The sulphur limestones from the Lorca Basin (SE Spain): new sedimentological and petrological data.

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1 Introduction

The Lorca Basin is a Neogene post-orogenic pull-apart basin located in the Betic Cordillera (SE Spain) (***Fig. 1***). It is filled with Serravallian/Lower Tortonian-Pliocene sediments, up to 1500 m thick in the depocenter, which record the progressive isolation of the basin during the late Tortonian (Krijgsman et al., 2000). The sedimentary succession starts with shallow water coarse-grained transgressive sediments, which are followed by open marine marls (**Hondo Fm.**), in turn overlain by alternations of diatomites and marls (**Varied Member**, Geel, 1976, or **Tripoli Formation**, Rouchy et al., 1998) and an evaporitic unit consisting of gypsum (**Main Gypsum Unit**) (***Fig. 2A***); halite was found in the subsurface (Geel , 1976; Garcia Veigas et al., 1994; Rouchy et al., 1998).

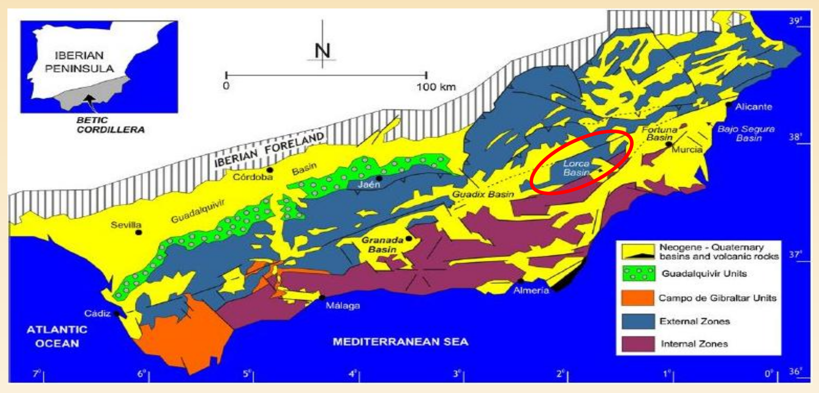


Fig. 1 - Geological map of the Betic Cordillera with location of the Lorca Basin (red circle)(modified from Corbì et al., 2012).

2 The Varied Member/Tripoli Formation

The Varied Member or Tripoli Formation, about 180 m-thick, can be further subdivided in two units: the lower one (**Lower Member**) shows a cyclic stacking pattern evidenced by the alternation of homogeneous marls and diatomite packets (***Fig. 2B***). The upper unit (**Upper Member**) is mostly made up of marls and subordinated diatomite layers (***Fig. 2C***).

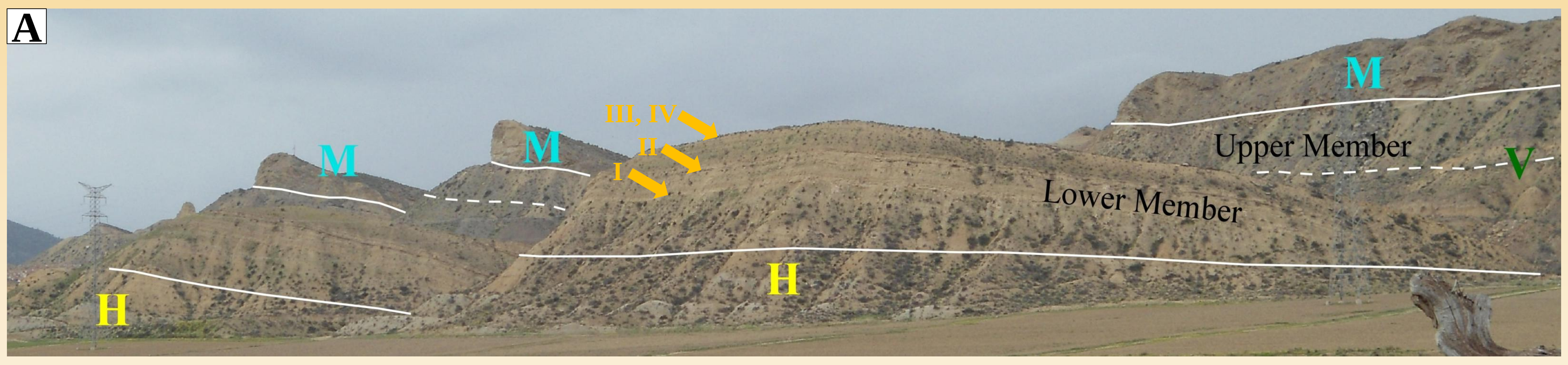


Fig. 2A – Panoramic view of the SW sector of the La Serrata ridge. Arrows indicate the sulphur limestones I to IV. H=Hondo Fm. V=Varied Member. M=Main Gypsum Unit.

