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Diagenesis and Geochemistry of Upper Muschelkalk (Triassic) Buildups and Associated Facies in Catalonia (NE Spain): a paper dedicated to Francesc Calvet

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ABSTRACT

Carbonate buildups are well developed in the Triassic Upper Muschelkalk of eastern Spain in the La Riba Unit, but they are completely dolomitised. These mud-mounds with reefal caps have well-developed fibrous and botryoidal marine cements which were probably high-Mg calcite and aragonite originally. The dolomite is fabric retentive indicating an early origin, but the $\delta^{18}O$ values are quite negative (average -3.‰), interpreted as indicating recrystallisation during shallow burial, but without fabric destruction. Low Sr and Na contents support this. The $\delta^{13}C$ signature is quite uniform (~ +1‰) and this is probably the inherited, original marine $CaCO_3$ value. The Alcover Unit, deposited between and above the La Riba buildups after a sea-level fall terminated mound growth, is an organic-rich laminated dolomicrite with exquisitely-preserved fossils. The $\delta^{18}O$ signature (average –3.4‰) is similar to the La Riba dolomites, also interpreted as suggesting recrystallisation. The $\delta^{13}C$ values, however, show a stratigraphic trend of increasingly negative (to –5.5‰) and then more positive to marine values (~0‰), over a thickness of 10 metres. This is interpreted as a reflection of increasing stratification and developing anoxia, which would have led to the preservation of the special fossils, and then a return to conditions of more open-marine circulation. The dolomicrites of the Alcover unit may well have been formed on or close to the sea-floor. Recrystallisation of the dolomites took place during shallow to moderate burial, with the resetting of the $\delta^{18}O$ signatures and loss of Sr. The dolomitisation of the La Riba Unit is attributed to circulating seawater, probably driven by sea-level change, during deposition of the Alcover Unit or shortly thereafter.

KEYWORDS **Muschelkalk. Triassic reefs. C and O isotopes. Trace element geochemistry. Catalonia.**

INTRODUCTION

The formation of carbonate mud-mounds and the origin of dolomites are still two of the outstanding problems in carbonate sedimentology. The Upper Muschelkalk of Catalonia (NE Spain) has well-developed buildups with a variety of associated facies, and the majority of these carbonate rocks are completely dolomitised. The sedimentology and sequence stratigraphy of the mud- mounds in the La Riba Unit have been described in several papers by Francesc Calvet and Maurice Tucker (1988, 1995), in some cases with other authors (Calvet et al. 1990, 1993). However, although we did study the diagenesis and geochemistry, the results were not published. This paper, addresses these topics and in particular the dolomitisation of the Upper Muschelkalk rocks.

GEOLOGICAL AND STRATIGRAPHICAL SETTING

Triassic rocks of the 'Germanic' facies were deposited extensively in western Europe and occur in several basins in Spain. They are particularly well developed in the Catalan Basin (Fig. 1), with excellent outcrops occurring in the Catalan Coastal Ranges near the cities of Tarragona and Reus in eastern Spain. As a result of regional variations in the stratigraphy and sedimentology, three distinct regions (termed *domains*) have been recognised in the Catalan Basin, bounded by faults (Marzo and Calvet, 1985). They are the Gaià-Montseny domain in the north-east; Prades domain in the central part and Baix Ebre-Priorat domain in the south-west (Fig. 2). The thickness of the Triassic succession in the Catalan Basin is very variable, from 500 m to more than 800 m, as a result of the strong tectonic control on deposition, particularly of the siliciclastic facies.

The Triassic in the Catalan Coastal Ranges has been divided into six lithostratigraphic units (Fig. 1 and Virgili, 1958; Marzo and Calvet, 1985; Calvet et al., 1990), as follows:

FIGURE 1 **Map showing the location of the Catalan Basin in Spain and the general geology of the area with the 3 domains. The broad stratigraphy of the Triassic succession is also shown. After Calvet and Tucker, 1995.**

6: Imon Formation: mostly dolomites, 40-70 m thick, probably Rhaetian.
5: Keuper: evaporites, marls, carbonates and locally volcaniclastic sediments and lavas, 50-150 m thick. Carnian-Norian.
4: Upper Muschelkalk: limestones, dolomites and shales, 100-140 m thick. Ladinian.
3: Middle Muschelkalk: sandstones, mudstones and evaporites, with rare volcanics, 50-130 m thick. Upper Anisian to lower Ladinian.
2: Lower Muschelkalk: limestones and dolomites, 70-120 m thick. Anisian.
1: Buntsandstein: conglomerates, sandstones, mudstones and rare evaporites, 60-310 m thick. Upper Permian (?) to lower Anisian.

In the Catalan Coastal Ranges, the thickness of the Upper Muschelkalk varies from around 100 m in the north to more than 140 m in the south. There is a rapid transition from the Middle Muschelkalk fluvial-playa lake siliciclastics and evaporites into the Upper Muschelkalk carbonates and a gradual transition from these carbonates into overlying Keuper evaporitic, mostly sulphate facies. Deposition of the Upper Muschelkalk carbonates took place on a ramp-type platform with a homoclinal ramp, barrier-bank type, evolving into a homoclinal ramp with buildups (Calvet et al., 1993).

The carbonates of the middle part of the Upper Muschelkalk show important lithological and sedimentological differences in the three domains (Calvet et al., 1990), whereas the lowermost stratigraphic units of the Upper Muschelkalk (Rojals and Benifallet) and the uppermost unit (Capafons) are present in all the domains (Fig. 2). In the Gaià-Montseny domain, the middle part of the Upper Muschelkalk consists of coarsely dolomitised domal stromatolites in the Querol Unit. In the Prades domain, the La Riba buildups and Alcover laminated dolomicrites occur in the central part; in the Baix Ebre-Priorat domain, ramp cycles of storm-dominated limestones and shales with *Daonella* constitute the Rasquera Unit (Calvet and Tucker, 1988), with Tivissa muddy lagoonal limestones/dolomites and shales above.

The age of the Upper Muschelkalk is Ladinian (Calvet and Tucker, 1995). The Rojals and Benifallet units are probably lower Ladinian (Fassanian). The La Riba buildups are of upper Ladinian (Longobardian) age on the basis of foraminifera, as is the Rasquera Unit from conodonts and ammonoids. The Capafons Unit is also dated as upper Ladinian by palynomorphs.

LA RIBA BUILDUPS AND ALCOVER DOLOMICRITES

The special feature of the Upper Muschelkalk in the Prades domain is the presence of buildups described in detail by Calvet and Tucker (1995). However, the overlying Alcover Unit is also very special, since it contains beautifully preserved and unusual fossils.

