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Isotopic Signature of the Diagenetic Fluids and Cement in the Tortachilla Limestone, South Australia

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Abstract

Stable isotope analysis of carbonate rocks and fossils can be employed for reconstruction of the ancient sedimentary environments and their diagenetic history, estimation of the isotopic composition, origin and temperature of seawater and diagenetic fluids. In this study, relying upon earlier investigations by authors and others in the Tertiary sequences of St. Vincent Basin of South Australia, the diagenetic setting, isotopic compositions, origin of diagenetic fluids and cement are constrained. The isotopic signature of meteoric cement is controlled by the isotopic composition of the original marine calcites (e.g., calcareous organisms) and the meteoric fluids. The isotopic composition of this meteoric cement is used to constrain the isotopic signature of diagenetic fluids. The isotopic composition of diagenetic Low Mg-Calcite (dLMC) meteoric cement of the Tortachilla Limestone represents an isotopically light composition (highly depleted) relative to the isotopic composition of marine calcite. This suggests that seawater had no significant contribution to the formation of this cement. On the other hand, the isotopic value of this cement is close to the values reported for the calcite precipitated from modern coastal and island meteoric water in similar latitude (51.5°). The meteoric calcite cement of this unit shows the inverted-J pattern, which is characterized by concomitant invariability in $\delta^{18}O$ and variability in its $\delta^{13}C$ signature.

The isotopic composition of seawater is also estimated by using the well-preserved fossil materials.

Key words*: stable isotopes, meteoric cement, Australia, diagenesis*

1. Introduction

The chemical and isotopic composition of meteoric waters vary during passage through sedimentary carbonate sequences due to water-rock interactions (mineralogical stabilization), uptake of organically derived CO_2 and mineralogical discrepancies of different carbonate sequences. Accordingly, the $\delta^{18}O$ values of meteoric groundwater are mainly invariable (constant) in a given geographic location, whilst the $\delta^{13}C$ values are variable mainly due to variations in the amount of dissolved soil-gas CO_2 and in the extent of water-rock interaction. This concomitant invariability in $\delta^{18}O$ and variability in $\delta^{13}C$ signatures of meteoric waters are reflected in their diagenetic products, producing a distinct geochemical trend, termed "the meteoric calcite line" or inverted-J pattern (Lohmann 1988). Lohmann (1988) suggested that this line could serve as a baseline for distinguishing different diagenetic environments, using the isotopic signature of their products.

Meteoric calcite cements are usually 2.0‰ lighter in $\delta^{18}O$ than their contemporaneous marine counterparts in the nearby environments (e.g., Frank et al., 1995). Craig (1961) and Dansgaard (1964) have shown that the $\delta^{18}O$ values of meteoric waters generally become lighter with increasing latitude (Rayleigh Fractionation Effect). The $\delta^{18}O$ values of shallow meteoric cements (shallow burial) are controlled by the isotopic composition of rainwaters in the region, climatic variations and temperature. Modern rainwaters vary in $\delta^{18}O$ values, from as much as 0.0‰ (low latitude in arid regions) to - 5.0‰ (in humid monsoon climates -e.g., Aharon 1983, Anderson and Arthur 1983).

Therefore, the $\delta^{18}O$ values of meteoric cements can vary drastically and are only partially dependent on the rock reservoir $\delta^{18}O$ signature (e.g., Saller and Moore 1991). In this paper, some of the diagenetic implications of meteoric cement from Tortachilla Limestone of St. Vincent Basin are investigated and the isotopic signature of diagenetic fluids is estimated.

2. Geological setting

Studied area is located in the southern section of the St Vincent Basin of south Australia, in the Maslin-Aldinga area (Fig. 1). Thickest sedimentary successions of the Tertiary of south Australia accumulated in passive continental margin basins, such as the St. Vincent and Murray Basins, where they unconformably overlie Mesozoic rift-basin sediments. In these Tertiary basins sediments are mainly deposited in marginal setting as widespread thin sheets of diverse origin. A consequence of the separation of Australia from Antarctica was the initiation of marine transgressions into the southern marine basins and deposition of marine sediments with considerable thickness. Therefore, the Tertiary succession in southern Australia passes upwards and seawards from Early Tertiary nonmarine clastic sediments into marine temperate carbonate sediments (Fig.2). These carbonate sediments, which are up to 1.5km thick, contain copious macro-and microfossils, which in many cases are well-preserved. The St. Vincent Basin represents a continuous record for lower Tertiary of South Australia (Fig.2). Tortachilla Limestone is one of the important units in the St. Vincent Basin which its geochemical diagenetic implications are studied here.