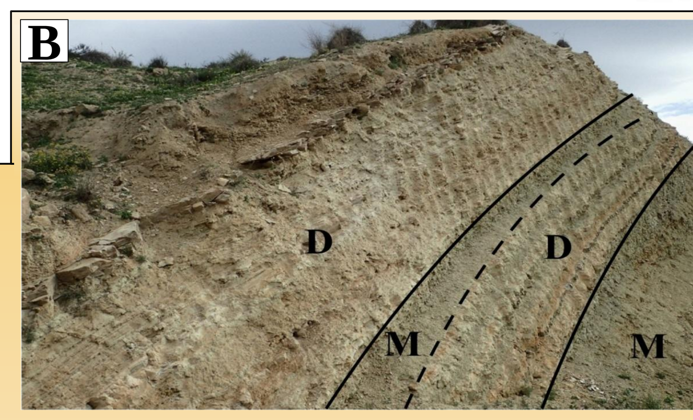


Fig. 2B – Lithological cyclicity in the Lower Member. D: Diatomite; M=Marl;

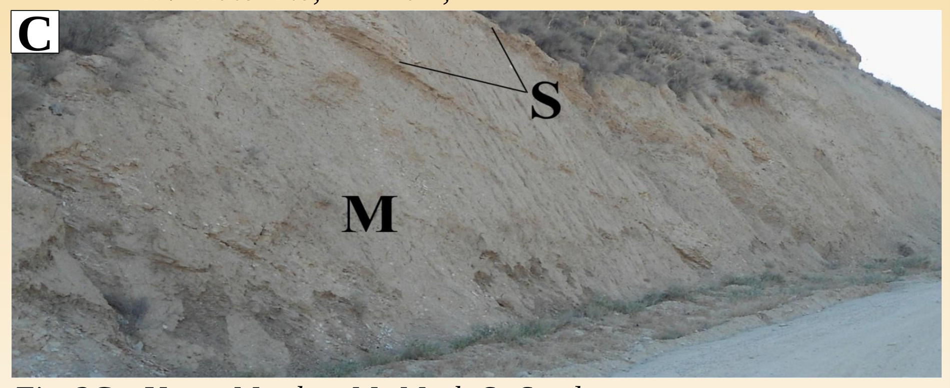


Fig. 2C – Upper Member. M=Marl; S=Sandstone.

3 The sulphur limestones

Seven layers of sulphur-bearing limestones were found within the Varied Mb/Tripoli Formation (six in the Lower Mb. and one in the Upper Mb.) and correlated to seven/eight gypsum beds (Rouchy et al., 1998) cropping out on the NE margin of the basin (***Fig. 3***).