The Benifallet Unit beneath the La Riba Unit is quite variable in lithofacies, from lime mudstone to oolitic grainstone. Generally, it is partially to totally dolomitised, and the thickness varies from 20 to 50 m. The Benifallet consists of metre-scale shallowing-upward, coarsening-upward parasequences. Bioturbated lime mudstone-wackestone generally grades up into peloidal-bioclastic

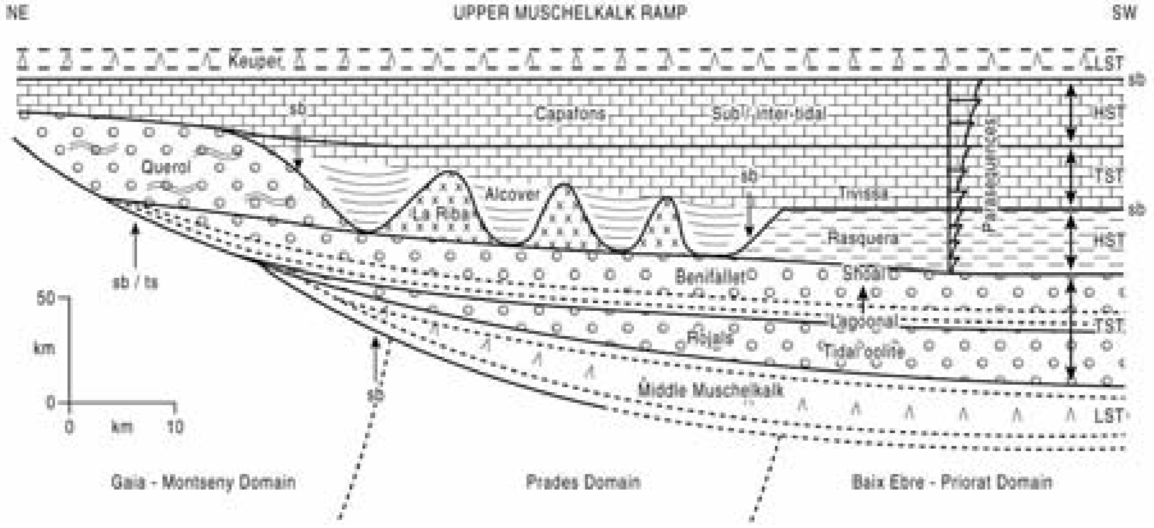

FIGURE 2 **Cross-section of the Upper Muschelkalk in the Catalan Basin showing the 3 domains and their different stratigraphies, and the sequence stratigraphy. After Calvet and Tucker, 1995.**

wackestone-packstone. The Benifallet Unit was deposited on a shallow, mostly low-energy carbonate ramp.

La Riba Unit Facies

The La Riba reefal mud-mounds are well developed in the eastern part of the Prades domain with their number and size decreasing towards the west. They were formed in moderate water depths and evolved into more complex facies mosaics as they grew into shallow water. They range from isolated, circular structures a few 100 m across, to elongate ridges parallel to the palaeo-strike of the basin. They reach 60 m in height and while growing, virtually nothing (0.1 m of sediment) was deposited in the inter-mound areas (Fig. 3A).

The mound-core is dominated by massive peloidal mudstone and wackestone, although packstones and even grainstones do locally occur. The mound-core contains scattered bioclasts, sponge spicules and *Tubiphytes*. There are many clotted peloidal aggregates within the mud mounds (Fig. 3B), as well as micritic encrustations around bioclasts, 'lacey' crusts, micritic laminae and micritic cements, much of which could be included in the term automicrite (coined by Wolf, 1965 for autochthonous micrite, in-situ formed fine-grained carbonate). Many of these micritic fabrics are probably microbial in origin, being in-situ precipitates of bacteria, fungi and other microbes (Reitner and Neuweiler, 1995). Automicrite is a feature of Triassic reefs in general; indeed in the stratigraphically-equivalent Sella Platform in the Dolomites, automicrite is the dominant component of platform-margin and upper-slope facies (Keim and Schlager, 2001).

The mound-core facies passes up into a skeletal-rich reefal facies which in places is a framestone-cementstone. This more reefal facies may also occur on the flank of the mound. Corals, bryozoans, sponges, microbial laminated crusts and calcareous algae are common frame-builders and binders, and molluscs, echinoderm debris and foraminifera are also present. Peloidal-skeletal grainstone lenses are common. Fibrous marine cements are conspicuous as are internal sediments (Fig. 3C and later section).

The upper parts of the buildups consist of well-bedded dasyclad grainstones and peritidal stromatolitic, fenestral, intraclastic and pisolitic dolomites. There is plenty of evidence of exposure, in the form of desiccated horizons, tepees, blackened laminites, intraclasts and floe carbonate (thin sheets of carbonate precipitated on the surface of small ponds).

Flank facies are poorly-developed in some buildups whereas in others, much flank progradation has taken place and clinoforms are prominent. Sediments are peloidal, skeletal packstones, with much automicrite; dasyclads are common, as are corals and crinoids. Lenticular, muddy patch reefs with corals are also present on the buildup flanks. Coarse debris beds are rare.

The buildups were subjected to exposure, limited erosion and karstic dissolution as a result of a major sea-level fall which terminated mound growth.

Alcover Unit Facies

The La Riba buildups are onlapped and overlapped by laminated dolomicrite of the Alcover Unit. The boundary is a sharp, undulating, locally erosive unconformity, interpreted as a palaeokarstic surface. The Alcover Unit fills the depressions between the mounds and the upper part then overlies the buildups. In the lower part, the Alcover dolomicrite is a lithographic stone, finely laminated, organic rich, and black in unweathered samples. Thicker beds (up to 0.5 m) of dolomicrite are the result of resedimentation. Some slump folds occur in marginal areas close to the slopes of the buildups. In the upper part of the unit, the beds are thicker, more peloidal and grainy, and have a pale grey colour. There are several layers of chert nodules, which contain evidence of being replaced evaporites.

The Alcover strata contain exquisitely preserved fossils (Fig. 4), especially osteichthyan fish, sauropterygian reptiles, arthropods, echinoderms, mollusca, insects, plants and soft-bodied organisms at certain levels in the lower part (Cartaña, 1994; Martínez-Delclòs, 1995).

The lower part of the Alcover Unit was clearly deposited under anoxic and periodically hypersaline conditions. The extremely fine-grained nature of the dolomicrite would be consistent with extremely early replacement of calcite mud, possibly even on or just below the sea-floor.

DIAGENESIS OF THE LA RIBA BUILDUPS

The diagenesis of the buildups is noteworthy for the early marine cementation, the meteoric diagenesis in reef-top strata and the total dolomitisation, which is mostly fabric retentive, taking place in this order.

Marine diagenesis

The reefal framework facies of the upper parts of the buildups has two distinctive types of marine cement (both dolomitised): A) well-preserved fibrous isopachous and non-isopachous cements, and B) poorly-preserved botryoidal cements originally of large fibrous crystals.

