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Epigenetic, low-temperature, carbonate-hosted Pb-Zn-Cu-Ba-F-Sr deposits in México: A Mississippi Valley–type classification

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ABSTRACT

The low-temperature epigenetic and stratabound Pb-Zn-Cu-Ba-F-Sr–bearing ore deposits enclosed within sedimentary columns historically have been major sources of metals. Exploration companies still find these deposits to be a profitable exploration target due to their simple mineralogy as well as the large tonnage that can present, always considering the mineral districts as a whole.

In northeastern México, several nonmagmatic, low-temperature Pb-Zn-F-Ba deposits have been systematically considered as magmatic-related (skarns, high-temperature replacement deposits, epithermal deposits, etc.). Recently, these deposits

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have been restudied and placed within a scenario of deep fluid circulation of basinal brines through the Mesozoic sedimentary series, enriched in Ba, F, and metals during fluid flow and water-rock interactions. These fluids gave rise to a series of strata-bound epigenetic ore deposits scattered throughout the whole Mesozoic carbonate platform and can be shown to be unrelated to any period of magmatism. There is no intense alteration to the host rocks. Commonly there is a close association with organic matter, either liquid hydrocarbons or bitumen; they have a very simple mineralogy of barite, celestine, fluorite, sphalerite, galena, and have low formation temperatures (90–105 °C) combined with variable salinities. These characteristics make these deposits similar to the Mississippi Valley–type deposits, possibly most similar to the Alpine-Appalachian subtype.

Keywords: low temperature, carbonate-hosted, Mississippi Valley–type (MVT) deposits; geochemistry; México.

INTRODUCTION

The existence of Mississippi Valley–type (MVT) deposits in México has been largely unrecognized by Mexican ore geologists and mining companies until quite recently, even though these deposits first attracted attention at the end of the nineteenth century. This is partly because these deposits contain small amounts of base metals (e.g., El Diente, Nuevo León; Sierra Mojada, Coahuila), barite (Múzquiz, Coahuila), celestine (distrito de Cuatrociénegas, Coahuila) and/or fluorite (La Azul, Taxco, Guerrero: Tritlla et al., 2001; La Encantada-Buenavista, Coahuila: González-Partida et al., 2003; Tritlla et al., 2004a, 2004b), compared to precious metal deposits (skarn, epithermal) or the larger tonnage base metal deposits (sedimentary exhalative mineral deposits [sedex], volcanogenic massive sulfide [VMS]).

De Cserna (1989) was the first to suggest the presence of MVT deposits in his review of the geology of México, but this was mostly ignored by both the scientific and mining communities in México. Due to the omnipresence of Tertiary intrusive bodies that crosscut the whole of the Mesozoic series in the center and NE of México, the genesis of the MVT ore deposits has been confused with deposits linked with magmatism. The recognition of MVT deposits is important and requires a new assessment of the metallogenic processes that affected the Mesozoic carbonate platform series of central and NE México.

LOW-TEMPERATURE CARBONATE-HOSTED DEPOSITS IN MÉXICO

The vast majority of MVT deposits in México are located within the Mesozoic carbonate sediments outcropping in the states of Guerrero, San Luis Potosí, Coahuila, and Chihuahua (Fig. 1). Due to the lack of research on this type of ore deposition in México, some ore deposits previously classified as magmatic-related can, after reevaluation, probably be reassigned as MVT deposits, broadening their distribution in Mexican territory.

The MVT ore deposits in México are mainly stratabound and represented by barite-bearing, celestine-bearing, fluorite-bearing, and base-metal-bearing ore bodies, the latter always associated with a deep supergenic alteration that, eventually, transformed the whole of the primary sulfides into a secondary nonsulfide Zn-Pb deposit.

The better known deposits are located in the state of Coahuila. Their location is mostly controlled by the position of the paleogeographic structures—mainly basement highs, associated basins, the presence of evaporitic horizons and reefal formations, as well as regional faults (Puente-Solís et al., 2005). Based upon their main substance, these deposits present a marked basin-scale vertical zoning and distribution, probably reflecting the different mobility of the cations throughout the sedimentary pile as well as slightly different genetic mechanisms. The barite-bearing deposits are located in the lower part of the Mesozoic limestone series, enclosed mainly within the Kimmeridgian Olvido Formation and are occasionally reported within the Barremian limestones (Cupido Formation; Puente-Solís et al., 2005) (Fig. 2); Pb-Zn-bearing deposits are found scattered throughout the entire Mesozoic sequence (Fig. 2), even though the main deposits are found within the carbonates of the Cupido Formation, of Hauterivian to Aptian age. Similarly, celestine deposits are mainly located within platform limestones (Aurora and Acatita Formations) of Aptian to Albian age, and mixed fluorite-celestine and fluorite-dominated deposits are located near the top of the Mesozoic sedimentary succession, within the last limestone horizons (Georgetown and Del Rio Formations) of Upper Cretaceous age (Cenomanian; Fig. 2).

Stratiform Barite-Dominated Deposits

North of the state of Coahuila (NE México), a series of stratiform barite deposits appear enclosed within the Olvido Formation (Kimmeridgian). These barite "mantos" (flats) present a significant lateral extension (several hundred meters to some km) and a very constant thickness of between 1 m and 3 m. They are made up exclusively of high-purity microcrystalline barite, with minor amounts of calcite and, locally, barite-celestine (Barosa, 2004, personal commun.).

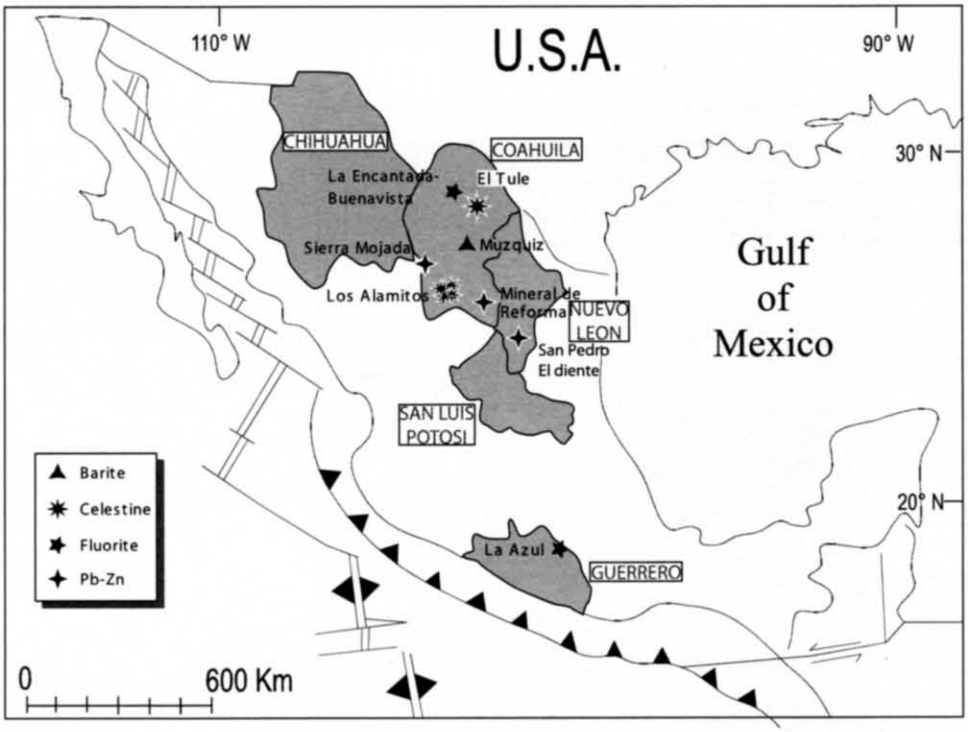

Figure 1. Location of the Mississippi Valley–type celestine, fluorite, and base metal deposits recognized in México.

The main stratiform bodies are mined near the town of Múzquiz (Coahuila). They consist of two stratiform to strata-bound barite mantos (Cocina and Potrero mines), vertically separated from each other by ~50 m, enclosed within the limestones of the Olvido Formation. Both the limestones and the barite horizons show concurrent folds produced during the Laramide Orogeny. This folding produces the partial obliteration of the barite horizons at the fold's hinge, as well as the generation of late fractures filled by coarse blocky calcite. It is noteworthy that the contact between the barite body and the enclosing limestone is always sharp (Figs. 3A and 3B) and marked by a pervasive discoloration zone a few decimeters thick, affecting the limestone. This color alteration grades from whitish at the contact to the original (non-altered) dark gray limestone (Fig. 3C), mainly reflecting the oxidation of the organic matter contained within the limestone due to the excess of sulfate during the barite formation. It has to be pointed out that both the barite and the fresh limestone are fetid (presence of H_2S).