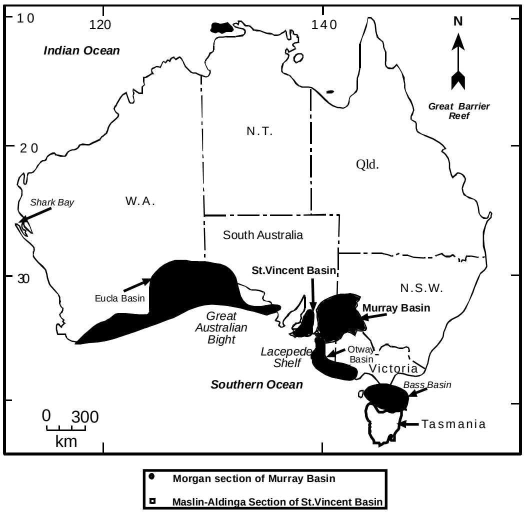

Figure 1 - Location map of the study area and some other Tertiary basins of southern Australia.

The Tortachilla Limestone overlies the South Maslin Sand, which is a marginal marine glauconitic unit and contains bryozoans, molluscs, echinoids and foraminifera (Fig.2). The Tortachilla Limestone in the southern district of the St. Vincent Basin announces the Tortachilla Transgression (McGowran 1989, 1991).

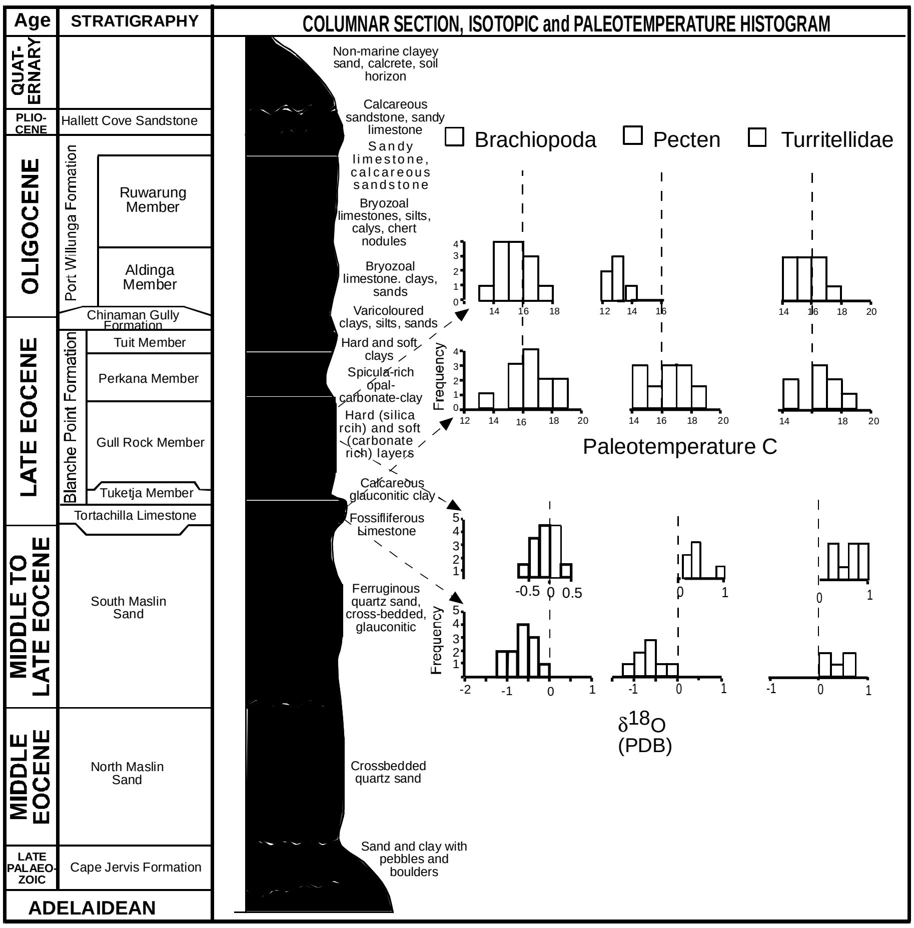

Figure 2 - Generalized stratigraphic column of the Tertiary units of St. Vincent Basin of South Australia in the Maslin-Aldinga area (not to scale). The isotopic and paleotemperature histograms of Tortachilla Limestone and Gull Rock Member is also shown.