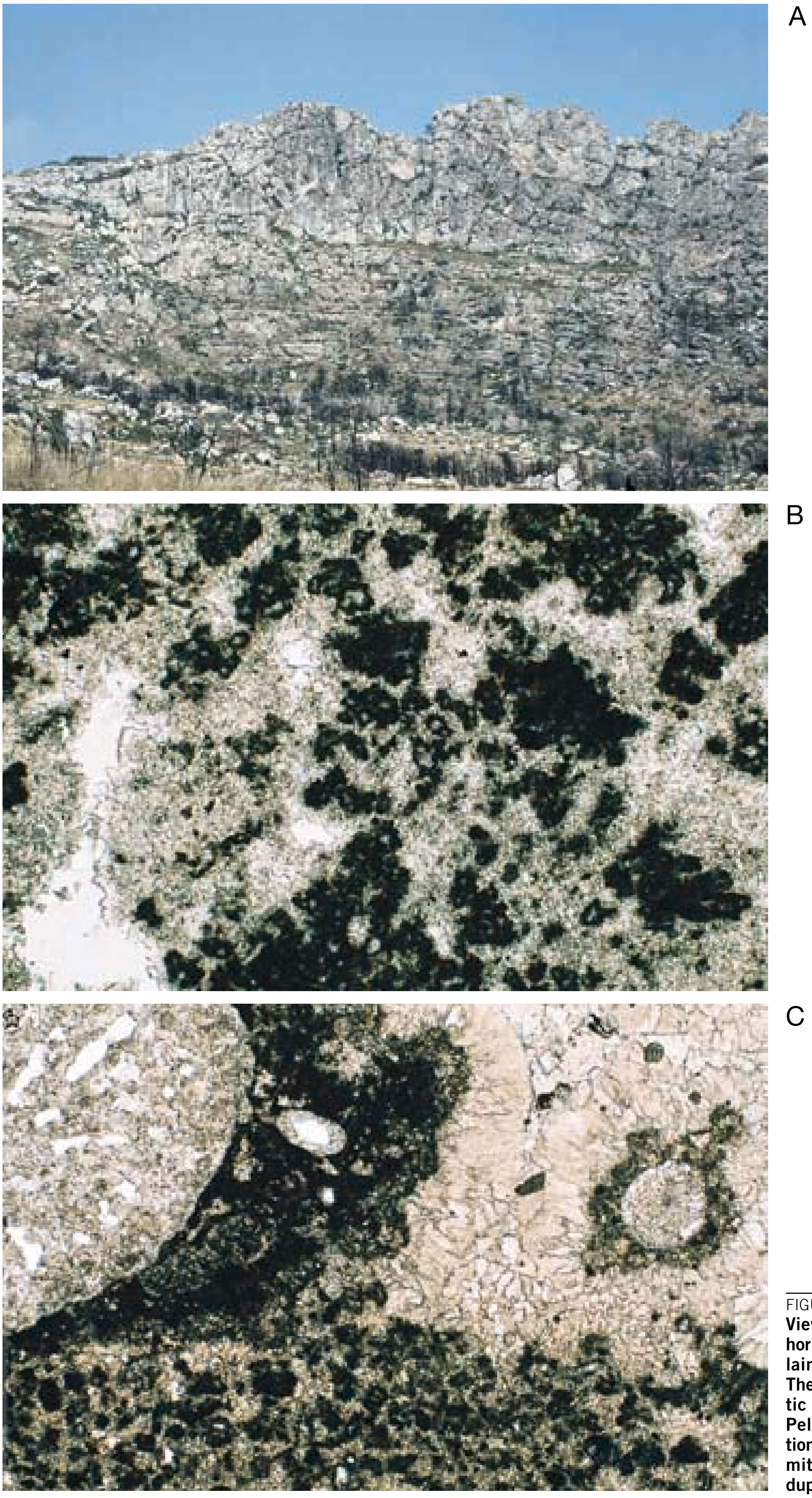

FIGURE 3 **La Riba buildup outcrops. A) View of a La Riba buildup, resting on horizontal Benifallet Formation and overlain by onlapping Alcover dolomicrites. The buildup is 50 metres high. B) Micritic aggregates in mound-core facies. C) Peloids, a coral with micritic encrustation and fibrous marine cement, all dolomitised, from the upper part of a buildup. Fields of view 5 x 3 mm.**

FIGURE 4 **A well-preserved holothuroidean fossil *(Oneirophantites tarraconensis)*, 10 cm in length, from the Alcover Unit.**

The fibrous cements occlude small cavities in the reefal framestone and line larger cavities with isopachous fringes (Figs. 5 and 6). However, some fibrous cement layers are non-isopachous, showing thickness increases into cavity corners and the filling of sub-cavities off major ones first (Fig. 6). Although dolomitised, the columnar crystals preserve the undulose extinction and curved twin-plane fabrics typical of many ancient fibrous calcite cements (Fig. 5B).They were probably high-Mg calcite originally.

The botryoidal cements form mamelons and fans with fibres up to 10 cm long; the fibres themselves are poorly preserved through the dolomitisation, with vugs commonly present (Figs. 6 and 7A). The fans may occur within the sediment (Fig. 7B) or fill large growth cavities in the reefal framework (Fig. 6). They were often precipitated after the fibrous cements (Fig. 6).