In general, both barite horizons are composed of an isotropic mesh of fine grained, tabular crystals of barite. A close inspection reveals that the occurrence of these barite crystals is closely related to the pseudomorphosis of relic textures: (1) pseudo-stratification, marked by the disposition of residual minerals, mainly clays (Figs. 3A and 3B); (2) convolute surfaces, often boudinaged; (3) changes in the grain size or in the disposition of the pseudo-stratification from bottom to top of the mineralized body (Fig. 3D); (4) banded structures texturally similar to rythmites, made up by the disposition of white and dark barite bands that, occasionally, comprise the whole manto (Fig. 3E); and (5) the most revealing texture of all, globular accumulations of barite, with radial internal textures, with morphologies similar to the "chicken-wire" texture of anhydrite (Fig. 3F), typically from evaporitic series of gypsum that have undergone diagenetic dehydration and compaction. Also, the complete absence of cavities within the barite mass is notable. Locally, some thick calcite veins appear to be arranged close and parallel to the limestone contact within the barite horizon. These calcite veins predate the Laramide orogeny and seem to represent discrete zones of maximum fluid flow during the late stages of barite formation. This entire assembly is post-dated by some calcite veins that are closely related to the late folding and fracturing of the Mesozoic sediments.

Fluid inclusions in barite are scarce, small ($<10\mu m$) and are affected by post-trapping changes due to both the perfect cleavage of the barite and the deformation events. Homogenization temperatures (without pressure correction) for the Cocina mine are between 60 and 150 °C, suggesting that these fluid inclusions are affected by leakage. Homogenization temperatures in the Protrero mine have a smaller range of between 60 and 100 °C. In both cases, hydrohalite and ice melting temperatures indicate an electrolyte composition dominated by $CaCl_2$; the calculated total salinity is ~20–23 wt% with 18–22 wt% corresponding to $CaCl_2$ and 1–2 wt% to NaCl (E. González-Partida, 2004, personal commun.; Tritlla et al., 2005).

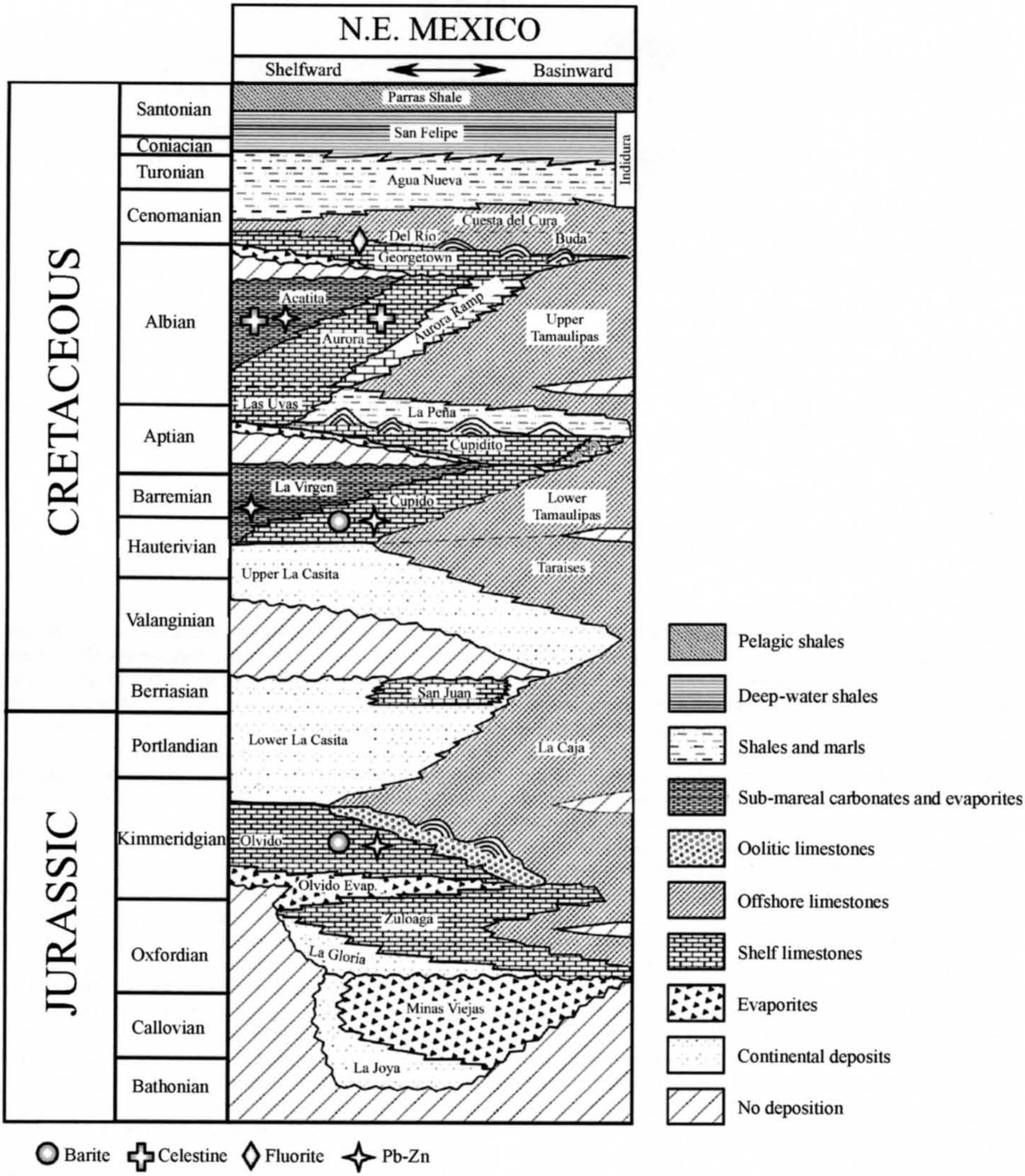

Figure 2. Chronostratigraphic table of the Mesozoic sediments in the NE of México with the position of studied stratabound deposits. Modified after Goldhammer (1999) and Puente-Solís et al. (2005).

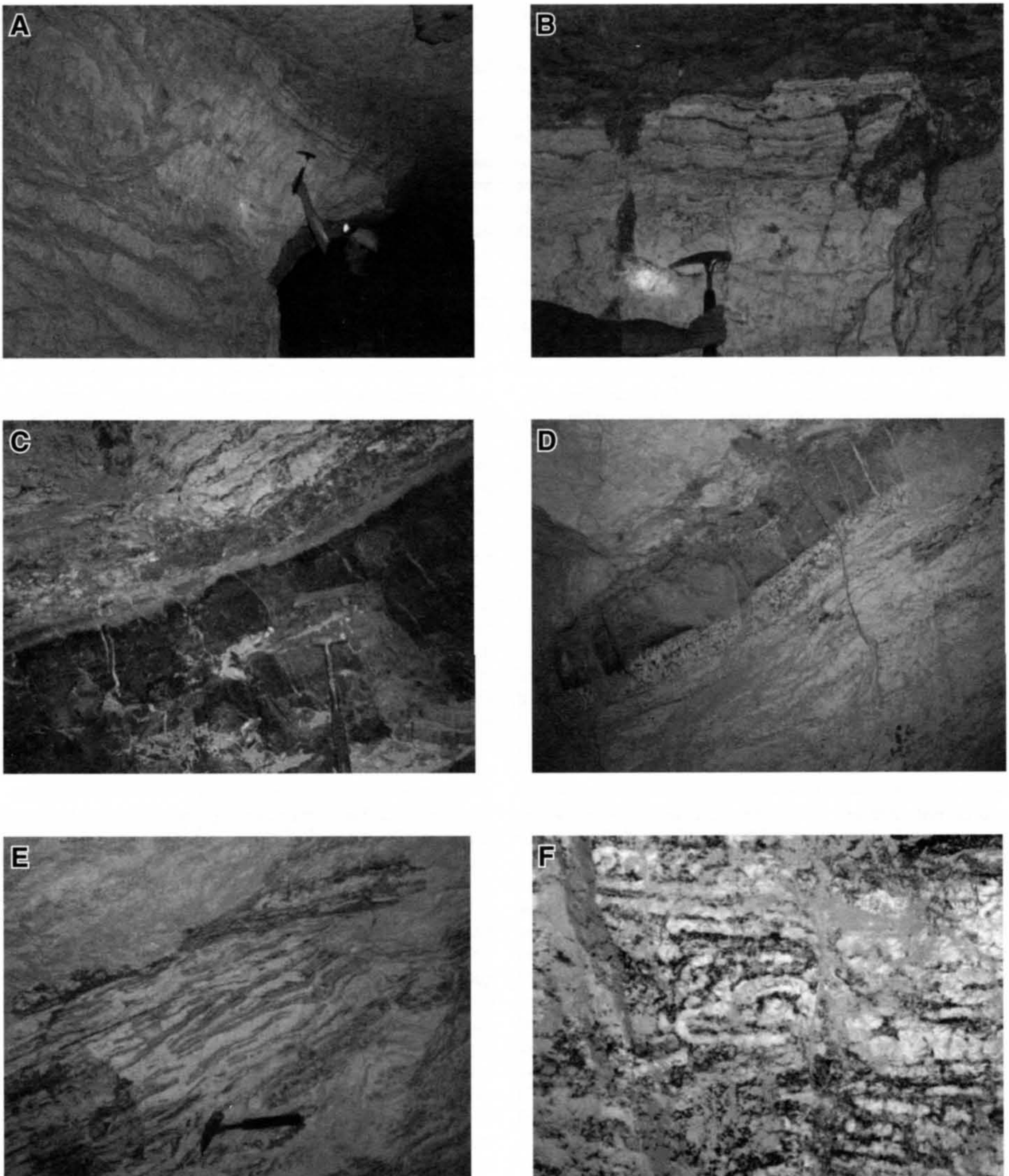

Figure 3. Barite deposits from Múzquiz (Coahuila). (A) General view of the stratiform barite manto, with the presence of rhythmites located both at the top and bottom of the body. (B) Detail of the barite rhythmites close to the contact with the enclosing limestone; this contact is disrupted by later fracturing. (C) Detail of the barite manto lower contact with the limestone; note the intense color alteration, several cm thick, affecting the limestone. (D) Limestone boulder within the barite manto; note the barite facies changing underneath the carbonate block with enterolithic textures, probably reflecting some primary diagenetic textures. (E) Detail of the "zebra" rhythmites developed in barite. (F) Remains of a clearly recognizable "chicken-wire" texture in barite, after anhydrite.