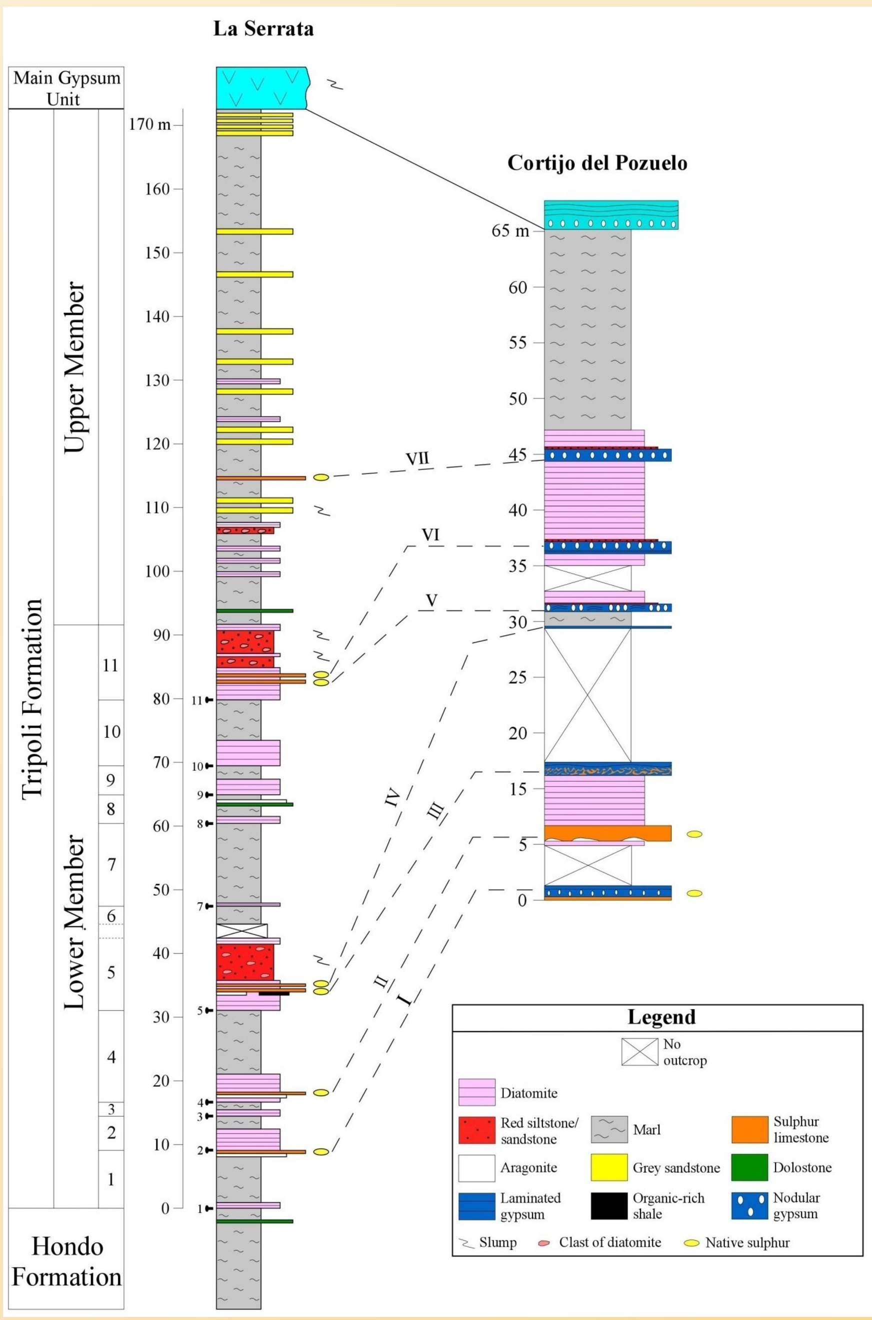


Fig. 3 - Correlation of the sulphur limestones of the La Serrata ridge with the gypsum layers at the NE margin of the basin (Cortijo del Pozuelo section).

To elucidate the origin of this layers we carried out new sedimentological and petrological studies of two sections exposed along the La Serrata ridge.

4 Field characteristics

- The sulphur-bearing limestones from the Lower Mb. occupy different positions within the lithological cycles (***Fig. 3***):
  - at the base of diatomites layers (I);
  - within the diatomites (II, III, IV, V, VI).

  In the Upper Mb. Layer VII is found within the marls.
- All the layers exhibit lateral thickness variations and evidence of sinsedimentary deformation (slumps) (***Figs. 4A, 4B, 4C***).
- Layers I and II contain intraclasts of diatomites and marls (***Fig. 4D***).
- The unconsolidated sediments above layers III, IV, V, VI display chaotic arrangement and contain clasts of diatomites of different size flooting in a reddish silty matrix (***Figs. 4E, 4F***).

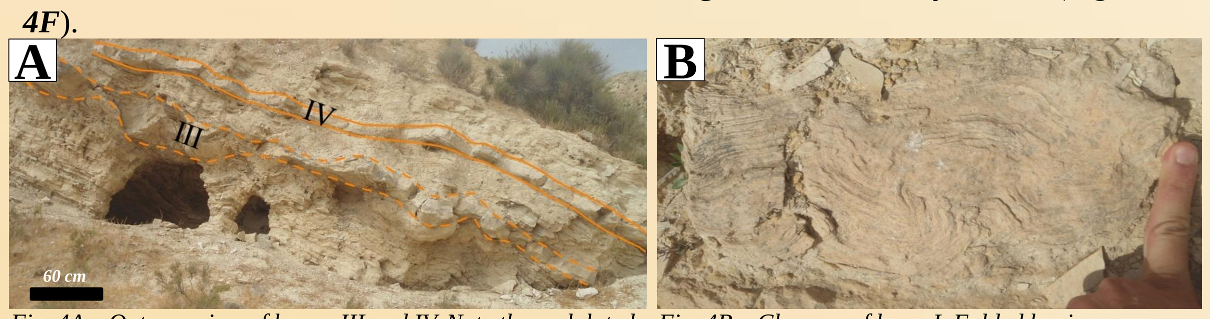


Fig. 4A – Outcrop view of layers III and IV. Note the undulated lower and upper boundary and the lateral thickness variation.

Fig. 4B – Close up of layer I. Folded laminae can be observed.