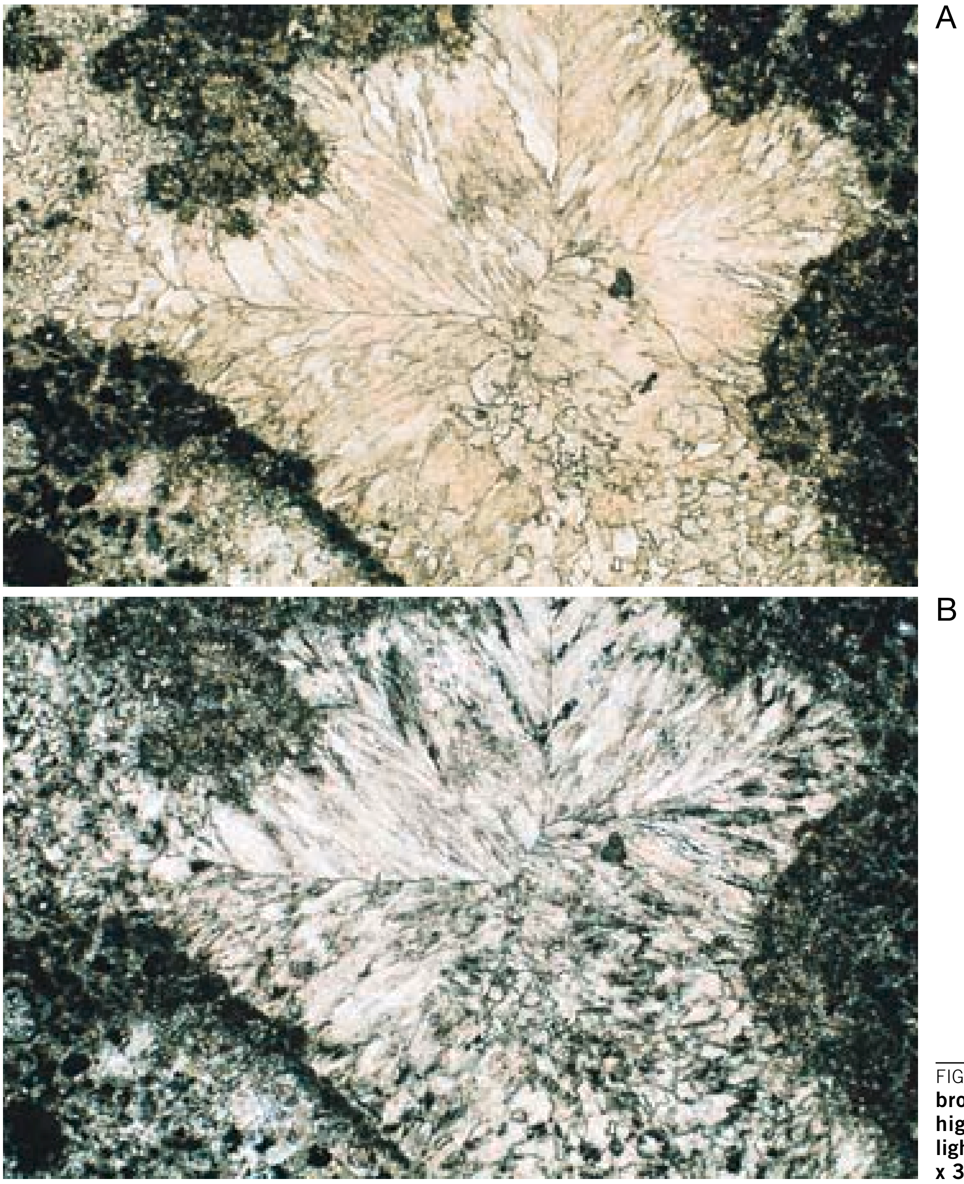

FIGURE 5 **Well-preserved dolomitised fibrous cement, interpreted as originally high-Mg calcite. A) Plane polarised light. B) Crossed polars. Fields of view 5 x 3 mm.**

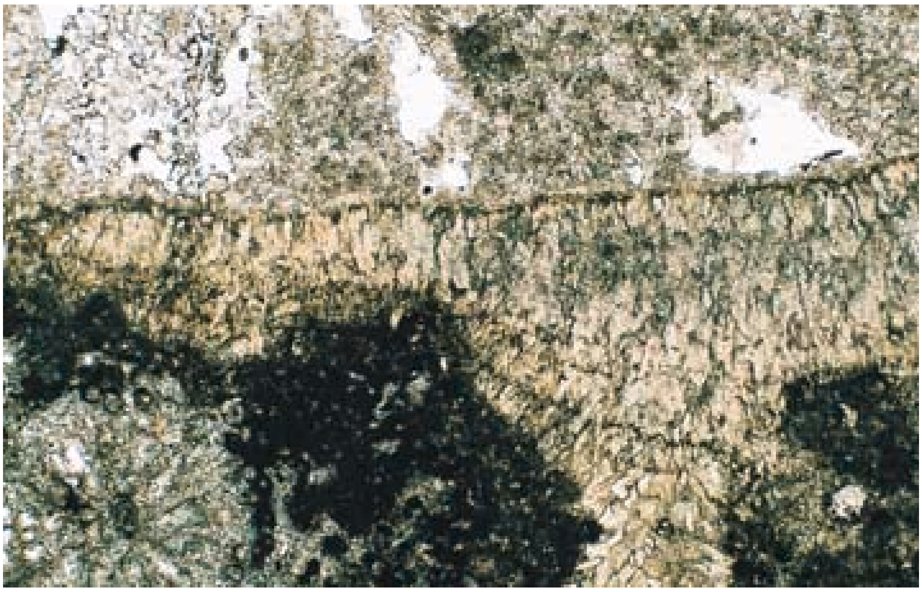

FIGURE 6 **Dolomitised early fibrous cement fringes (interpreted as original high-Mg calcite) followed by cavity-filling cement, originally aragonite. Coral lower left. Field of view 5 x 3 mm.**