The stratiform character of the barite bodies, their diagenetic-like textures, and the omnipresence of organic matter or its degradation products, both within the barite and limestone, suggest that these barite deposits formed due to the substitution of former anhydritized gypsum horizons, subsequently transformed to barite by highly modified basinal brines that were mobilized during the first stages of the Laramide compression. The origin of Ba is uncertain, although formation waters can scavenge Ba released after feldspar breakdown during diagenesis and transport it in low-sulfate reducing fluids. In our case, the evaporitic horizons acted as a sulfate-rich, oxidant trap for a hot, saline, and Ba-rich solution. Their interaction produced pseudomorphs of the former anhydrite body by barite, partially preserving the original diagenetic textures. Also, the presence of a mobile, hot, sulfate-rich residual fluid, after barite formation, flowing through the evaporitic horizon, could account for oxidation of the organic matter contained within the adjacent limestone, resulting in the discoloration observed. The calcite-filled fractures could also act as channelways for the expulsion of the residual Ca-rich fluids.

Stratabound Celestine-Dominant Deposits

The Mesozoic platform sediments found in the states of Coahuila, San Luis Potosí, and Chihuahua contain one of the biggest accumulations of celestine deposits in the world; yet, this district has received little attention from the scientific and mining communities mainly due to the small and dispersed nature of the single ore bodies.

These celestine-dominant deposits in NE México are mainly found enclosed within the Acatita and Aurora Formations (Albian) in the central part of the Coahuila Platform (Alamitos, Australia, and La Paila Ranges); some other small and isolated celestine deposits are also found north of the San Marcos fault and in the SE margin of the Parras Basin (Puente-Solís et al., 2005).

Previous studies of the celestine deposits in México are scarce. Salas (1973) made the first thorough description of the Sr deposits, based on the mineralized lenses of the La Paila Ranges (Coahuila). Following Salas (1973), these celestine deposits appear as mantos made up of medium-sized, white celestine crystals that contain variable amounts of remnants of the enclosing limestone. When the celestine lenses are pure, it is usual to find pockets and cavities filled with idiomorphic crystals of celestine up to 10 cm in length, with minor quantities of native sulfur, fluorite, and gypsum. Salas (1973) and Rickman (1977) suggested that the La Paila celestine "mantos" are epigenetic and formed after the replacement of the enclosing limestones. Later, Kesler and Jones (1981), based on the S and Sr isotopic composition of gypsum, barite, and celestine (13 samples), concluded that the celestine deposits, formed from Sr derived exclusively from the limestone series, were probably expelled during diagenesis. More recently, Ramos-Rosique (2004), Ramos-Rosique et al. (2005), and Tritlla et al. (2004a, 2005) studied some of the celestine lenses from the Los Alamitos Ranges (El Venado, El Volcán, La Tinaja, La Víbora, El Diablo mines), presenting the first microthermometric data on these deposits and preliminary results on the brine halogen composition.

One of the main features of these deposits is their small to medium size. This not only prevents them being mined on an industrial scale, but also leads to the impossibility of knowing the total number of celestine bodies enclosed within the Mesozoic basins in Coahuila, San Luis Potosí, and Chihuahua. Moreover, it is notable that a huge amount of small mineralized lenses can appear in a single mining area and it is very common to see more than three different celestine-bearing lenses in the same sedimentary column, but in slightly different stratigraphic positions.

The celestine typically appear as stratiform to stratabound bodies within the Cupido (Aptian) and Acatita (Albian) limestone formations, with a general lense-shaped morphology, thicknesses up to 5 m, and total lengths exceeding 500 m (Fig. 4A). They are composed of euhedral to subhedral, prismatic to tabular, blue to black celestine crystals, up to 20 cm in length and 5 cm in width (Fig. 4B), with minor, late selenitic gypsum filling the remaining cavities, and subordinate calcite and traces of native sulfur. Occasionally, a very late, non-tabular celestine generation is found co-precipitating with the late selenitic gypsum. The ubiquitous presence of selenite as a late phase indicates either an excess of sulfate or the cessation of the Sr-bearing brine flow. The crystal size increases from the contact with the limestones (sucrose celestine) to the center of the bodies, forming large, euhedral celestine crystals with abundant intercrystalline voids. As a general pattern, crystals are arranged as rhythmites defined by the alternation of organic matter–rich (fetid, black) and organic matter–poor (blue) celestine (Figs. 4C and 4D). Both black and blue bands are fetid due to the presence of H_2S, probably trapped within fluid inclusions. It is significant that no remnants of precursor gypsum bodies or lenses have been found within the sedimentary series containing the celestine deposits.

A fluid inclusion study was undertaken to reveal the nature of the fluids involved in the genesis of these deposits (Ramos-Rosique, 2004; Ramos-Rosique et al., 2005; Tritlla et al., 2004a, 2005). Fluid inclusions in celestine are abundant but have frequently been affected by post-trapping changes, mainly necking-down and leakage due to the perfect cleavage of the host mineral. Fluid inclusions are mainly biphasic, with a visually estimated degree of filling of 0.9–0.95. Homogenization temperatures are constant, ranging from 80 to 130 °C, with variable calculated salinities ranging between 4 and 13 wt% NaCl eq.

The brine halogen composition, on a Cl/Br versus Na/Br molar ratio diagram, plots beneath but parallel to the trend defined by the evaporation of seawater (Tritlla et al., 2004a) (Fig. 5). This suggests that the electrolytes came from seawater modified by evaporation. These brines probably entered into the sedimentary pile as formation waters. Their salinity is less than would be expected compared with the salinity expected for the degree of seawater evaporation indicated by their halogen ratios. Thus, the fluid has been modified by dilution.