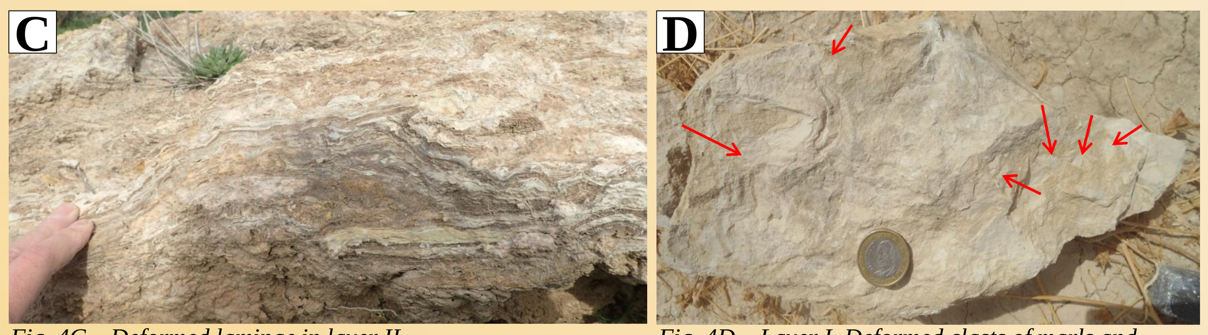
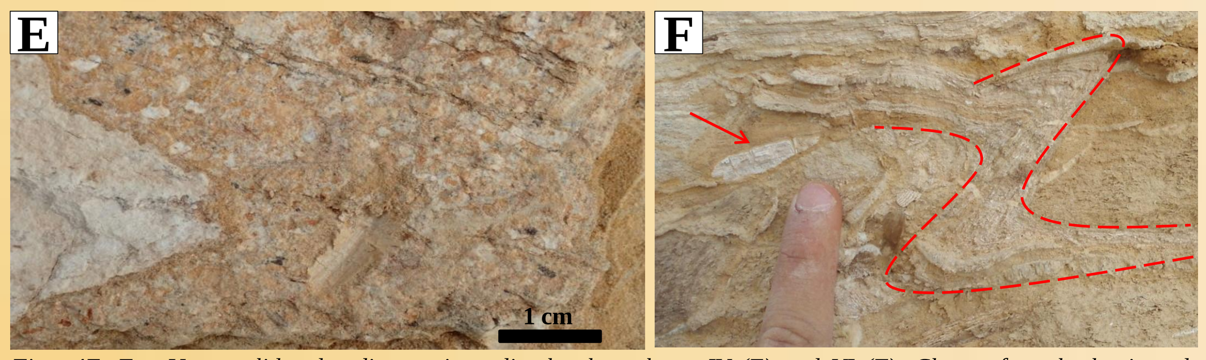


Fig. 4C – Deformed laminae in layer II.

Fig. 4D – Layer I. Deformed clasts of marls and laminated diatomite (red arrows) are recognizable.



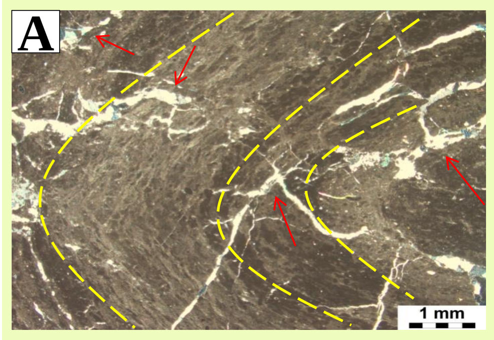
Figs. 4E, F – Unconsolidated sediments immediately above layer IV (E) and VI (F). Clasts of marls, laminated diatomites (red arrow and dashed lines) and plant remains can be observed.

5 Petrographic observations

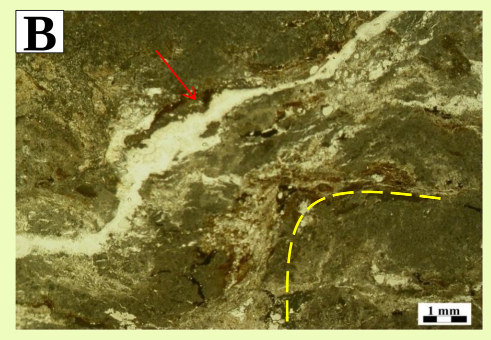
Sulphur limestones from Lorca display different compositional and sedimentological characteristics. Three microfacies have been distinguished:

1) Fine-grained carbonates with sinsedimentary deformation and locally clastic gypsum;
2) Carbonates with calcite pseudomorphs after gypsum;
3) Gypsarenites with sponge spicula and radiolarians.

5.1 Fine-grained carbonates (layers I, II)



Layers I (***Fig. 5A***) and II (***Fig. 5B***) are characterized by a strongly deformed, fine-grained carbonate matrix (*dashed lines*), mostly consisting of low-Mg calcite. A network of mm-large fractures and veins filled with calcite is present (*red arrows*).