This unit contains shallow water temperate benthic foraminifera, molluscs and bryozoans (mainly Packstone partly graded into

Grainstone) and is succeeded by the Late Eocene Blanche Point Formation, which in turn is a fossiliferous calcareous mudstone with a few thin limestone lenses.

3. Sample Preparation and Analytical Methods

All sample preparations and experiments, including petrography of rock samples in thin sections, XRD and Cathodoluminescence studies and stable isotope analysis for carbon and oxygen were carried out in the laboratory of department of Geology, the University of Adelaide. Samples of dLMC meteoric cements, fossils of Pecten sp. and Terebratellidae brachiopoda from Tortachilla Limestone were used for this study. Prior to analysis, all samples were brushed, soaked and washed in commercial bleach (4‰ sodium hypochlorite concentration) by the method recommended by Love and Woronow (1991) and Gaffey and Bronnimann (1993) for removal of organic material, then rinsed several times by deionised water and dried. Samples were then powdered using a dental drill or with a pestle and mortar. In the case of cements, sampling was carried out under binocular microscope using a dental drill and / or scalpel.

The mineralogy of the samples was determined by X-Ray diffraction (XRD) using a Phillips PW 1050 Diffractometer. A few drops of water were added to the finely pulverized sample and about 1/3 of a spatula full of powdered quartz was also added and then mixed. The spiked quartz acts as an internal reference. This mixture was ground again by mortar and pestle to form the required slurry. The slurry was then smeared over half of a cleaned and labeled glass slide. Samples were subjected to XRD analysis under the following conditions:

Graphite Monochromator, Cobalt Ka radiation source, Wavelength 1.7902 A, 2-0 Scanning range of 3 to 75 with a steep interval of 0.05.

JCPDS Manuals and an X-Plot (developed by the CSIRO Division of Soils) computer package were used in the identification of the minerals.

The following equation was used to aid in determining mineral percentages:

$$R = hA.wA / hA.wA + hC.wC \quad R = \text{carbonate mineralogy}$$

$$hA = \text{height of aragonite peak} \quad hC = \text{height of calcite peak}$$

wA = width of aragonite peak *wC = width of calcite peak*

These results were compared to a standard curve for aragonite determination using peak height and width analysis (Milliman 1974). In most instances the standard deviation is considerably less than 5‰. Mole ‰ $MgCO_3$ was determined by running the sample carefully using the gwbasic mgcalc program.

Samples were analyzed for their oxygen and carbon isotopes using and Optima Micromass Spectrometer that was equipped with an Isocarb autorun device for carbonate samples. This equipment needs 0.2 mg of powered sample for analyzing carbon and oxygen isotopes. The isotope results are presented in the standard form of per mil Pee Dee Belemnite (PDB) for carbonates (Tables 1,2 and 3). Standards (NBS. 19 and NBS. 18) and duplicate samples and several blanks were used to ensure high equipment precision and appropriate corrections have been applied to the results. All values are reported in the standard (δ) notation where:

$$?\&^{18}O = [(^{18}O/^{16}O)\ sample/(^{18}O/^{16}O)\ standard - 1]\ (10^{3})\ per\ mil$$

Determination of $\delta^{13}C$ were made concurrently with $\delta^{18}O$. Average reproducibility, as evidenced by duplicate analyses and a standard run before and after sample strings, was approximately ± 0.1‰ for Optima Micromass Spectrometer. The precision is ± 0.05 for $\delta^{13}C$ and ± 0.1 for $\delta^{18}O$.

Luminescence in carbonates has been shown to be correlative primarily with the presence of certain trace elements, namely manganese (Mn^{2+}). The substitution of Ca^{2+} by Mn^{2+} typically gives rise to luminescence in calcites at the orange-yellow to orange red end of the spectrum. The maximum CL intensity appears to be determined by the iron to manganese (Fe^{2+} / Mn^{2+}) ratio. After all supposedly well-preserved fossil samples examined, by staining, microscopic study and XRD analysis, they were further re-examined by CL to distinguish any diagenetic alterations. All fossil samples, which were here claimed to be pristine, did not show any luminescence under the CL.

CL studies were carried out in a Technosyn Cold stage Luminoscope, model 8200MkII, using a cold cathode electron gun to supply the electrons. The resultant electron beam was fixed. In the vacuum chamber of the CL stage, the electron beam is absorbed by the surface it hits. Much of the incident energy is absorbed at the atomic level by electrons. Luminescence often results. Uncovered thin sections (100 micron thick) with high quality polished surfaces were used to obtain optimal details under CL. The extra thickness is needed for heat dissipation since the standard thin sections have a tendency to crack and burn. Abnormal heating of thinner sections can alter the color of cathodoluminescence. Thin sections were prepared using a glue/cement that is stable at the moderate temperature generated in the process. Luminescence was recorded on Ektapress PC 1600 color film.