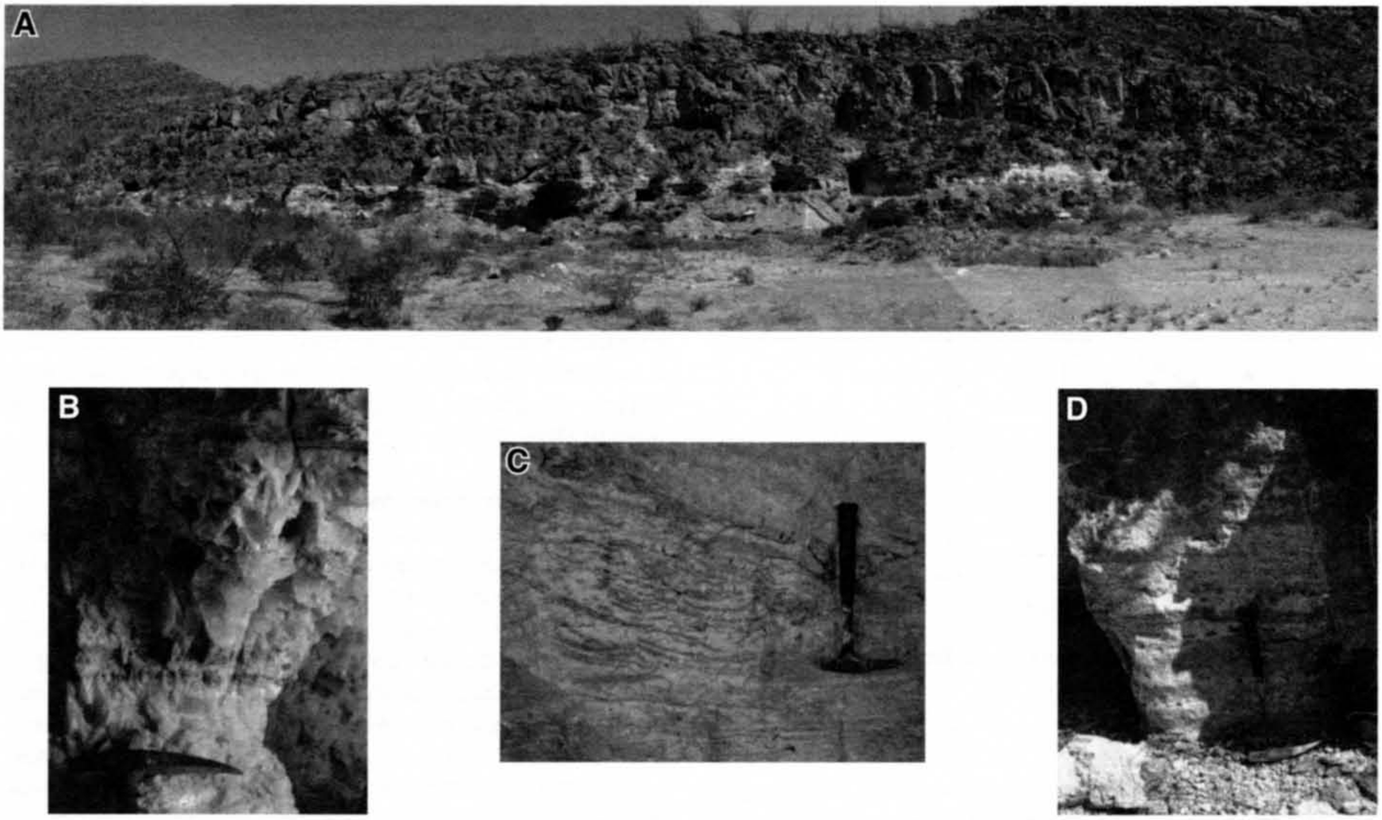

Figure 4. Celestine deposits. (A) General view of the stratabound, lenticular celestine body of La Víbora mine, Los Alamitos Ranges, Coahuila. (B) Celestine rhythmite located in the central part of the ore body, marked by the alternation of blue (O.M.-free) and black (O.M.-bearing) zones mostly within the same decimetric crystals; El Volcán mine, Los Alamitos Ranges, Coahuila. (C) Massive rhythmite zone, La Víbora mine, Los Alamitos Ranges, Coahuila. (D) Detail of the rhythmites located at the edge of the ore body, passing to the recrystallized host rock; La Víbora mine, Los Alamitos Ranges, Coahuila.

An unusual celestine deposit is located at El Tule, north of Muzquiz (Coahuila; Kesler, 1977) enclosed within the limestones of the Buda Formation (Washita Group). It comprises a single stratabound mineralized body whose disposition is controlled by a subhorizontal stratification joint with clear evidences of layer-parallel slip, acquiring a "pinch and swell" overall shape, with local mineralized zones up to 2 m in thickness. The deposit is celestine-dominated and has similar textures to the celestine-bearing deposits discussed above (rhythmites, tabular centimetric to decimetric crystals, fetid, etc.). The main difference is the presence of an early celestine generation with evidence of deformation during crystal growth (crystals bends, undulose extinction), while the latest, dominant celestine generation grew in a deformation-free environment. After celestine precipitation ceased, minor quantities of fluorite formed as a late phase, partially filling the remnant cavities and vugs in passive succession. This fluorite always appear as bluish to colorless, zoned, idiomorphic cubic crystals growing on top of the celestine crystals. No final selenitic gypsum has been recognized in this deposit.

Celestine contains abundant aqueous, two-phase fluid inclusions with evidences of post-trapping changes (necking-down). Homogenization temperatures are between 80 and 120 °C with very variable salinities between 5 and 11 wt% eq. of NaCl (Lamadrid, unpublished personal data). Raman analyses indicate that the gas phase is mainly composed of water vapor; no traces of other gases were found. Data plotted in a Th versus salinity plot suggest fluid mixing as the main mechanism for celestine precipitation, despite the somewhat scattered nature of the data.

Fluorite contains two distinct fluid inclusion types. The brine-bearing fluid inclusions are biphasic (L + V) to polyphasic ($L + V + S_{trapped}$). The trapped solids can be tiny quartz crystals or very small, high-birefringence minerals, thought to be calcite crystals. Raman analyses indicate the presence of variable amounts of CH_4, H_2S, and CO_2 within the gas phase. The hydrocarbon-bearing fluid inclusions are dark brown (heavy oils) and usually polyphasic (L + V + B) due to the presence of variable amounts of solid bitumen. Homogenization temperatures and salinities for the aqueous fluid inclusions are between 120 and 150 °C, and salinities are between 11.7 and 16 wt% eq. of NaCl, respectively (Lamadrid, unpublished personal data), showing much less variation than in the celestine inclusions. In a Th versus salinity plot, the data suggest that fluorite precipitated mainly by cooling after

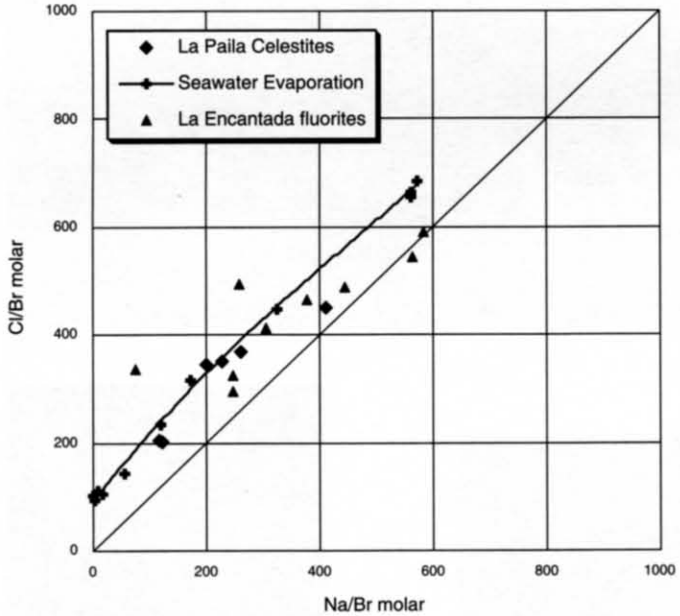

Figure 5. Na/Br versus Cl/Br compositions for the fluorite and celestine fluids. See text for explanation.

mixing of two different fluids. The petrographic analyses give clear evidence of coeval trapping of hydrocarbon-bearing and brine-bearing fluid inclusions within the same growth zone.

Thus, the mineralogical change from celestine to fluorite precipitation is also reflected in the change of the fluid composition and regime. Celestine precipitated within open sedimentary joints during and after the Laramide deformation, partially substituting the enclosing limestone. Fluorite precipitated after a dramatic change in the fluid composition, which probably inhibited the formation of celestine. During the mixing of the brine, most likely enriched in Ca^{2+} remaining after celestine precipitation, with an external emulsion of brine and hydrocarbons, partial degradation of the organic matter by means of thermochemical sulfate reduction (TSR) reactions occurred and generated the CH_4, H_2S, and CO_2 found in the gas phase of the brine-bearing fluid inclusions. An in situ origin for the small amounts of hydrocarbons found is unlikely, as the local source-rock for the organic matter was almost certainly depleted by the excess of sulfate during celestine formation.

Therefore, the El Tule deposit represents a rare example of a deposit that is transitional between the celestine lenses and mantos, well represented in the south of the state of Coahuila (La Paila and Alamitos Ranges), and the fluoritic mantos that are characteristic of the upper Cretaceous sediments in the north of the state of Coahuila (i.e., La Encantada-Buenavista).

Stratabound Fluorite-Dominant Deposits

A series of stratabound fluorite deposits and other occurrences are found in Cretaceous platform carbonates scattered all over México. These deposits are classified as: (1) MVT deposits, of syn- to post-orogenic Laramide age, related to basinal brines and organic matter (oil and gas), including the La Encantada–Buenavista district and the El Tule deposit in the state of Coahuila (Gonzalez-Partida et al., 2003, Tritlla et al., 2004b, 2005) and the La Azul deposit in the state of Guerrero (Tritlla and Levresse, 2006); (2) post-orogenic, nonmagmatic, very low-temperature fluorite bodies, including the Las Cuevas world-class deposit and several minor occurrences in the State of San Luis Potosí (Levresse et al., 2003); and (3) extremely unusual and very small fluorite-bearing skarns developed around F-rich rhyolitic necks in northern Coahuila (Levresse et al., 2006). Due to the ubiquity of magmatic rocks spatially close to these deposits, they were formerly classified as belonging to a single, magmatic-related category. Here, we only discuss the MVT-related typologies.

Fluorite Deposits in the State of Coahuila

La Encantada–Buenavista is the most representative fluorite-dominant MVT district deposit in México. It is located 180 km north of Muzquiz in the state of Coahuila (northern México). The district consists of several fluorite bodies and other occurrences scattered among the different limestone horizons that outcrop in the Sierra de la Encantada; the economic deposits appear mainly within the limestones of the Aurora Formation, of early Cretaceous age (Gonzalez-Partida et al., 2003). This formation is overlain by the Washita Group (Albian-Cenomanian), which is ~130 m thick and split into three formations, from bottom to top: (1) the Georgetown Formation (mudstone to wackestone limestones, 40 m thick); (2) the Del Rio Formation (thin-bedded shale, 10 m thick); and (3) the Buda Formation (impure wackestone-packstone, 80 m thick). The Laramide Orogeny affected the entire sedimentary pile, displaying two major folding styles: (1) asymmetrical and elongated anticline folds, and (2) domal anticlines with steep dips. During the middle Oligocene (Levresse et al., 2006), rhyolitic bodies intruded the sediment, affecting the previously formed fluorite bodies and causing a local enrichment of silica that makes these deposits unsuitable for industrial exploitation.

Because the upper limit for fluorite mineralization is always marked by the occurrence of the first strata of the Washita Group, these sediments are thought to act as a seal or flow barrier for the ore fluids, thus providing an explanation for the anomalously high occurrence of mineralized bodies near the Aurora-Georgetown Formations transition.