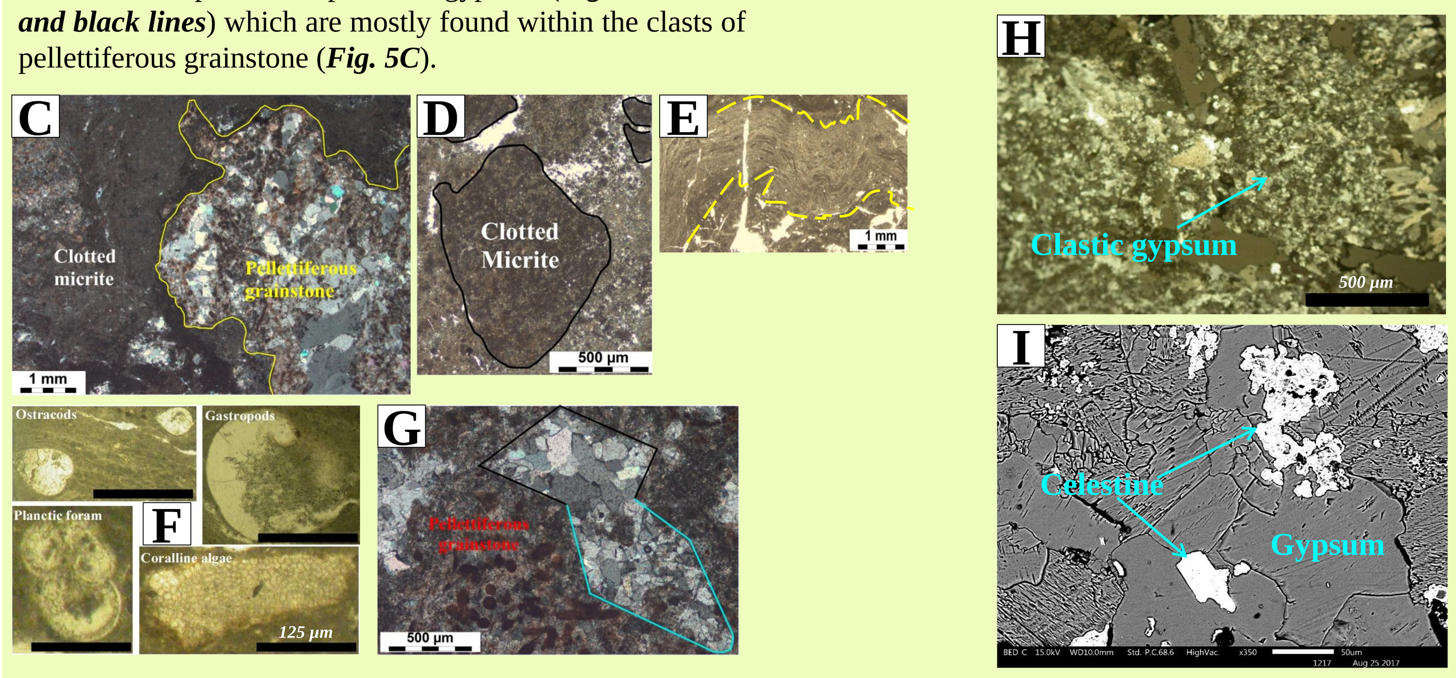


Layer I shows these additional features:

- Clasts of pellettiferous grainstone (***Fig. 5C***), clotted micrite (***Fig.5D***), and of strongly deformed laminated diatomites (***Fig. 5E***).
- Remains of ostracods, gastropods, foraminifers and coralline algae (***Fig. 5F***).
- Rare calcite pseudomorphs after gypsum (***Fig. 5G – blue and black lines***) which are mostly found within the clasts of pellettiferous grainstone (***Fig. 5C***).

Layer II shows these additional features:

- Occurrence of fine-grained gypsum possibly of clastic origin (***Figs. 5H, 5I***), beside satin-spar filling cavities and fractures and of probable late diagenetic origin.
- Celestine replacing gypsum (***Fig. 5I***).
- No fossils.