4. Tortachilla Limestone; Discussion

In the Tortachilla Limestone most of the primary and secondary porosity (including intergranular, intragranular and fractures) are filled by a sparite void-filling LMC cement which exhibits approximately bright luminescence under CL and has shallow burial meteoric origin (Figs. 3, 4 and 5). The stable isotopic composition of this coarse diagenetic Low Mg-Calcite cement (dLMC) from the Tortachilla Limestone is plotted in Figure 6. Also shown are the average values of the isotopic composition of well-preserved Pecten sp. and Terebratellidae brachiopoda from Tortachilla Limestone (as baselines for marine calcite). By detailed petrography and cathodoluminescence studies only LMC fossil samples that showed no evidence of the diagenetic alterations have been chosen. Taking into account that equilibrium isotopic precipitation of calcareous shells of these organisms is substantiated (e.g., Veizer et al., 1986, Popp 1986, Brand 1989a, b and c, Grossman et al., 1991, Carpenter and Lohmann 1995, Bone and James 1997, Rahimpour-Bonab et al., 1997a and b), their isotopic signatures (after applying appropriate fractionation factors for water and calcite) is pondered as proxies for seawater isotopic composition of the early Late Eocene time.

Figure 3.A - Meteoric sparite, dLMC cement from Tortachilla Limestone which filled secondary porosity (solution cast of aragonitic gastropods) (PL).

B. CL photomicrograph of this cement that shows bright luminescence. Darker areas in the cement are due to subsequent exposure of this unit to vadose zone and consequent oxidation of iron ions that caused staining of meteoric cement. In hand specimens, due to oxidation this void filling cements are reddish brown (Fields of view 3mm, CL conditions: 195?ka, 20kv, 6mins. 15Sec. Exposure time).

Figure 4 - Transverse section through well-preserved Pecten sp. of the Tortachilla Limestone, which shows its original foliated microstructure (LN, Field of view 4mm).

Figure 5 - The longitudinal section of a brachiopod valve from Tortachilla Limestone shows is endopunctate microstructure (up). In the lower part of photomicrograph, remaining cast of a dissolved aragonitic gastropod that is partially filled by meteoric sparite cements is also shown (LP, field of view 4mm).

The majority of dLMC cements in this unit exhibit relatively invariant ?Ì^{18}O and highly variant ?Ì^{13}C. Their overall isotopic compositions range between -3.85 and -4.8C for ?J^{18}O and -3.85 and -7.8‰ for ?Æ^{13}C (Fig. 6). As shown, all dLMC cement isotopic values are depleted with respect to the Tortachilla Limestone marine calcite baselines (Pecten sp. and Terebratellidae brachiopoda).