Fluorite is found at the intersection of low permeability barriers with low angle faults (layer-parallel slip) developed where stratification joints contain abundant clays (S. Baca, 2004, personal commun.; Tritlla et al., 2004b). The precipitation of fluorite is preceded by a substantial increase in the permeability of the host rock due to hydraulic fracturing (Fig. 6A). The fragments of the enclosing rock, within the brecciated structure, are extensively recrystallized, with some evidence of corrosion rims in the limestone boulders. Fluorite probably precipitated very rapidly, precluding the ongoing carbonate replacement. A thin calcite blanket, a few centimeters to a few decimeters thick, is usually found at the boundary of the fluorite body, smoothly transitioning into the slightly recrys-

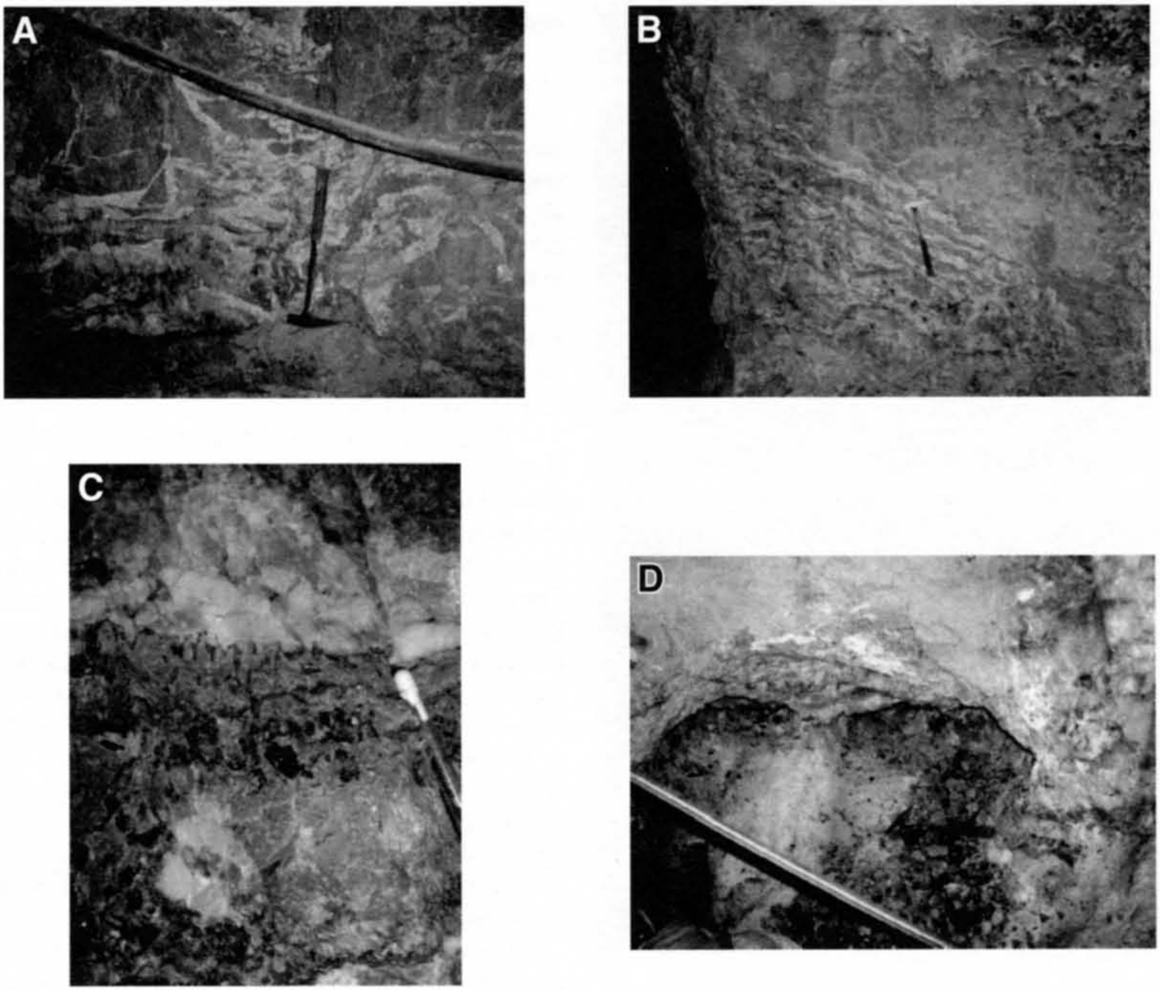

Figure 6. Stratabound fluorite ore bodies from La Encantada–Buenavista (Coahuila). (A) Hydraulic breccia within limestones at the front of a fluorite ore body. (B) Main stratabound fluorite manto exclusively made up of rhythmites of alternating white to colorless and purple fluorite. (C) Detail of the contact between the fluorite body (lower part) and the enclosing limestone (upper part); note the high degree of recrystallization of the limestone, with the development of a pure white calcite "blanket" at the front of the ore body. (D) Late cavity lined by idiomorphic, centimeter-sized purple fluorite crystals.

tallized enclosing limestone (Fig. 6A). The fluorite always appears as white to colorless, corrosion-free subhedral crystals indicative of passive mineral precipitation, usually arranged as rhythmites (Fig. 6B). Later cavities are filled by idiomorphic, cubic, heavily zoned fluorite crystals with a deep-purple color in their outer zones (Figs. 6C and 6D), minor idiomorphic calcite scalenohedrons, and extremely rare barite crystals (Tritlla et al., 2004b).

Aqueous and hydrocarbon-bearing fluid inclusions have been characterized by microthermometry (Gonzalez-Partida et al., 2003), crush-leach, Raman spectroscopy, Fourier Transform Infra-Red (FTIR) spectrometry, and confocal scanning laser microscopy (CSLM), and subsequently modeled using the Petroleum Inclusion Thermodynamics (PIT software; Thiéry et al., 2000).

Fluorite contains abundant primary fluid inclusions up to 50 μm in size, often distributed along growth planes (Fig. 7A). Three fluid inclusion types have been recognized (Figs. 7A and 7B): (1) biphase aqueous fluid inclusions (L + V); (2) brown to dark brown hydrocarbon-bearing fluid inclusions (L + V) that, occasionally, contain solid bitumen (L + V ± S); and (3) polyphase fluid inclusions comprising a saline fluid, liquid hydrocarbon, a gas bubble, variable amounts of solid bitumen and, rarely, minute calcite crystals. These three inclusion types are commonly found to be located in the same growth bands, indicating the coeval trapping of a brine-oil emulsion. Microthermometric data on this deposit (Gonzalez-Partida et al., 2003) indicate homogenization temperatures between 75 and 120 °C, with corresponding salinities between 10.5 and 14.9 wt% eq. NaCl. In some places, fluid inclusions are decrepitated due to the overheating caused by the intrusion of late subvolcanic rhyolite bodies, post-dating the mineralization events.

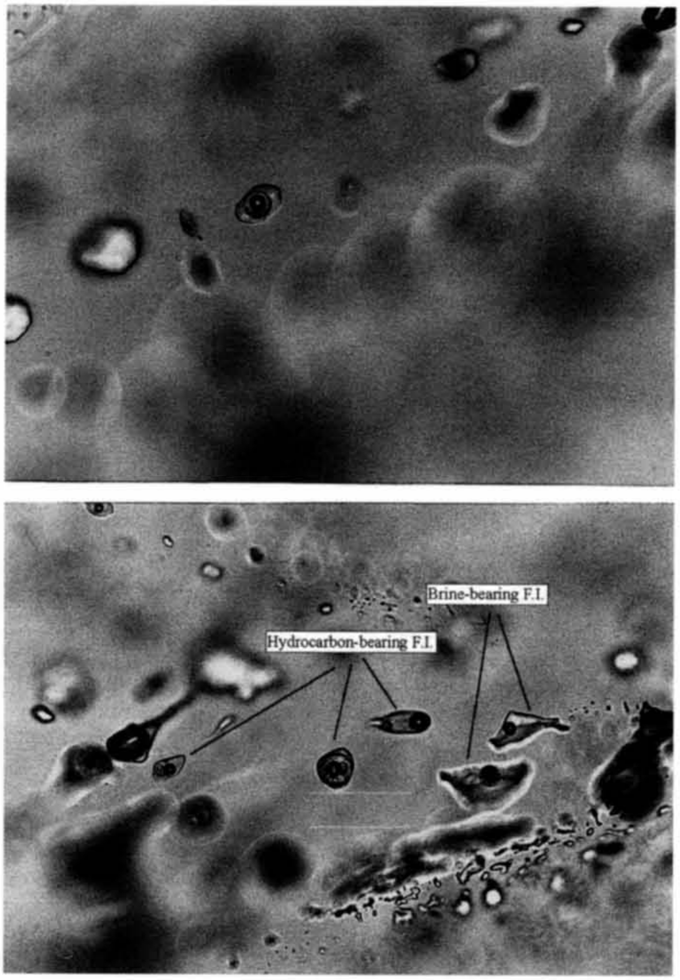

Figure 7. Fluid inclusions in fluorite, La Encantada–Buenavista district (Coahuila). Top: primary polyphase (brine + liquid hydrocarbon + gas + bitumen) fluid inclusions trapped within growth zones in fluorite. Bottom: coeval brine-bearing and hydrocarbon-bearing fluid inclusions trapped within the same growth bands in fluorite. Pictures taken by A. Ramos.