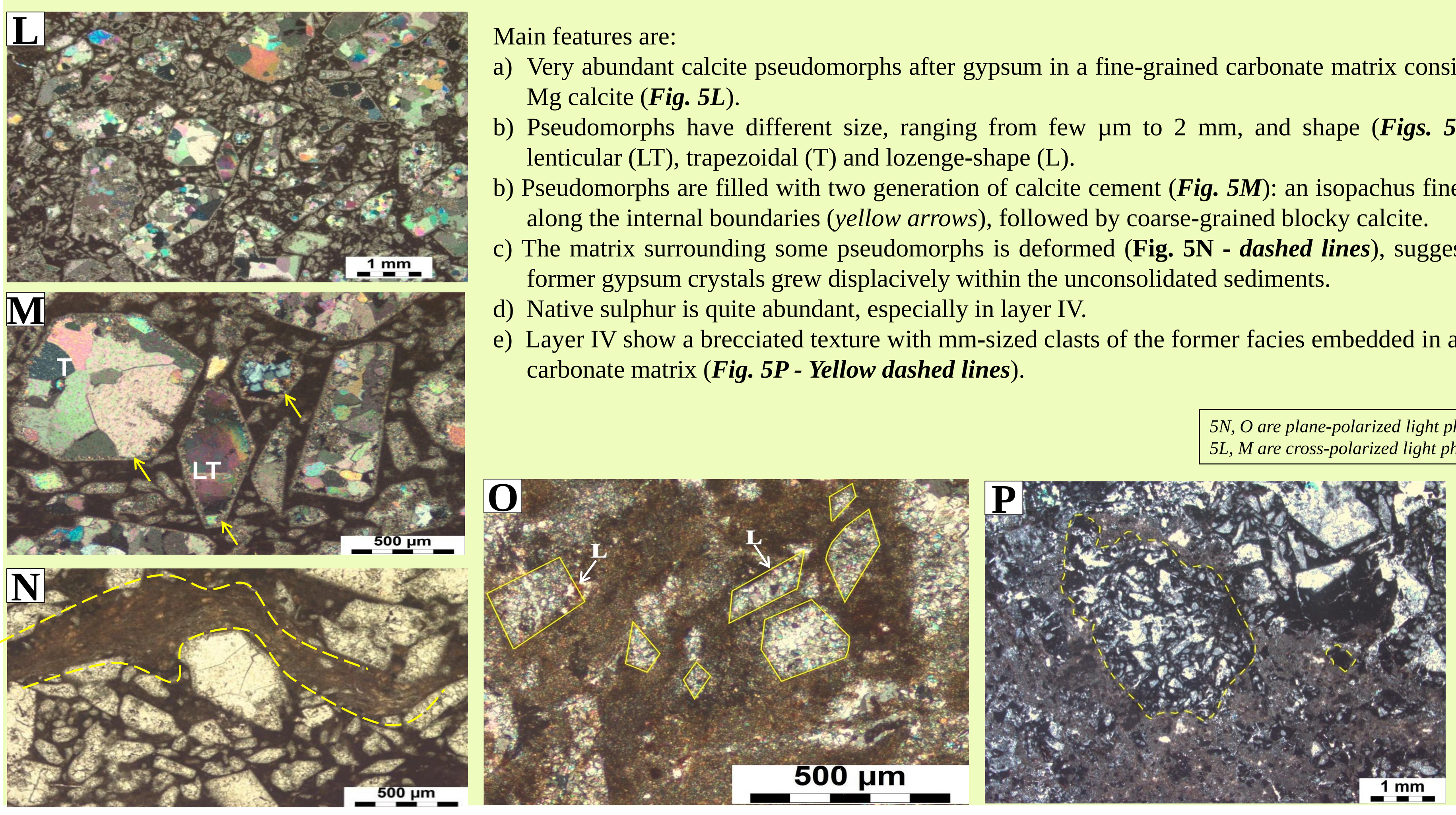


5A, B, D, E, F are plane-polarized light photomicrographs; 5C, G, H are cross-polarized light photomicrographs; 5I is a backscatter SEM image.

5.2 Carbonates with calcite pseudomorphs (layers III, IV, V, VI)

Main features are:

a) Very abundant calcite pseudomorphs after gypsum in a fine-grained carbonate matrix consisting of low-Mg calcite (***Fig. 5L***).
b) Pseudomorphs have different size, ranging from few μm to 2 mm, and shape (***Figs. 5L, 5M, 5O***): lenticular (LT), trapezoidal (T) and lozenge-shape (L).
b) Pseudomorphs are filled with two generation of calcite cement (***Fig. 5M***): an isopachus fine-grained rim along the internal boundaries (*yellow arrows*), followed by coarse-grained blocky calcite.
c) The matrix surrounding some pseudomorphs is deformed (**Fig. 5N - *dashed lines***), suggesting that the former gypsum crystals grew displacively within the unconsolidated sediments.
d) Native sulphur is quite abundant, especially in layer IV.
e) Layer IV show a brecciated texture with mm-sized clasts of the former facies embedded in a fine-grained carbonate matrix (***Fig. 5P - Yellow dashed lines***).