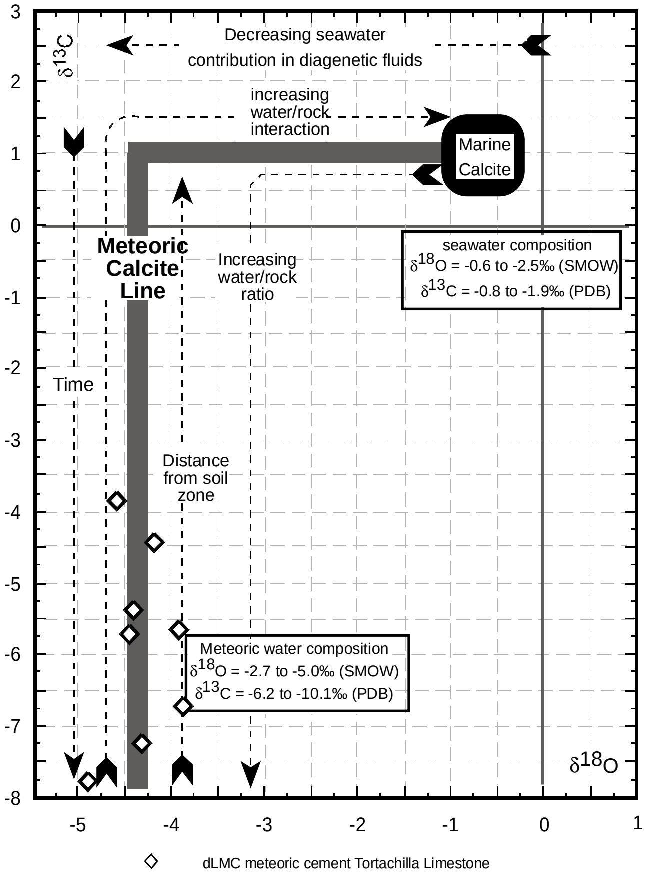

Figure 6 - The inverted - J pattern in the isotopic composition of the dLMC meteoric cement of the Tortachilla Limestone. The estimated average isotopic composition of meteoric water is based on the fractionation equation of Friedman and O'Neil (1977) at 25?C. The carbon isotopic composition is based on the most negative values of dLMC cement and applying a fractionation factor of 2.3‰ for calcite - bicarbonate (Turner 1982). The oxygen isotopic of seawater is also constrained by using average ?18O

marine calcite in that equation at 16?C and the carbon isotope resulted from the average ?<^{13}C marine calcite after 2.3‰ correction.

In Figure 7, the ?¾^{18}O range of this dLMC cement is overlain on an equilibrium fractionation diagram which relates calcite ?9^{18}O PDB values to the temperature for a range of pore fluid (diagenetic pore fluids) compositions (relative to SMOW). If the temperature of dLMC cement precipitation is constrained between 20 to 30°C, which is rational for such a shallow depth diagenetic realm, the ?[^{18}O values of the diagenetic fluids range from -2.7 to 5‰ (SMOW). The only curve that passes throughout the entire range of cement compositions is the -4.0 ‰ (SMOW) curve, which presumably demonstrates the average ?/^{18}O value of the diagenetic fluids.

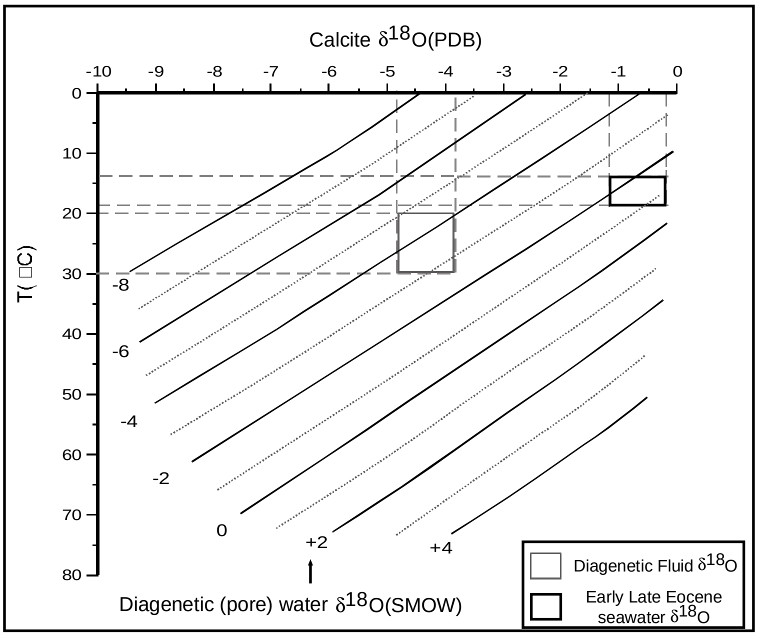

Figure 7 - The calculated ?^{18}O composition of calcite precipitated at equilibrium from waters of various compositions over a range of temperatures, using the calcite water oxygen isotope fractionation equation of Friedman and O'Neil (1977). The range of isotopic values of water from which the Tortachilla limestone cement could have been precipitated is defined by the curves which pass through the stippled box between the 20 to 30?C temperatures, in this case, about -2.6 to -5‰ SMOW. Only a single curve (?W̃=-4‰) can account for the entire range of cement composition within the permitted temperature values.

The seawater isotopic composition of the early Late Eocene at temperatures of 14 to 18C, which was the range of the bottom water temperature for that high latitude basin (Rahimpour-Bonab 1997) is also shown.