Both microthermometric and halogen analyses of brine-bearing fluid inclusions show that the fluids involved in the genesis of the La Encantada fluorite deposit are of meteoric origin (Tritlla et al., 2004a, 2004b, 2005), probably seawater that has undergone some degree of evaporation. Mixing of fluids is clearly supported by both microthermometric and halogen data, where the salinities are too low for the halogen ratios found, indicating mixing with a low-salinity end-member.

Hydrocarbon-bearing fluid inclusions are composed of yellow to brown "black oils" with low methane (30 mol%) and high CO_2 (5–30 mol%) contents and commonly contain solid bitumen, indicative of CO_2-asphaltene interaction or thermal degradation. Deformation of inclusions is probably due to post-trapping events consistent with pressure variations from 180 to 320 bar. The solubility of fluorite in NaCl solutions increases with temperature at all ionic strengths up to ~100 °C (Richardson and Holland, 1979) and at higher temperature increases with increasing $CaCl_2$ and $MgCl_2$ concentrations in NaCl-dominant solutions. Transport of fluoride is then favored and maximized by (basinal) brines enriched in Ca^{2}. Hydrocarbon-bearing fluid inclusions repeatedly show the presence of solid bitumen trapped along with heavy oils (Fig. 7), indicative of thermal degradation (Gonzalez-Partida et al., 2003). Both mixing and thermal degradation of hydrocarbon-rich fluids along with hydraulic fracturing of the host rock points to an in situ maturation of organic matter (Tritlla et al., 2004b) by means of TSR, due to the mixing of a saline, oxidized, sulfate-rich fluid, and $CaCl_2$-rich bittern. The latter fluid probably transported fluoride together with an organic matter–rich fluid present in the Cretaceous carbonates.

The products of TSR include H_2S (HS^-) and HCO_3^- (CO_2) (Machel, 2001). The production of volatiles would have resulted in a large volumetric expansion of the fluids (Dubessy and Ramboz, 1986), increasing the fluid pressure and, consequently, favoring the hydraulic fracturing of the enclosing rock. The presence of alkali earth metals and a reduction in the pH of the remaining brine often result in the formation of carbonates, particularly calcite and/or dolomite. In the La Encantada mine, calcite is present as minute solid inclusions, trapped contemporaneously with brine and hydrocarbon-bearing fluid inclusions in fluorite or as centimeter-sized scalenohedrons filling voids within the late-fluorite cavities. If F^- was transported as alkali complexes (CaF^+, for instance) in the bittern, then TSR could have produced sufficient CO_2 after maturation of organic matter to account for the destabilization of F-complexes and fluorite precipitation (Tritlla et al., 2004b).

It is noteworthy that the halogen ratios of the brines present in the celestine-dominated and fluorite-dominated deposits are comparable and overlap in a Cl/Br versus Na/Br plot. This indicates that both types of deposits were formed by the flow of the same highly modified evaporated seawater through the sedimentary pile. As suggested earlier (see the El Tule discussion), the predominance of celestine or fluorite can be controlled by a change in the fluid regime. This was initially controlled by formation waters (Sr-enriched) expelled from and through the sedimentary column during and immediately after the peak of the Laramide deformation. Later, the fluid regime changed to one dominated by gravity-driven flow in an extensive tectonic regime, where F could be scavenged from arkoses or the granitic basement.

Fluorite Deposits in the State of Guerrero

The fluorite deposits in the state of Guerrero are thought to have originated via the same processes discussed in the previous paragraph and are located along a broad NW-SE lineament between Acamixtla, Huajojutla, San Miguel Acuitlapán, and San Francisco de Acuitlapán. All the deposits and occurrences of fluorite are hosted by the limestones of the Morelos Formation (Cretaceous). Several small mines and workings are scattered throughout this zone, but only the La Azul mine open pit is of economic importance.

Research on the La Azul deposit has been carried out by several authors (Skewes-Saunders, 1938; Fowler et al., 1948; Gonzalez-Reyna, 1956; Osborne, 1956, Fernández, 1956; Florenzani, 1974; De Cserna and Fries, 1981; Clark, 1990; Pi et al., 2005; Tritlla et al., 1999, 2001; Tritlla and Levresse, 2006). The main reason for this research is La Azul's proximity (~30 km) to the important Taxco Ag-Zn-Pb-Cu district. The deposit consists of a single stratabound fluorite body that replaces the fossil-rich limestone of the Morelos Formation (Fig. 8A). The upper limit of the mineralization is marked by an irregular reaction front between the fluorite and the limestone. The fluorite mass passes into the fresh limestone by means of a thin recrystallization front (Fig. 8B), a few centimeters thick, with minute fluorite crystals located at calcite grain boundaries and whose abundance rapidly decrease toward the un-recrystallized limestones (Tritlla and Levresse, 2006; Fig. 8C). The lower contact does not outcrop. No fracture-related mineralization is associated with this deposit.

The fluorite contains alternations (rhythmites) of deep purple, black, and white bands (Figs. 8B and 8D) with rare quartz-rich bands and minor quantities of accessory minerals (barite, uraninite; Fig. 8E). Most of the fluorite found at La Azul is characteristically fetid due to the presence of H_2S. The gas is largely contained within the abundant primary biphase fluid inclusions and is interpreted to be a byproduct of organic-matter destruction, as has been recorded in similar fluorite deposits within comparable lithologies throughout México (El Tule deposit and the La Encantada–Buenavista district, Coahuila State; Gonzalez-Partida et al., 2003; Tritlla et al., 2004b). The "black & white" rhythmites contain abundant dark inclusions, probably degraded organic matter. The entire deposit is affected by a high number of hydrothermal fracturing episodes subsequently followed by the precipitation of additional fluorite layers. The substitution of the limestone by fluorite is not complete, and remnant blocks of limestone are found, partially corroded, within the fluorite mass. Carbonate replacement also increases the porosity of the limestone, creating abundant cavities within the fluorite mass, which are occasionally covered by minute cubes of a late yellow fluorite. The rhythmitic textures characteristic of this deposit are similar to those found in carbonate-hosted, fluorite-rich deposits throughout México (Gonzalez-Partida et al., 2003; Levresse et al., 2003; Tritlla et al., 2001, 2004b) and worldwide (i.e., MVT deposits).

This deposit, as in the La Encantada–Buenavista fluorite district (Coahuila) discussed above, is intruded by a tertiary rhyolitic dyke, a few meters wide and heavily altered to a mixture of clays, quartz fragments, and some recognizable ferromagnesian minerals. This rhyolite clearly crosscuts and postdates the fluorite manto, including some brecciated fluorite blocks (Fig. 8D). These fluorite blocks as well as the fluorite adjacent to this dyke are heavily recrystallized and have acquired a characteristic grayish to reddish color, in contrast with the original bluish or whitish color found in the undisturbed fluorite. In addition, this recrystallized fluorite does not present the characteristic fetid odor found throughout the rest of the deposit. Some rare small veinlets of remobilized fluorite can also be found crosscutting the grayish recrystallized fluorite blocks. These textures were mistakenly identified as a dissolution breccia by several authors (Fowler et al., 1948; Fernández, 1956; Osborne, 1956; Florenzani, 1974). However, Skewes-Saunders (1938) and Tritlla and Levresse (1999, 2001, 2006) consider this structure to be a piecemeal stoping developed after the intrusion of a felsic subvolcanic body into the rigid fluorite mass.

Fluorite and quartz from La Azul contain abundant, negative crystal-shaped, primary biphase fluid inclusions. Microthermometric studies indicate that the fluids are $NaCl-CaCl_2$–rich fluids with a medium salinity (10–13wt% eq. NaCl) and temperatures (without pressure correction) between 120 and 150 °C (Tritlla and Levresse, 2006). In general, the homogenization temperatures from La Azul have a large range, mainly between 90 and 200 °C as a consequence of the rhyolite dyke intrusion.

Recently, Pi et al. (2005), disregarding the intrusive cross-cutting relationships of the limestone, the fluorite body, and the rhyolitic dyke, reported a supposed deposit age of 32 ± 2 Ma (1σ) using the (U-Th)/He method. Tritlla and Levresse (2006) demonstrated that this age does not represent the deposit formation age but a resetting age due to emplacement of the rhyolite.

Stratabound Base-Metal Deposits

The stratabound, low-temperature base metal deposits have been largely ignored until very recently. Information on these deposits is very scarce and old, as they were mined during the second half of the nineteenth and the first decades of the twentieth centuries. Moreover, most of the low-temperature, base-metal carbonate-hosted deposits in México are located in a desert-like environment and have a deep, supergenic alteration, making it difficult to study the primary mineralization features. The primary sulfides are partially or completely replaced by "calamines," a mixture of anhydrous (smithsonite) and hydrated zinc carbonates (hydrozincite). This style of mineralization is typical of the deposits in Sierra Mojada, Sierra de la Purísima, and San Marcos deposits in Coahuila and Minas de San Pedro (also known as "El Diente") in Nuevo León. The base metal deposits (Pb-Zn) are roughly located around the Coahuila paleohighs and do not have the same strong stratigraphical control shown by the nonmetallic deposit. They are mainly hosted by the Cupido Formation but can also be found within the limestones of the Aurora, Acatita, and La Virgen Formations (Upper Jurassic to Cretaceous; Puente-Solís et al., 2005).