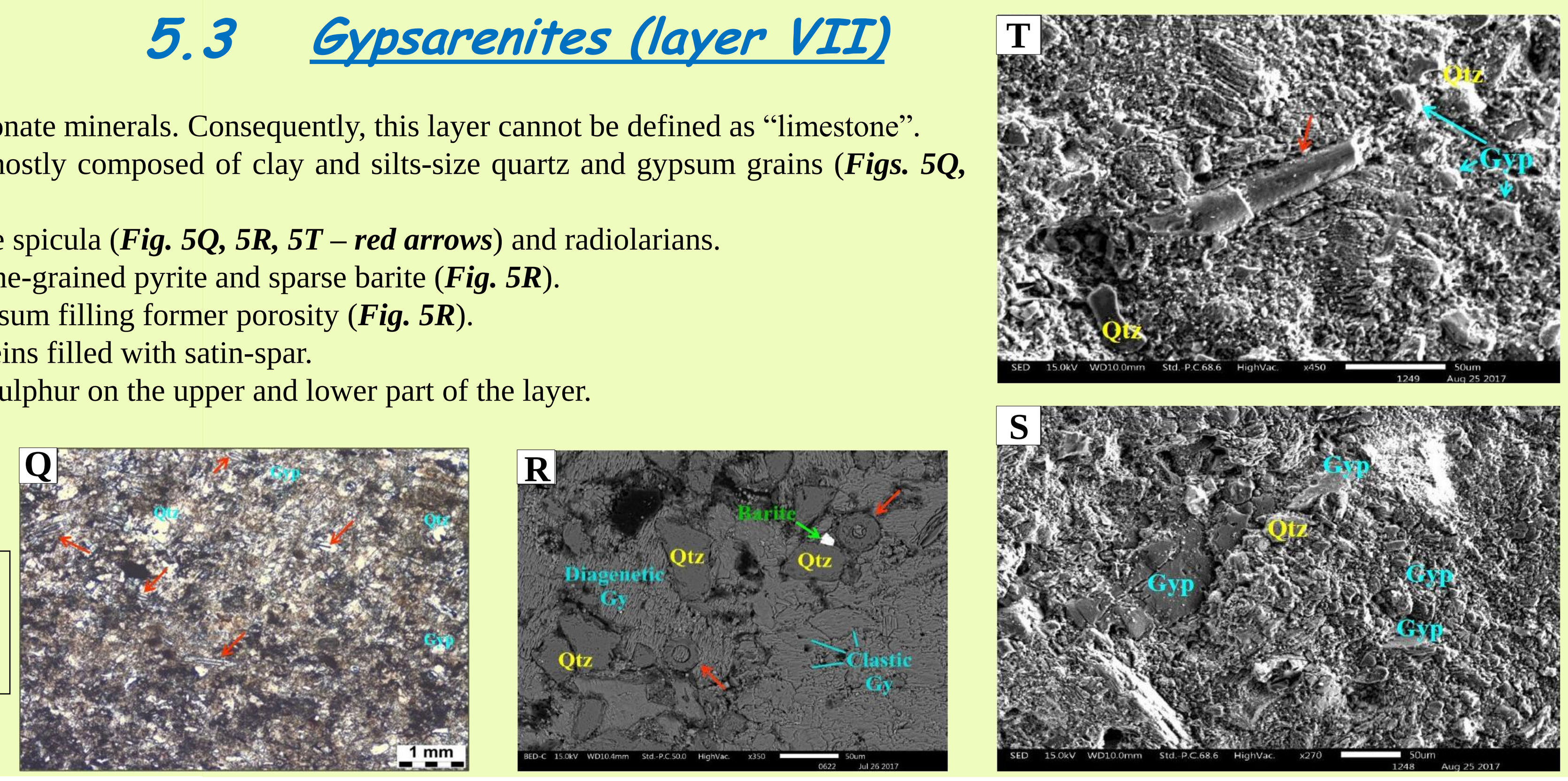


5N, O are plane-polarized light photomicrographs; 5L, M are cross-polarized light photomicrographs;

5.3 Gypsarenites (layer VII)

Main features are:

- Absence of carbonate minerals. Consequently, this layer cannot be defined as "limestone".
- Clastic texture mostly composed of clay and silts-size quartz and gypsum grains (***Figs. 5Q, 5R, 5S, 5T***).
- Abundant sponge spicula (***Fig. 5Q, 5R, 5T – red arrows***) and radiolarians.
- Occurrence of fine-grained pyrite and sparse barite (***Fig. 5R***).
- (Diagenetic) gypsum filling former porosity (***Fig. 5R***).
- Occurrence of veins filled with satin-spar.
- Glaze of native sulphur on the upper and lower part of the layer.



5P is plane-polarized light photomicrograph; 5Q is backscatter SEM image; 5R, S are SEM images.