Assuming an early diagenetic marine origin for the cement in the Tortachilla Limestone is incompatible with the petrographic evidences and paleotemperature estimates, as even the maximum ?^{18}O values of cement (-3.9‰ PDB) could only have precipitated from diagenetic fluids with ?^{18}O values of -2.7‰ SMOW at a maximum temperature of 30°C (Fig. 6), which is lighter even than the lightest ?^{18}O$_{seawater}$ (-2.5‰). Moreover, this cement has coarse equant blocky texture, LMC mineralogy and bright luminescence under CL (Fig. 3) which are characteristic of the meteorically precipitated cements. The bright luminescence of this cement under CL, which denotes precipitation in a reducing shallow-depth terrestrial environment (meteoric phreatic zone), is a cogent indicator of its meteoric diagenetic setting. Therefore, ?^{18}O and ?^{13}C values of the diagenetic cement in Tortachilla Limestone indicates its precipitation in the meteoric phreatic zone from a meteoric groundwater with a characteristic ?^{18}O signature (-2.7 to -5‰ SMOW).

The meteoric origin for these pore fluids is also supported by considering the ?^{13}C signature of this dLMC cement (Fig. 6). The negative ?^{13}C signatures of this cement are indicative of the introduction of isotopically depleted bicarbonate to the pore fluids. The isotopically light carbons could have been introduced to the diagenetic pore fluids by thermal degradation of organic matter, which then are incorporated into the subsurface carbonate cement. However, the process of thermal degradation of organic matter (decarboxylation) requires relatively higher (geothermal) temperature (about 150°C, Hesse 1990) which is not consistent with the shallow burial depth of the studied sedimentary sequence. The compaction of the basinal shales is another alternative source for ?^{13}C depleted bicarbonate but there is no evidence of this. The most conceivable source of negative carbons for such shallow burial dLMC cement are organically derived CO_2 during meteoric water infiltration through the soil zone (e.g., Anderson and Arthur 1983, Lohmann 1988). Therefore, both carbon and oxygen isotopic data indicate that this dLMC cement is precipitated mainly from diagenetic pore fluids of the meteoric origin. Additional important evidence for a meteoric origin of the diagenetic pore fluids and the prevailing meteoric system in the sedimentary sequence, is the wholesale dissolution of skeletal aragonite in this unit, which in many cases is replaced by dLMC cement (Figs. 3 and 5).

The isotopic composition of meteoric waters depends on the latitude and geographical setting (coastal versus continental settings). The isotopic fractionations during frequent evaporation - precipitation (Rayleigh effect) give rise to the progressive depletion in ?k^{18}O values of rainfall towards the interior of continents and higher latitudes, compared with the coexisting marine reservoir (oceans). In marginal basins (such as the studied area) this difference is only a few per mil (Anderson and Arthur 1983, Lohmann 1988). Figure 7 demonstrates that the most negative ?!^{18}O signatures of the diagenetic pore fluids, that could have precipitated this dLMC cement of the Tortachilla Limestone, originated from a water with -5.0 ‰ (SMOW) value. This composition is close to the values reported for the modern meteoric water of the coastal areas for a similar latitude (51.5°) (Smith et al., 1981) which are about - 7‰ (cf. Hays and Grossman 1991). However, only the lightest dLMC cement could have been precipitated from the estimated meteoric water composition of -5‰ SMOW, and the heaviest dLMC cement, apparently, precipitated from more positive meteoric water with a composition of -2.7‰ SMOW (Fig. 7). There are two possibilities for such circumstances (e.g., Hendry (1993):

1) Mixing of meteoric water with marine water or compactional fluids prior to or during cementation.

This presumption that the relatively heavy ?•^{18}O of dLMC is due to mixing of meteoric fluids with marine water cannot be the case here, because such mixing would result in undersaturation with respect to calcite and, therefore, dissolution rather than precipitation (e.g., Lohmann 1988). In addition, as mentioned earlier, the ?a^{13}C of dLMC is too light and so a significant contribution of marine water in its precipitation seems unlikely.

2) The meteoric waters are considerably more enriched in ?@^{18}O compared to normal values, due to some processes such as evaporative enrichment or lack of the latitude-related fractionation of meteoric waters in coastal areas.

Meteoric waters originated from coastal precipitation show minimal altitude-related isotopic fractionation (minimum of Rayleigh Fractionation Effect) (e.g., De Wet 1987). On the other hand, figure 7 shows that a diagenetic pore fluid of -4‰ (SMOW) could have produced all of the dLMC cement, if cementation continued from near-surface temperatures to maximum burial and so maximum temperature of 30°C. Consequently, heavy ?A^{18}O values for the dLMC cement was generated by a diagenetic meteoric water which had relatively heavy ?E^{18}O (~ -4‰ SMOW). This fluid acquired its signature due to its geographic setting (marginal marine realm and so minimum of the Rayleigh fractionation).