The Sierra Mojada was probably the biggest and best known mining district of this kind. It is located in the west central part of the state of Coahuila, near the Coahuila-Chihuahua state border in northern México. The district has a long history of mining activity since its discovery in 1879 and was historically considered a high-grade silver district. The initial discovery was the "Lead Manto" composed of silver-bearing cerussite. Later, in 1906, a Cu-Ag mineralization was discovered, and subsequently, in the 1920s, an oxide-zinc mineralization ("Red Manto") was found. The ores of the district have been selectively mined for bodies of sufficiently high grade to be shipped directly to the smelters (Metalline Mining Company, 2004, www.metalin.com).

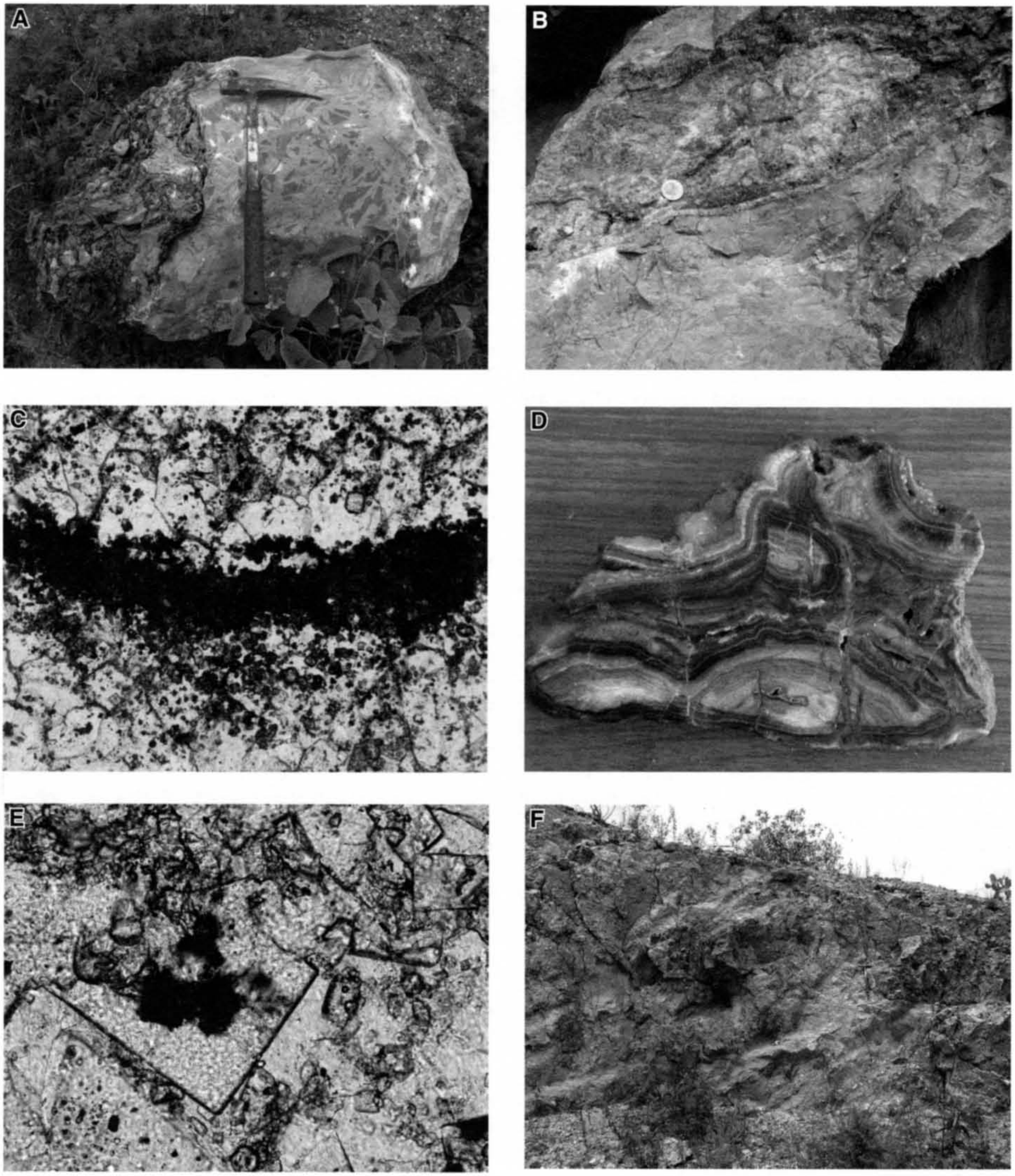

Figure 8. La Azul fluorite stratabound body (Guerrero state). (A) Detail of the contact between fluorite mineralization (left) and the enclosing Morelos Formation limestone, heavily recrystallized. (B) Detail of the fluorite replacement front; this is marked by the presence of a thin, white recrystallized calcite rim. (C) Detail under the petrographic microscope of the recrystallization front; the calcite crystals developed well-connected grain borders and triple points, where tiny crystals of fluorite formed. (D) Fluorite rhythmites brecciated by hydraulic fracturing and subsequently recemented by late generations of fluorite. (E) Idiomorphic crystal of fluorite containing several anhedral crystals of uraninite; around these uraninite crystals a metamictic aureole developed due to fluorite lattice destruction. (F) Detail of the rhyolitic dyke, heavily altered and containing fragments of the highly recrystallized fluorite.

The ore deposits are located on the southern margin of the Sabinas Basin and comprise two stratabound mineral systems separated by the east-west–trending Sierra Mojada Fault (Fig. 9). North of the fault, the deposits contain disseminated to massive Cu-Ag-sulfide–bearing mineralization (tetrahedrite, sphalerite, and galena) with celestine-rich zones mostly altered to powdery strontianite. South of the fault, the mineralization is mainly composed of supergene bodies of secondary zinc (hemimorphite, smithsonite, and sauconite) and lead (cerussite) minerals. North of the fault, mineralization is hosted by the Upper Jurassic and lower Cretaceous sediments; in the south, it is hosted by the limestones of the Aurora and La Peña Formations (Middle Cretaceous) (Metalline Mining Company, 2004, www.metalin.com). The deposition of the ores is not associated with any hydrothermal alteration of the host rocks, except for some dolomitization affecting the host rocks of the Red Ore Manto. The absence of a pervasive hydrothermal alteration, the composition of the primary mineralization, and the morphology of the ore bodies suggest that these deposits can be classified as MVT.

The Sierra Mojada is the only MVT district presently undergoing economic reevaluation in México by the Metalline Mining Company. With a total of 7108 ha and its potential for low-grade, high tonnage Zn deposits, mainly calamines, as well as minor Zn-Pb-Cu-Ag primary ores, it may prove to be exploitable.

The Mineral de Reforma District is located in the La Purísima and San Marcos Ranges and includes the Reforma, Ojo de Agua, and Juárez mines. This district acquired some importance between the end of the nineteenth and the beginning of the twentieth centuries. The ore bodies that were exploited are stratabound and enclosed within the oolitic and reef facies of the Cupido Formation (González-Ramos, 1984). The emplacement of the ore deposits is marked by a strong alteration of the host rock by a pervasive dolomitization event, clearly seen as an abrupt change in the color of the rock (Figs. 10A and 10C). This dolostone is fetid (presence of H_2S) and surrounds the base-metal accumulations. The primary mineralization is dominated by galena, sphalerite, barite, and siderite, with traces of chalcopyrite and pyrite. This is almost completely altered to an assemblage of supergene minerals, smithsonite, hydrozincite, limonite, cerussite, etc. (Fig. 10B), and only some rare remnants of primary sulfides are found. Scarce fluid inclusions found within primary minerals indicate formation temperatures of between 100 and 150 °C with salinities between 7.5 and 20 wt% eq. NaCl (González-Ramos, 1984).

