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Carbon and oxygen isotopic variations applied to the study of carbonate diagenesis in the Landraves Formation (Thanetian, Burgos, Northern Spain)

Variaciones isotópicas del carbono y oxígeno aplicadas al estudio de la diagénesis de los carbonatos de la Formación de Landraves (Thanetiense, Burgos, Norte de España)

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ABSTRACT

We have studied the dolomitization and calcitization processes that have widely affected the Landraves Formation sediments (Thanetian) at Valdivielso Valley (Burgos). The unit was deposited in a shallow marine environment with eventual tidal retouchings. The top of the unit coincides with an important sedimentary gap marked by the deposition of an Oligocene fluvial conglomerate. Whereas dolomitization could be early in origin and continuously and completely affected the sediments, the late calcitization processes originated from the mentioned rupture. In addition, some evaporitic nodules are indicative of subaerial exposure episodes towards the upper part of the unit. Dolomite isotopic values show slight variations ($\delta^{13}C$ = +0.6 to +2.6‰PDB y $\delta^{18}O$ = -1.1 to +2.2‰PDB), suggesting the temporal persistence of marine-evaporitic conditions; on the contrary, the calcite ones are lighter ($\delta^{13}C$ = -5.9 to +2.2 ‰ PDB y $\delta^{18}O$ = -7.5 to +0.4 ‰ PDB) and denote a phreatic meteoric environment associated to a strong fresh-water input.

RESUMEN

Se han estudiado los procesos de dolomitización y calcitización que afectaron extensamente a los sedimentos de la Formación de Landraves (Thanetiense) en el valle de Valdivielso (Burgos). La unidad se depositó en un ambiente marino somero con eventuales influencias mareales. Su techo coincide con una importante ruptura, marcada por el depósito de conglomerados fluviales de edad oligocena. Mientras que la dolomitización pudo ser temprana y afectó a los sedimentos de manera contínua y completa, los procesos de calcitización, más tardíos, se originaron en relación con la ruptura mencionada. Además, algunos nódulos evaporíticos delatan episodios de exposición subaérea hacia la parte superior de la unidad. Los valores isotópicos de la dolomita experimentan ligeras variaciones ($\delta^{13}C$ = +0.6 a +2.6‰PDB y $\delta^{18}O$ = -1.1 a +2.2‰PDB), lo que sugiere la persistencia en el tiempo de condiciones marino-evaporíticas. Por el contrario, los de la calcita son más ligeros ($\delta^{13}C$ = -5.9 a +2.2 ‰ PDB y $\delta^{18}O$ = -7.5 a +0.4 ‰ PDB) e indican un ambiente freático-meteórico ligado a una fuerte entrada de agua dulce.

Key words: *Thanetian , Basque-Cantabrian Basin, sedimentary rupture, carbonate diagenesis, stable isotopes, dolomitization, calcitization.*

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Introduction

The dolomitization processes at the Landraves Formation (Thanetian, 20-40 m of thickness) have been, documented by several authors: Ramirez del Pozo (1971), García Garmilla (1979), Floquet (1991, 1992), Pluchery (1995), Rioja *et al.* (1996) and García Garmilla and Elorza (1998). The unit constitutes a very sharp topographic ridge that has been mapped along the Valdivielso Valley and studied in detail at the Quintana, Valdenoceda, Tejada, Quecedo and Arroyo sections, and covers discordantly the Torme and/or Sobrepeña Formations (Fig 1). The first one (Upper Maastrichtian, 5 m. of thickness) includes shallow-marine carbonate sediments poorly shown in the studied sections; and the second one is composed of reddish and blue marls bearing *Charophyta* oogonia, fresh-water gasthropods and several vertebrate remains: turtle plates and crocodilia teeth (Astibia and Murelaga, com. pers.). The Landraves Formation is unconformably overlaid by Oligocene fluvial polymictic conglomerates bearing both siliceous and carbonate pebbles and grains consisting on fossil-enriched rocks, red-algae, algal-mats, nummulitids and orbitoidids. Although normally massive, the Landraves dolomite sometimes includes sets from 30 cm to 1 m in thickness showing planar cross-lamination and «herringbone» laminae. Massive beds are moderately-to-strongly bioturbated. The most plausible depositional environment may have been marine littoral with tidal influences, alternating areas reworked by currents (small "sand-waves") with others having low-energy that favoured