During meteoric diagenesis, progressive water-rock interaction leads to wholesale dissolution of metastable marine carbonates (e.g., aragonite) by undersaturated recharging meteoric waters and precipitation of calcite cements when supersaturation is attained. This process can produce characteristic compositional patterns in dLMC cement known as “inverted J” trends (Meyers and Lohmann 1985; Lohmann 1988). This trend arises from the smaller concentration of Dissolved Inorganic Carbon (DIC) in diagenetic pore fluids compared with the rock (reactive marine carbonate) carbon reservoir, associated with a significant larger reservoir of ?D^{18}O in the fluid phase compared to a much smaller reservoir of ?Ç^{18}O in the solid phase (rock). Thus, because mole fractions of carbon differ significantly in the water and rock reservoir (oxygen concentrations, in contrast, are roughly equal), the isotopic composition of meteoric water (and cement) should evolve such that the fluid’s carbon isotopic compositions equilibrate more rapidly with the marine carbonate than do fluid’s oxygen isotope compositions (e.g., Lohmann 1988; Banner and Hanson 1990). Consequently, as a result of the larger reservoir of ?ó^{18}O of water and adversely, larger reservoir of ?f^{13}C of rock, meteoric cements precipitated in a carbonate aquifer show relatively invariant ?d^{18}O, coupled with strongly variant ?g^{13}C (e.g., Lohmann 1988; Saller and Moore 1991). The isotopic composition of the dLMC cement of the Tortachilla Limestone presents such a trend, which denotes the high water / rock interaction due to the wholesale alteration of all aragonitic components in this unit and their partial replacement by dLMC cement (Fig. 6).

The isotopic composition of the Tortachilla Limestone dLMC cement shows a pattern of strongly variable ?·^{13}C (-3.85 to -7.8‰) and relatively invariant ?¶^{18}O values (-3.8 to -4.8‰ - Fig. 6) that is typical for cement with the meteoric origin. The ?^{18}O variation is about 1.0‰, which is not unusual for meteoric groundwater in modern carbonate terrains (e.g., Frank et al., 1995). Therefore, this pattern of approximately invariant ?Ê^{18}O coupled with variant ?Ê^{13}C in the cement of this unit indicates its meteoric origin (e.g., Allen and Matthews 1982, Lohmann 1988). In this regard, the most negative values of ?é^{13}C$_{\text{meteoric cement}}$ can be considered the best estimate for the value of pure meteoric calcite (?¾^{13}C = -7.8‰), which suggests light ?¾^{13}C values for soil-CO_2 (-18.0 to -20.0‰ - Romanek et al., 1992). The low ?Ó^{13}C values of this cement reflect decreasing water-rock exchange as the primary marine metastable aragonitic components (aragonitic gastropods, for example) were diagenetically stabilized. The extent of water - rock interaction can be quantified as rock to water volume. This ratio represents the relative volume of rock permeated by a single volume of water in response to dissolution - precipitation reactions. Hence, a low water/rock ratio exemplifies a system in which fluid chemistry is dominated by the composition of the dissolving rock phases. Therefore, due to the small total concentrations of dissolved carbon in water, the ?µ^{13}C value of water rapidly converges to the values of the dissolved metastable carbonate phases (Lohmann 1988).

The carbon isotope in meteoric cements could originated from different sources such as atmospheric CO_2 (about -8.0‰); dissolution of metastable carbonate minerals such as aragonite, and CO_2 from soil/calcrete organic matter decay (?^{13}C ≥ -20‰). Carbonate precipitated in surface or shallow diagenetic settings with an open-system exchange with atmospheric CO_2, will have an isotopic composition, which reflects the air-CO_2 signature. In general, calcite precipitated in an open-system equilibrium with soil-gas CO_2 is limited to about - 15‰ ?^{13}C (Rightmire and Hanshaw 1973).

The ?^{13}C isotopic signature of meteoric water percolating through the soil zone containing organic CO_2 (produced by oxidation of soil-organic matter) rapidly shifts towards negative values. The ?^{13}C isotopic value of the organically produced CO_2 has values of about -16 to - 25‰ which is quite different compared to atmospheric CO_2 (?^{13}C = -8‰). The contamination of meteoric water by soil-CO_2 produces a distinguishing isotopic signature for meteoric water, compared to other diagenetic fluids. On the other hand, the final isotopic composition of meteoric cement precipitated from this highly depleted (light ?^{13}C) meteoric water is controlled by the isotopic composition of the dissolved phase, which is usually metastable marine carbonates. Accordingly, during dissolution of the metastable carbonate phases, isotopic exchange between the fluid (meteoric water) and rock reservoir (metastable carbonate phase) modifies the highly depleted meteoric waters.