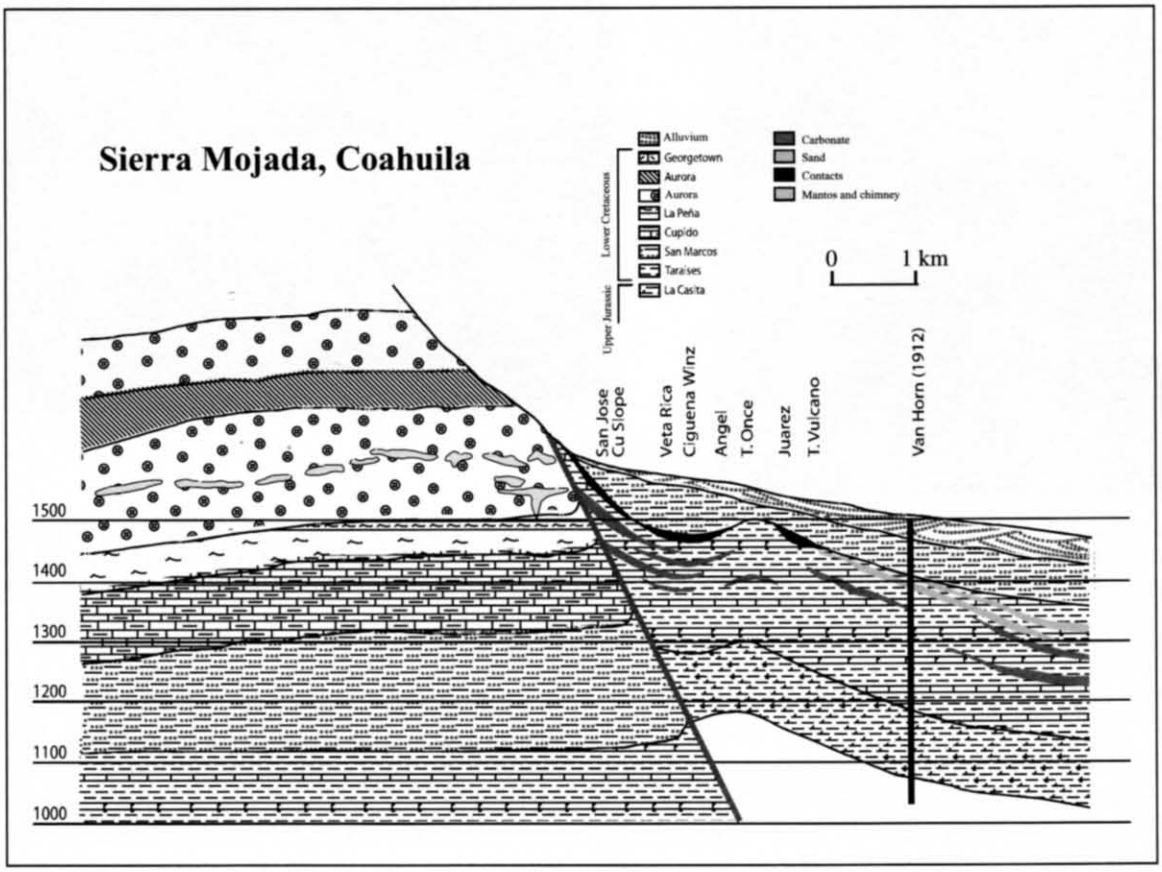

Figure 9. Geological cross section (not to scale) showing the general geology and disposition of the Pb-Zn stratabound deposits at Sierra Mojada (state of Coahuila). Modified after Metalline Mining Company (2004, www.metalin.com).

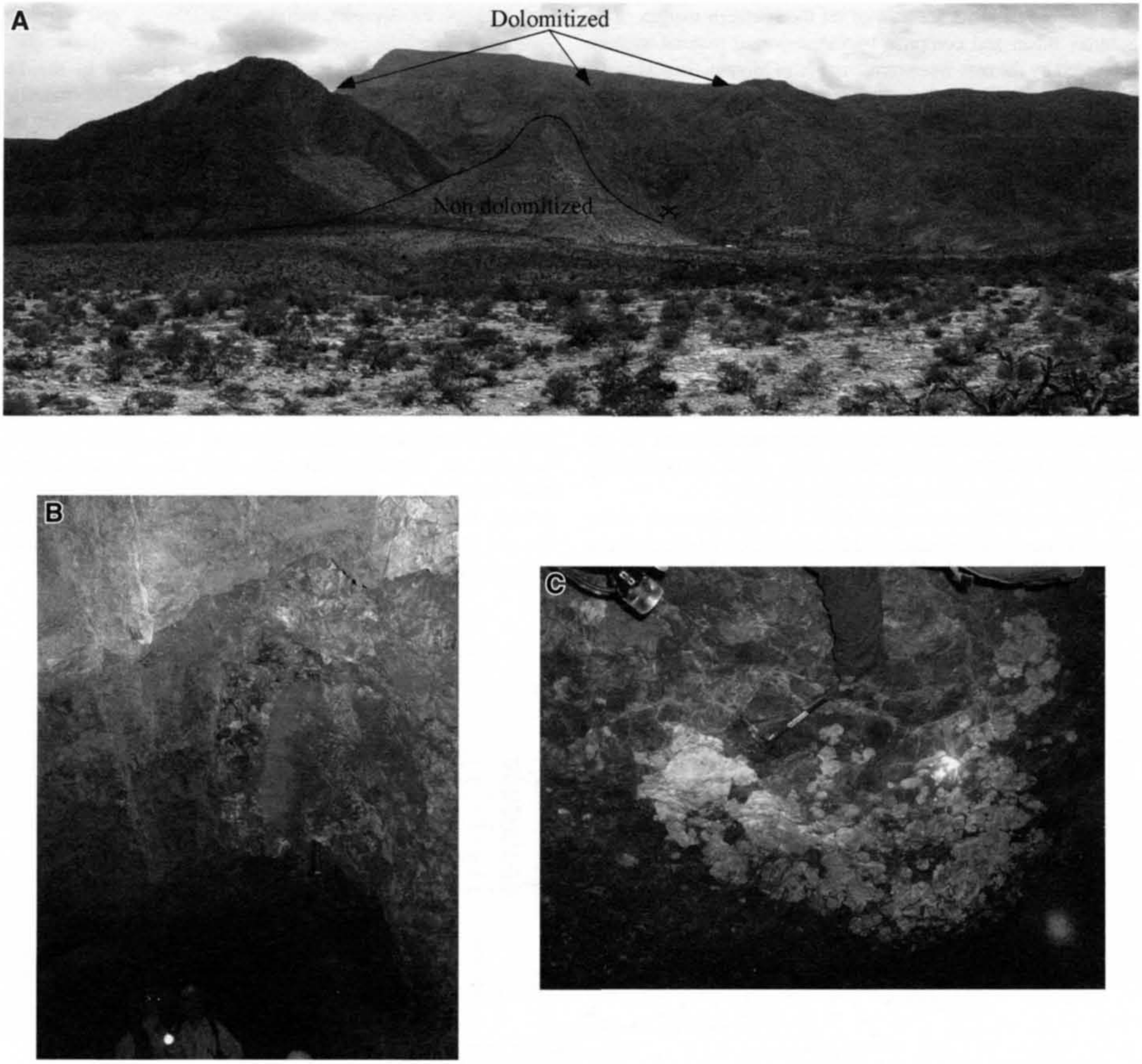

Figure 10. Mineral de Reforma Pb-Zn deposit, Purísima and San Marcos Ranges (Coahuila state). (A) View of the enclosing Mesozoic series; the darkening in color near the mineralization is due to the dolomitization of the limestone. Crossed pickaxes denote the location of the mineshaft. (B) Detail of the heavily oxidized mineralization (calamines). (C) Contact zone between the ore deposit and the enclosing dolostones.

CONCLUSIONS

This review of the geological and geochemical characteristics of the low-temperature, stratabound deposits in México allows us to propose the occurrence of, at least, four groups of deposits: (1) stratiform barite bodies of great purity, located at the lower parts of the sedimentary pile, that replace former anhydrite horizons, preserving some of the evaporite diagenetic textures; (2) stratabound, lens-shaped celestine-dominated bodies enclosed within the limestones of the Cupido Formation or their analogs; (3) stratabound fluorite-dominated mantos and bodies, mainly controlled by low-angle faults and associated hydraulic breccias, within the reefal limestones of the Aurora and Morelos Formations; and (4) Zn-Pb-(Ag-Cu-Ba-Sr) stratabound ore bodies enclosed within limestones that may be dolomitized, of Upper Jurassic and Cretaceous age, often deeply altered to supergene "calamines" and iron oxides.

All of these deposits are closely related to compressional (Laramide) or extensional post-tectonic events that instigated the flow of highly modified basinal brines that interacted with the sedimentary pile at a variety of levels. Locally, the major controls on the ore distribution seem to be (1) presence of reefal limestones rich in organic matter; (2) availability of sulfate, either in basinal brines or, in the case of barite deposits, former evaporitic (anhydrite) horizons; (3) dilation along sedimentary joints due to an increase in pressure from the fluids and crystallization of the minerals; (4) hydraulic fracturing related to fluid overpressure. Halogen systematics, when applied, indicate that these brines are bitterns originating after evaporation of seawater passed halite saturation. These entered the sediments, probably as formation waters that eventually interacted with the sediments along the flow path and during expulsion, drastically changing their cation composition. The involvement of organic matter during the genesis of these deposit is ubiquitous and it is often detected by the presence of liquid hydrocarbons (heavy oils) trapped as hydrocarbon-bearing fluid inclusions, very frequently with bitumen and traces of H_2S, whose abundance is indicative of the thermal degradation of the organic matter.

In all the studied cases, these deposits are clearly genetically unrelated to any magmatic episode whatsoever, even though they can be physically close and intruded by Late Tertiary rhyolitic dykes and domes (La Encantada–Buenavista, Coahuila state; La Azul, Guerrero state) that induce physical and chemical changes in the deposits (silicification, fluid inclusion decrepitation, age resetting, etc.).

The occurrence of mineralized bodies with features similar to those of the classical MVT is much more common than previously thought. As shown in this paper, these deposits have been clearly identified within the undisturbed Mesozoic carbonate sedimentary platforms outcropping in the states of Guerrero, Chihuahua, Coahuila, and Nuevo León. Probably, some other deposits, outcropping in areas where the Mesozoic sediments have been affected by the widespread Tertiary volcanism will be also proven to belong to this type once the disturbing influence of later magmatic events is recognized. Therefore, a thorough revision of the geological and geochemical controls of the carbonate-hosted deposits in México is warranted, especially deposits that do not have any clear and close relationships with magmatism.

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