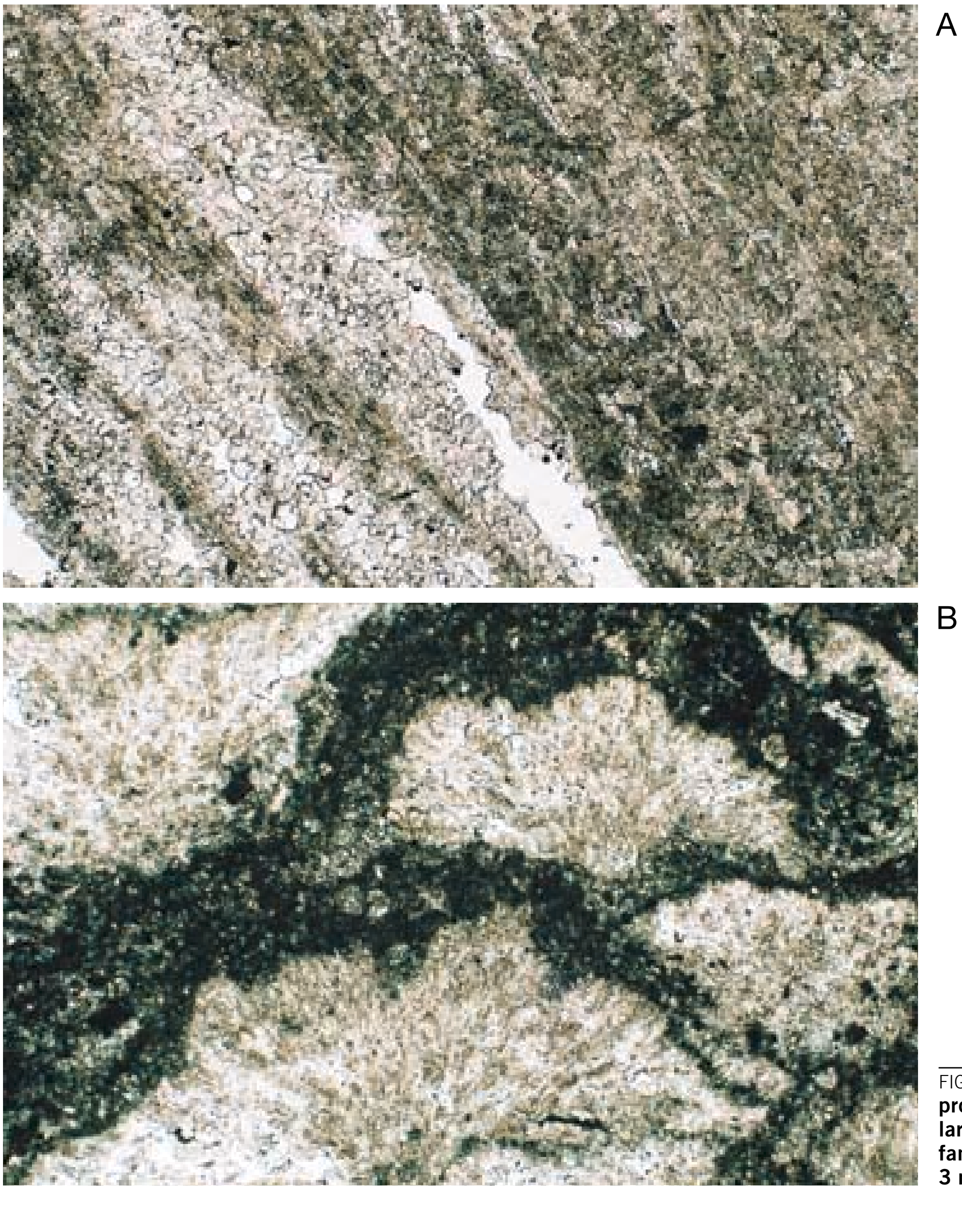

FIGURE 7 **Dolomitised botryoidal cement, probably originally aragonite. A) Part of large cavity-filling fibrous fan. B) Small fans within sediment. Fields of view 5 x 3 mm.**

Exposure diagenesis

After the growth of the La Riba buildups, there was a fall in sea-level and some karstification during the accompanying subaerial exposure (Calvet and Tucker, 1995). A sharp undulating surface was generated on the top of the buildups and there is minor brecciation. Some cavities may have been formed in the reefal facies as a result of meteoric dissolution. However, the palaeo-karstification was not extensive, probably since the climate was relatively arid.

Dolomitisation

The La Riba buildups are completely dolomitised but the fabric retention is generally excellent (Figs. 3B, 3C, 5 and 6). Many of the original features are faithfully preserved, just as if the rock was still a limestone. Bioclasts that originally had a cryptocrystalline fabric and were calcitic, often high-Mg calcite, look pristine. Original aragonitic grains, such as bivalve and gastropod fragments, and corals, are usually preserved as molds filled with dolomite cement showing a drusy fabric, again, just as they would be in any limestone. They are the result of aragonite dissolution-dolomite cementation. The cement between grains and in cavities is a dolomitised fibrous cement mimetically replaced, and/or dolomite spar cement with a drusy fabric. The automicrite is dolomitised with perfect textural preservation (Fig. 3B).

Under catholuminescence, the dolomite replacing the original sediment, bioclasts and micrite has a uniform dull luminescence. The cavity-filling dolomite spar shows the usual growth zones to be expected of a cement. There are later veins of brightly luminescing coarse dolomite crystals cross-cutting the dull dolomite.

The fabric-retentive nature of the dolomite replacing the micritic sediment and the high-Mg calcite grains, along with the more fabric-destructive replacement of original aragonitic grains, would indicate early dolomitisation, before the sediment was stabilised to calcite.

Late Sulphate Replacement

The mud-mound core facies does contain many vugs (irregular in shape and up to 10 cm across) and in some cases these contain quartz crystals and chert. They may also be partly filled with coarse calcite crystals. The quartz crystals contain small inclusions of anhydrite.

The vugs are interpreted as the result of dissolution of local patches of gypsum/anhydrite which replaced the dolomite. This could have been contemporaneous with deposition of the Alcover Unit, when the basin was periodically hypersaline, or later during shallow burial when, for example, the evaporitic Keuper facies were being deposited. The sulphate could have been precipitated even later still, from circulating basinal brines. After all, there are evaporites at many levels within the Triassic succession, and in younger formations nearby, such as the Tertiary of the Ebro Basin. The quartz is a diagenetic replacement of the sulphate and the silica may well have been derived from sponge spicules, which are common in the buildups.

ISOTOPE AND TRACE ELEMENT GEOCHEMISTRY STABLE ISOTOPES

Some 50 whole-rock samples of the Upper Muschelkalk were analysed in the isotope lab of Liverpool University for their carbon and oxygen isotopic signatures in the standard procedure: 10 mg powder in 4 ml anhydrous 100% phosphoric acid for 24 hours at 55ºC, all samples being dolomite. The average reproducibility on duplicates was 0.06 for $\delta^{18}O$ and 0.03 for $\delta^{13}C$ dolomite. Values give here are $‰_{PDB}$.

Upper Muschelkalk Limestones

Parts of the Rojals, Benifallet and Rasquera Units are still composed of calcite and their average isotopic compositions are shown in Table 1. Basically, the $\delta^{18}O$ values and $\delta^{13}C$ values are all quite constant for the three formations at -4.2‰, -3.3‰ and -3.9‰ for $\delta^{18}O$ for the Rojals, Benifallet and Rasquera Formations respectively, and 2.0‰, 2.2‰ and 2.2‰ for the $\delta^{13}C$ values respectively

TABLE 1| **Average isotope signatures for Upper Muschelkalk Units ($‰_{PDB}$).**

Unit	$\delta^{13}C$	$\delta^{18}O$
Querol Dolomites	+1.5	-3.9
Rasquera Limestones	+2.2	-3.9
Alcover Dolomites	-1.9	-3.4
La Riba Dolomites	+1.0	-2.8
Benifallet Dolomites	-1.9	-2.8
Benifallet Limestones	+2.2	-3.3
Rojals Limestones	+2.0	-4.2

Upper Muschelkalk Dolomites

La Riba Unit Dolomites

The whole-rock La Riba samples chosen for analysis were those appearing to be dominated by early dolomite

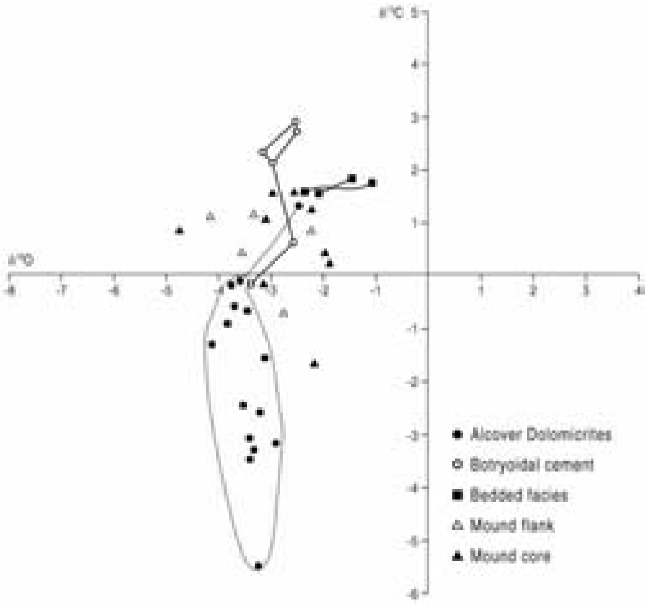

FIGURE 8 **δ^{13}C-δ^{18}O cross-plot for the various dolomites from the La Riba facies and the Alcover dolomicrites.**

only (uniformly fine grained, good fabric preservation). The δ^{18}O values range from –1.2 to –4.7‰ (overall average –2.8‰) and the δ^{13}C from –1.7 to +2.9‰ (overall average +1.0‰).