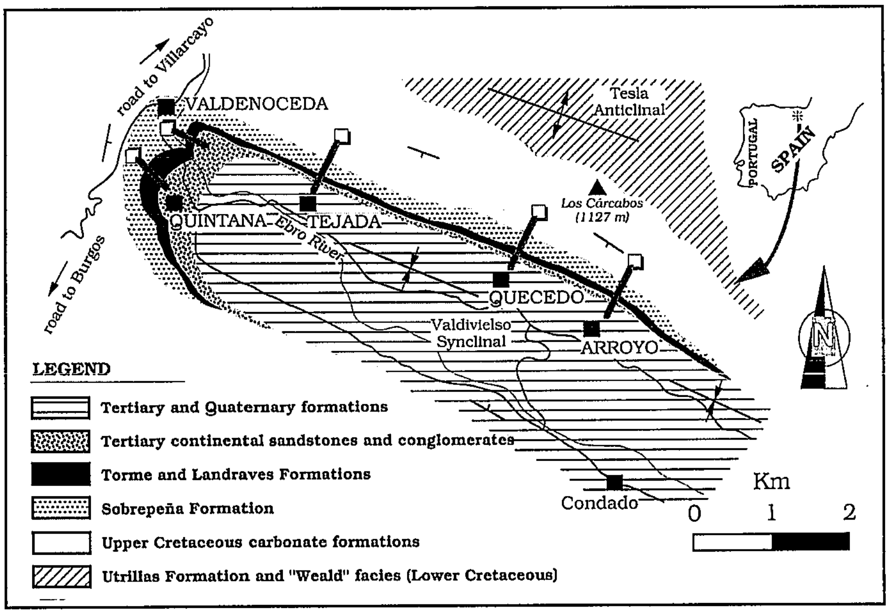

Fig.1.- Geological map and location of the studied sections.

Fig.1.- Mapa geológico y situación de los cortes estudiados.

bioturbation and vegetal settling. Further considerations about the depositional environment and diagenetic history of the Landraves Formation on the basis of sequential analysis, petrography, cathodoluminescence, and SEM observations can be found in Rioja *et al.* (1996).

Isotopic methods

Forty-five dolomite samples were isotopically analyzed (11 from Quecedo, 11 from Tejada, 12 from Arroyo, 6 from Quintana and 5 from Valdenoceda, fig 1, table 1). We will concentrate on the first three, which are the most complete and representative sampled sections. Carbon and oxygen isotopic values were obtained at Salamanca and Barcelona Universities following the procedures described by McCrea (1950). The organic matter in samples was eliminated by heating at 300-400°C under vacuum conditions