6 Dolomite-rich layers

Apart from the sulphur limestones described above, three dolomite-rich layers were found in the La Serrata section. The lower one is in the upper part of the Hondo Fm, while the other in the Varied Mb. (***Fig. 3***). These layers are fine-grained, mostly composed of a silt-size terrigenous fraction (***Figs, 6A, B***) and sparse planctonic foraminifers (***Fig. 6A***). Rusty grains resulting from oxidation of pyrite are common. The intergranular cement is composed of euhedral or rounded-shaped dolomite crystals, ranging in size from 3 to 10 μm (***Fig. 6C***).

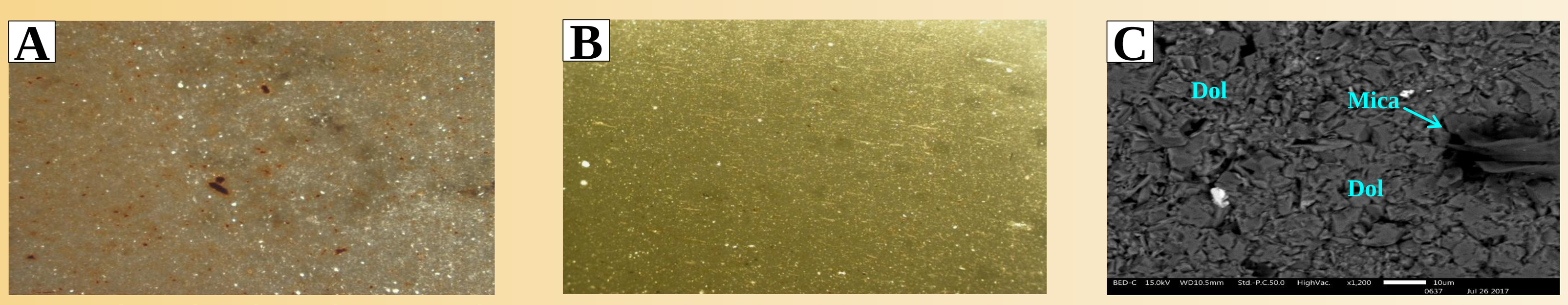


Fig. 6A - Plane-polarized microphotomicrograph of the lower dolomite-rich layer.

Fig. 6B - Plane-polarized photomicrograph of the lower dolomite-rich layer.

Fig. 6C - Backscatter SEM image of the dolomitic cement of the lower layer. Dol = dolomite

7 Discussion

The seven sulphur limestones layers from the Lorca Basin were considered as the product of diagenetic transformation, driven by bacterial sulphate reduction (BSR) of precursor gypsum layers formed in a shallow-water basin (Rouchy et al., 1998) in response to precession-driven climate change (Krijgsman et al., 2000) and were used to tie the succession to the astronomical polarity time scale. In particular, the sulphur-bearing limestones were correlated to arid phase at time of precession maxima (insolation minima), when evaporation exceeded precipitation. However, the interpretation of precursor gypsum layers as a product of seawater evaporation in a shallow-water basin is in contrast with the paleontological content of hosting sediments (marls and diatomites), which indicate a relatively deep marine environment, and with the sedimentological and petrological characteristics described above.
In particular:

1) the presence of **sinsedimentary deformations**, **clasts of diatomites** and **clastic gypsum** in layers I, II and VII, suggests that sediments were originally emplaced by **gravitative processes** involving organic-rich sediments (diatomites), and already deposited gypsum. As a matter of fact, an older gypsum unit is reported from the eastern margin of the basin (Playa et al., 2000). The gravitative origin is further supported by the presence of reworked stanoaline shallow-water biota like **coralline algae** (layer I) and **sponge spicula** (layer VII); these biota are not consistent with evaporitic conditions.

2) The abundant **calcite pseudomorphs after gypsum** preserved in layers III, IV, V and VI indicates the presence of gypsum-saturated interstitial pore-water in the basin depocenter, that could be related to periods of water-column stratification. **No bottom-grown selenite crystals were found in these layers.**

3) In both the case, the **mixing** of organic-rich sediments and sulphate (deriving from both detrital and displacive gypsum) provided the ingredients necessary for bacterial sulphate reduction (BSR), responsible for intense carbonate precipitation. BSR is furtherly supported by the presence of dolomite-rich layers which are possibly of biogenic origin. These diagenetic transformations did not affect layer VII, which actually corresponds to a gypsarenite. A possible explanation is the lack of organic matter in this layer, which is interbedded in homogeneous marls poor of organic carbon.

8 Conclusions

The sulphur limestones from Lorca Basin are the product of diagenetic transformations of original gypsum layers formed in a relatively deep basin and not of gypsum facies deposited in a shallow evaporitic environment.
Further geochemical investigations (C and O stable isotope composition of authigenic carbonates, as well as S and O stable isotope composition of gypsum) are needed to elucidate the origin of these enigmatic carbonates.

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