During carbonate dissolution following reaction occurs:

$$H_2CO_3+CaCO_3 \leftrightarrow Ca^{+2}+2HCO_3$$

In this reaction, half of the carbon atoms is derived from dissolving calcite and the rest from H_2CO_3 of the fluid. (e.g.,, Allen and Matthews 1982). Although, ?^{13}C composition of a meteoric water changes toward the negative values due to the influence of the soil-CO_2 (about -20‰ - Romanek et al., 1992), however, dissolution of isotopically heavy aragonitic fossils of this unit (?^{13}C about 2.2‰) has modified the meteoric water isotopic composition to the intermediate values. These intermediate values, which are reflected in the ?^{13}C composition of dLMC cement of the Tortachilla Limestone (-7.85 to -3.9‰), demonstrate that they are precipitated from meteoric water with ?^{13}C values about -10.15 to -6.2‰, which is much heavier than the ultimate negative signature (≥-20‰) that an organic reservoir (soil CO_2) can produce. This suggests that the meteoric water buffered isotopically by the dissolving carbonate precursors (i.e., aragonite) in this unit.

However, those cements with the lightest ?g^{13}C values, which are clustered at the depleted end of the inverted - J trend (Fig. 6), exhibiting absence of a high degree of rock / water interaction.

Therefore, the dLMC meteoric cements, which is depleted in ?^{13}C relative to marine calcite and their ?{^{18}O values are relatively invariant, defines the water - dominated (high water / rock ratio) portion of the inverted - J trend (Fig. 6). In such water - dominated systems, due to dissolution - precipitation reactions in shallow diagenetic settings, where ?£^{13}C - depleted fluids (resulted from the influx of soil gas derived CO_2) are prevalent, the final isotopic signature of dLMC meteoric cement shows highly variable ?^{13}C and relatively invariant ?(^{18}O (Fig. 6). The isotopic composition of marine calcites (marine well-preserved fossils) are clustered at the heavy end of the inverted - J pattern which demonstrates the origin of this secondary diagenetic cement.

The oxygen isotope values of seawater are also constrained by using ?¾^{18}O values of marine calcite and a temperature range of 14 to 18°C (Fig.2), which bestows -0.6 to -2.5‰ values for ?µ^{18}O$_{SW}$. In addition, the carbon isotopic signature of seawater in the early Late Eocene, which Tortachilla Limestone was deposited, can be constrained from the isotopic composition of equilibrium marine calcites. Using the ?ç^{13}C values of these biogenic equilibrium marine calcites and considering a fractionation factor of 2.3‰ between calcite and dissolved bicarbonate (Turner 1982), average values of -0.8 to -1.9‰ for ?^{13}C$_{Seawater}$ of early Late Eocene are concluded.

5. Conclusions

Carbonate sediments exposed in meteoric systems undergo post-depositional alterations, which eventually result in stabilization of the metastable components and precipitation of diagenetic calcites as cement. The isotopic composition of this meteoric cement is influenced by the isotopic composition of the original marine calcites and the meteoric fluids. Therefore, the isotopic composition of the diagenetic fluids is related to, and can be estimated from, that of the cement. The isotopic composition of seawater can also be estimated by using the well-preserved fossil materials and constraining relevant bottom water temperatures.

Table 1. Stable isotope composition of dLMC meteoric cements from Tortachilla Limestone.

$\delta^{13}C$	$\delta^{18}O$
-4.43	-2.17
-5.73	-3.45
-5.67	-3.52
-3.85	-2.58
-5.38	-3.40
-6.72	-3.86
-7.23	-4.32
-7.8	-4.85
-7.65	-4.80

Table 2. Isotopic composition of fossil Pecten sp. from Tortachilla Limestone.

$\delta^{13}C$	$\delta^{18}O$
0.68	-0.62
0.46	-0.27
0.58	-0.85
0.94	-0.55
0.5	-1.05
0.74	-0.23
0.46	-0.67
0.69	-0.95
0.75	-0.30

Table 3. Isotopic composition of fossil Terebratellidae brachiopods from Tortachilla Limestone.

$\delta^{13}C$	$\delta^{18}O$
0.68	-0.62
0.46	-0.27
0.58	-0.85
0.94	-0.55
0.5	-1.05
0.74	-0.23
0.46	-0.67

0.69	-0.95
0.75	-0.30

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