The analysed La Riba samples can be divided into four groups: the mound core, mound flank, botyroidal cements and mound-top bedded facies, and there are differences in the average isotopic signatures between these groups (Fig. 8). The mound-core samples average +0.6‰ δ^{13}C and –2.8‰ δ^{18}O. The flank facies are +0.9‰ δ^{13}C and –3.2‰ δ^{18}O. The botryoids are +1.8‰ δ^{13}C and –2.9‰ δ^{18}O and the bedded facies average +1.6‰ δ^{13}C and –1.8‰ δ^{18}O (Fig. 9).

Interpretation of La Riba Isotopes

The generally similar δ^{18}O values for all samples suggest that either there was one major phase of dolomitisation with similar porefluids involved for all facies or that all the dolomites recrystallised under similar conditions. The petrographic evidence of excellent preservation of original textures suggests that the dolomitisation was early. If this was through a seawater circulation mechanism (see later discussion), then taking mid-Triassic seawater to have had an isotopic composition of –2$‰_{\mathrm{SMOW}}$ (Veizer et al., 1999), and bearing in mind the uncertainties over the fractionation equations for dolomite (Tucker and Wright, 1990), the average value of δ^{18}O = -3.0‰ would indicate precipitation at a temperature of between 40-50ºC. This is too high for a near-surface environment. Looking at the problem another way, marine Middle Triassic calcite precipitates have a δ^{18}O value of –1.5 to –2.5$‰_{\mathrm{PDB}}$ (Scherer, 1977; Frisia et al., 1989), so that with a dolomite-calcite fractionation of ~3‰, Triassic seawater dolomite would be expected to have δ^{18}O in the range of 0 to +2‰. Indeed, many Upper Triassic marine dolomites do have these low positive values (Török, 2000).

The alternative explanation for the negative oxygen is that early dolomites recrystallised during burial and that this reset the δ^{18}O. If this took place in seawater, then the temperature of precipitation noted above could indicate a burial depth of up to 1 km, assuming a geothermal gradient of 25ºC per km. From the geological history of the region, such a burial depth would not be unreasonable.

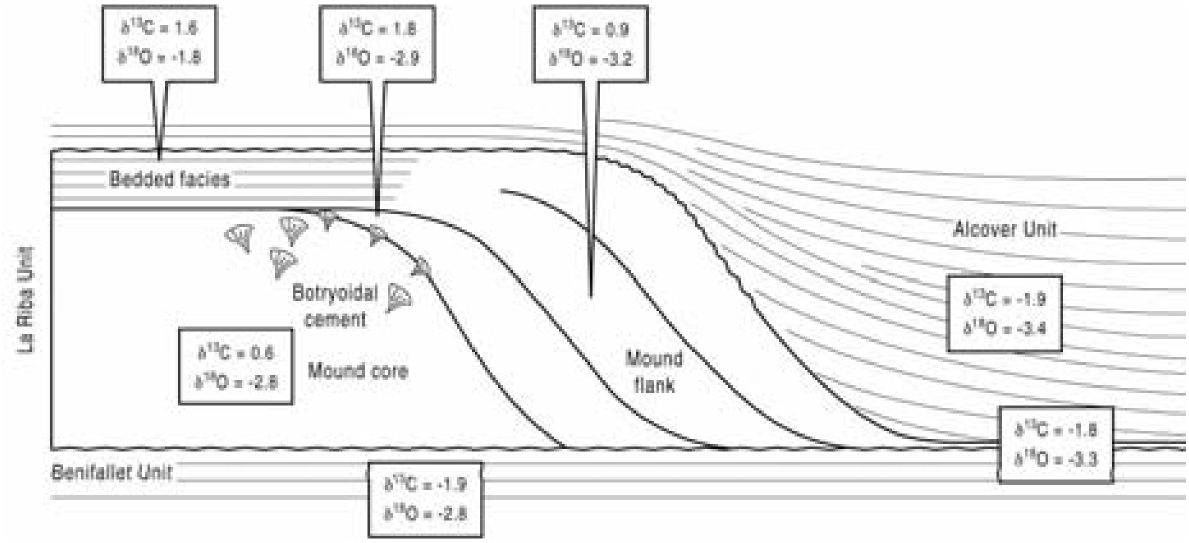

FIGURE 9 **Average isotope signatures for the La Riba buildup facies and Alcover dolomicrites.**

However, the good textural preservation might argue against burial recrystallisation.

Looking in a little more detail at the four groups of dolomite (Fig. 9), the less negative $\delta^{18}O$ value of the bedded facies could indicate some original evaporative carbonate precipitation giving a more positive $\delta^{18}O$ calcite or dolomite signature. This would be consistent with the tidal-flat environment of deposition of this facies.

The variations in the $\delta^{13}C$ values are most likely a reflection of original differences between facies in terms of the amount of microbial activity and organic matter degradation. The dolomitised botryoidal cements have higher $\delta^{13}C$ values (several around +2.8‰) than the other mound facies. In fact, botryoidal cements do commonly have more positive $\delta^{13}C$ values than their normal-marine host reef-rocks (James and Choquette, 1983).

Alcover Unit Dolomicrites

The $\delta^{18}O$ values for these fine-grained dolomites are remarkably similar; the range is between –2.2 and –3.9‰ (Figs. 8, 9) and average is –3.4‰. However, the $\delta^{13}C$ values are very variable indeed, from –5.4 to +1.5‰, with an average of –1.9‰. In fact, the values are not random; there is a distinctive stratigraphic trend in the data (Fig. 10). The basal layer of the Alcover Unit has a low negative value (-1.7‰) which is similar to that of the bed below (-1.8‰ $\delta^{13}C$); this is the thin (10 cm), lateral 'basinal' equivalent of the La Riba buildups. From the basal Alcover bed, the $\delta^{13}C$ becomes increasingly negative in the succeeding 2.5 metres of strata to a value of –5.4‰ $\delta^{13}C$. The carbon isotopic composition then becomes more positive to a value of +1.5‰ and then above this, $\delta^{13}C$ is close to 0‰.

