concentration. Also glauberite may be replaced by anhydrite. If dilution progresses even further, glauberite crystals will dissolve, leaving casts that are later infilled and cemented (pseudomorphed) by halite or polyhalite in the next stage of concentration.

During burial the most significant diagenetic process seems to be the transformation of any residual primary gypsum into anhydrite.

Exhumation of lake deposits produces new diagenetic (late diagenetic) reactions. The most important is the replacement of any sulfate (not only anhydrite) by secondary gypsum. If the process takes place slowly and in the subsurface, all replacement commonly occurs isovolumetrically, and pseudomorphs of precursor sulfates are clearly preserved in the secondary gypsum. But rapid hydration at the surface may destroy the most soluble minerals (halite, glauberite, polyhalite), and only anhydrite is replaced isovolumetrically by alabastrine or megacrystalline secondary gypsum. An example of replacement textures is illustrated in figure 14.2B, where a nodular layer of glauberite is being delicately replaced by secondary gypsum. It is also noted that in abandoned mine galleries the remaining glauberite layers may alter into secondary gypsum on exposed surfaces. In these near-surface mines the halite intercalations have already been leached away and are only present in the deeper boreholes.

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