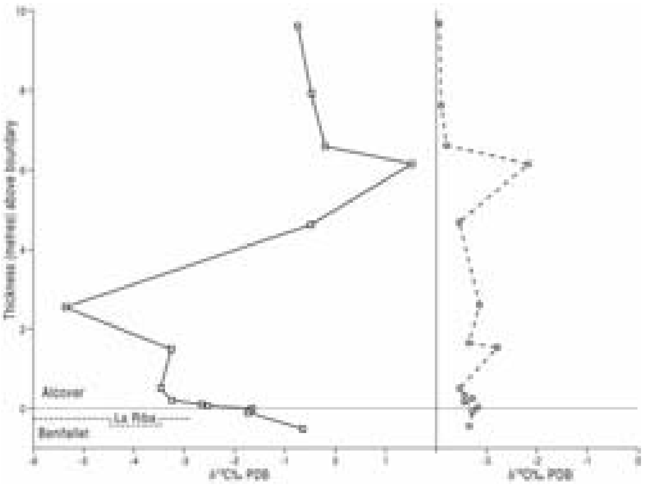

FIGURE 10 **Isotopic data for the lower part of the Alcover dolomicrites plotted stratigraphically.**

Interpretation of Alcover Isotopes

The similar values of $\delta^{13}C$ in the thin, La Riba buildup-equivalent bed and the basal Alcover bed suggest a similar degree of carbon cycling in the seawater. However, it is worth noting that the boundary between these two beds is a sequence boundary (Calvet and Tucker, 1995). It is the correlative conformity to the unconformity seen higher up on the buildup surface where the Alcover Unit onlaps the mound. The similarity of the $\delta^{13}C$ above and below the sequence boundary suggests that there was no subaerial exposure here in the depressions between buildups.

The increasingly negative upward trend in $\delta^{13}C$ in the lower few metres of the Alcover Unit could reflect developing anoxic conditions on the seafloor during carbonate precipitation and incorporation of light CO_2 into the carbonate from organic matter degradation. The occurrence and preservation of the special fossils in the lower part of the Pedra D'Alcover, also most likely the result of anoxic conditions retarding organic diagenesis, as well as the fine sedimentary lamination, are consistent with water stratification. The return to more 'normal-marine' carbon values higher up the succession could indicate increased circulation and a breakdown of stratification of the basin waters. The micrites there are a lighter grey colour too and the special fossils are rare or absent.

The average $\delta^{18}O$ value of the Alcover dolomicrites (-3.4‰) is a little more negative than that of the La Riba dolomites (-2.8‰), but not significantly so. The La Riba dolomites are clearly replacive, whereas the Alcover dolomicrites could be near-primary precipitates, that is sea-floor (or just below) alteration of calcitic/aragonitic muds. If the Alcover dolomites were 'primary' and precipitated from normal-marine Triassic seawater, then, as noted earlier, one would expect $\delta^{18}O$ values of between 0 and +2‰ with a dolomite-calcite fractionation of up to +3‰. However, again, perhaps the most likely explanation is that the Alcover dolomites were subjected to recrystallisation (although this did not result in any significant increase in crystal size) and this reset the $\delta^{18}O$ signatures. The really quite similar values of $\delta^{18}O$ in both the Alcover and the La Riba dolomites do suggest dolomitisation/recrystallisation under similar conditions of fluid composition and temperature/burial depth.

TRACE ELEMENTS

Trace element analysis was undertaken with ICP-OES on many of the samples analysed for their isotopes. Procedure was essentially 40 mg powder reacted

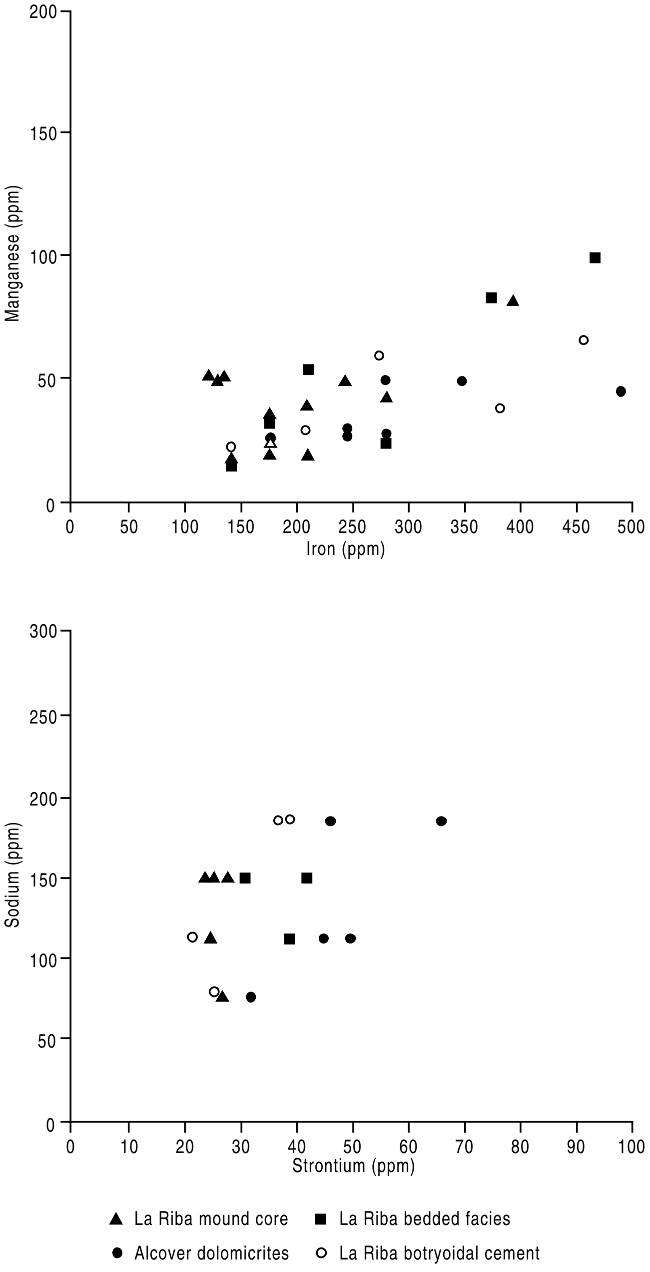

FIGURE 11 **Trace element data for La Riba buildup facies and Alcover dolomicrites.**

with 5mL 10% HCl at 60°C for 2 hours then 5 ml water added; errors are estimated as ~5%. Strontium, sodium, iron and manganese were determined and the results are shown in Fig. 11.

Iron and manganese

The iron values are all less than 500 ppm, with most less than 300 ppm; the Mn values are all less than 100 ppm, with the majority less than 50 ppm. These values are generally low compared with many other dolomites in the geological record. There is a fair amount of scatter for both the La Riba and Alcover dolomites. If anything, it could be said that the Alcover dolomites have a greater range of Fe (170-500 ppm), compared to Mn which is quite uniform (20-45 ppm). The La Riba mound-core dolomites generally have lower Fe and Mn compared to the La Riba reef-top facies, which are more variable in both Fe and Mn.

Strontium and Sodium

The strontium values are 25-70 ppm and the sodium values are 70-180 ppm. These trace elements are also on the low side compared with other published analyses of dolomites, especially young dolomites. Although there is little difference, the Alcover dolomites are slightly more enriched in Sr and Na compared to the La Riba dolomites. Of particular note is the low Sr (20-40 ppm) of the dolomitised botryoidal cements. If they were comparable to modern aragonite botryoids, they would originally have had values up to 10,000 ppm, and on dolomitisation, one would have expected some of this to be retained.

Discussion of Trace Element Data

Iron and manganese are generally present in low concentrations in marine carbonate precipitates, in view of the oxic nature of seawater and low contents of these elements. If precipitation or recrystallisation takes place in an anoxic environment, and these elements are available, then high values may occur in view of their high partition coefficients. In the case of these Triassic dolomites, the relatively low values of Fe and Mn could be the result of little recrystallisation (but this does not square with the $\delta^{18}O$ data) or a lack of Fe and Mn in the pore-fluids. The latter could be because the fluids were oxidising, or, if the dolomitising/recrystallising fluids were anoxic, then simply that Fe and Mn were not available; that is, there was little clay present. It is clearly the latter that is most likely.

The strontium and sodium values of the La Riba and Alcover dolomites are low compared to modern carbonates and to many ancient dolomites that had a marine origin. Loss of Sr and Na from the original mixed-mineralogy carbonate sediment could be the result of 1) stabilisation of the original metastable carbonate to calcite and then dolomitisation, or 2) dolomitisation of original carbonate sediment, then recrystallisation of the dolomite. Loss of these elements arises from their low (less than 1) partition coefficients.

Thus, the trace element data are actually very useful here. The low Sr and Na values can be interpreted in terms of dolomitisation after stabilisation of the original carbonate sediment or recrystallisation of early dolomite. The low Fe and Mn suggest low availability of these elements in the pore-fluids, in spite of the likelihood of anoxic conditions induced through the presence of organic matter.

DISCUSSION OF DOLOMITISATION

The Upper Muschelkalk buildups have been subjected to many phases of diagenesis: seafloor cementation, emergence and karstification, early dolomitisation, later dolomite recrystallisation, local sulphate replacement and then later dissolution-replacement of sulphate by silica and calcite.

The petrographic evidence from the La Riba Unit with the very well-preserved original fabrics in dolomite indicates that dolomitisation was an early event. Under this situation, the sediments would have been in their original metastable mineralogies, so that lime mud (aragonite or high Mg-calcite) and high-Mg calcite grains are well preserved by the replacement dolomite, but original low-Mg calcite and aragonite grains are poorly preserved. Since many of the grains and the sediment itself had a primary fine-grained texture, dolomitisation resulted in mimetic replacement, preserving the textures faithfully (see review of dolomite fabrics in Tucker and Wright, 1990).

The very fine-grained nature of the Alcover dolomicrites, and their beautifully preserved fossils, again indicates early dolomitisation, even seafloor (or just below) dolomite replacement of micritic carbonate.

The carbon isotopic data for the La Riba and Alcover dolomites are very variable and as suggested above, for the La Riba Unit, the $\delta^{13}C$ values are probably inherited from the original limestones. In fact, with many values around +1‰, they are quite typical for marine carbonates.

For the Alcover dolomites, the neat stratigraphic trend shown by the $\delta^{13}C$ analyses that can be interpreted in terms of changes in the depositional conditions, clearly shows that the values are original. Alcover deposition did take place in an anoxic environment, based on the presence of organic matter, fine lamination and exquisite preservation of fossils. It is now well accepted that microbes, anoxia and organic matter diagenesis are all factors favouring the precipitation of dolomite (Burns et al., 2000). Alcover deposition may well have been in a similar environment to the dolomite laminites recorded from the Gulf of Mexico (e.g., Kelts and McKenzie, 1982), although extreme $\delta^{13}C$ values as typify fermentation, are not recorded.

The $\delta^{18}O$ values for all the La Riba and Alcover dolomites are not really very different; they are all clustering around -3‰. There is scatter of course, but there do not appear to be different generations of dolomite from the petrography and CL, nor from the geochemistry. As discussed before, the best explanation for the negative $\delta^{18}O$ is one involving recrystallisation of an early dolomite, since the petrographic evidence points towards early dolomitisation. The La Riba dolomites do not show features of burial dolomite. The trace element data, in particular the very low Sr and Na values, are consistent with dolomite recrystallisation. As noted earlier, the re-setting of the $\delta^{18}O$ signatures would appear to have taken place at shallow-to-moderate depths of less than 1000 metres, but this did not involve any significant coarsening of crystal fabrics.

For the dolomitisation of the La Riba buildups, there are four possibilities: (1) dolomitisation by seawater being pumped through the buildups when buildup-top bedded facies were being deposited, (2) brine reflux during La Riba bedded-facies peritidal deposition, (3) dolomitisation by seawater circulating in the buildups during falling sea-level and lowstand, driven by circulation within the meteoric-marine mixing-zone and (4) dolomitisation by seawater, possibly with higher salinity and some degree of lowered oxygen, at the time of deposition of the Alcover Unit.

In view of the wholesale dolomitisation of the La Riba and Alcover formations, and much of the underlying Benifallet, the apparent early timing, and the similarity of $\delta^{18}O$ values of La Riba and Alcover dolomites, dolomitisation of the La Riba buildups from circulating seawater during Alcover deposition (or shortly after) is preferred, i.e. scenario (4) above.

CONCLUSIONS

The La Riba buildups of the Upper Muschelkalk in the Catalan Basin, eastern Spain, are completely dolomitised but with excellent preservation of original fabrics. Primary skeletal grains, various automicrite textures and fibrous marine cements, which were originally high-Mg calcite, are all faithfully recorded in the dolomite mosaic. Originally aragonitic grains such as corals and former aragonitic botryoids are poorly preserved by dolomite, but in a similar way to their preservation by calcite in a limestone. Although this suggests early dolomitisation, the oxygen isotope values are quite negative (~-3‰) and, with low Sr, recrystallisation at shallow to moderate depths is likely. The $\delta^{13}C$ signature (~+1‰) of the La Riba Unit is interpreted as an inherited marine value. The overlying Alcover laminated, organic-rich dolomicrites, with exquisitely preserved fossils, have similar negative $\delta^{18}O$ values indicating recrystallisation. However, they display a stratigraphic trend in $\delta^{13}C$ which records the development and breakdown of water stratification and anoxia. Dolomitisation of the La Riba buildups most likely took place through circulating seawater, probably induced by sea-level changes, during deposition of the Alcover Unit or shortly thereafter.

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