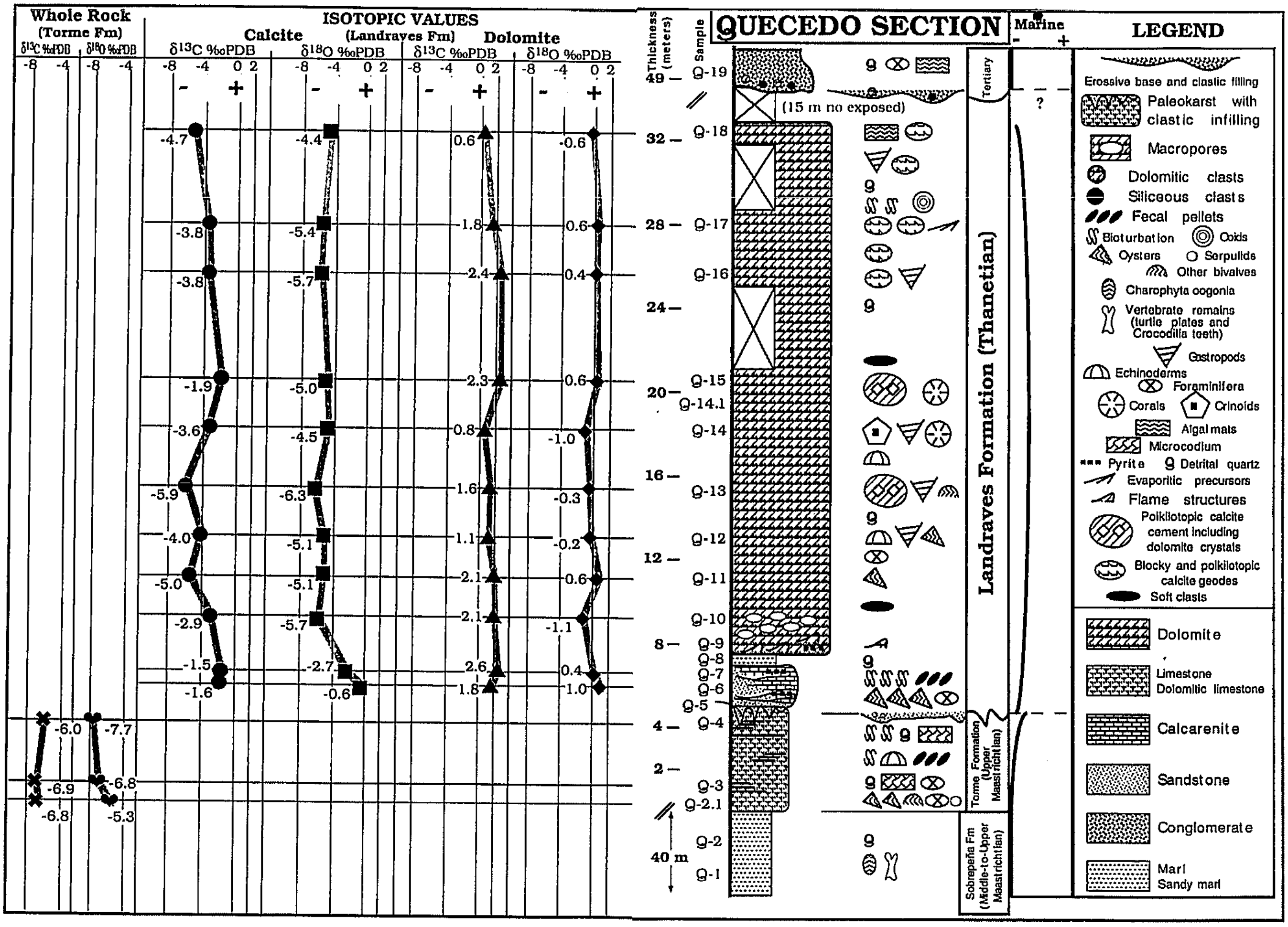

Fig.2.- Stratigraphic section and vertical C and O isotopic evolution at Quecedo locality.

Fig.2.- Sección estratigráfica y evolución vertical de los valores isotópicos de C y O en Quecedo.

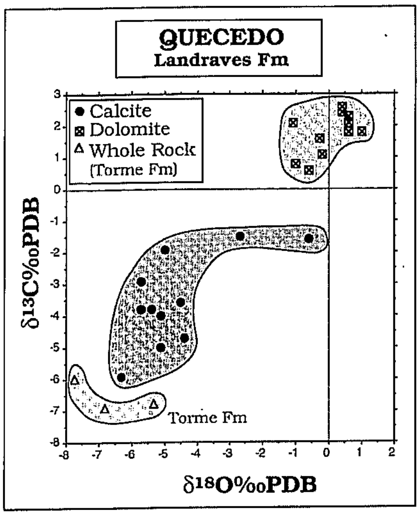

Fig.3.- $\delta^{13}C$ vs $\delta^{18}O$ plot for the Quecedo section samples.

Fig.3.- Diagrama $\delta^{13}C$ vs $\delta^{18}O$ para las muestras de la sección de Quecedo.

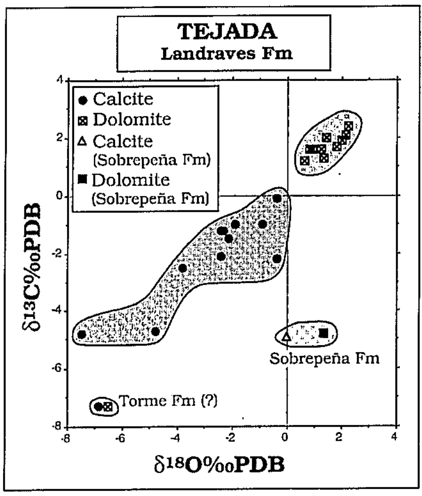

Fig.4.- $\delta^{13}C$ vs $\delta^{18}O$ plot for the Tejada section samples.

Fig.4.- Diagrama $\delta^{13}C$ vs $\delta^{18}O$ para las muestras de la sección de Tejada.

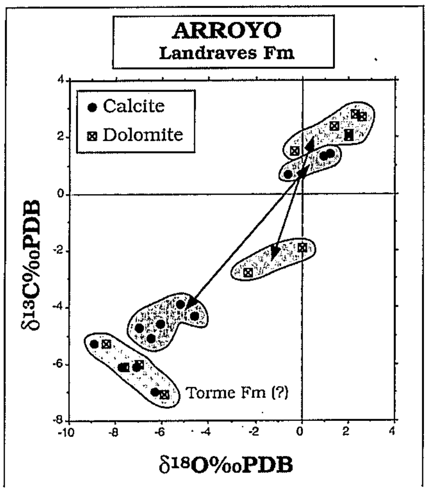

Fig.5.- $\delta^{13}C$ vs $\delta^{18}O$ plot for the Arroyo section samples.

Fig.5.- Diagrama $\delta^{13}C$ vs $\delta^{18}O$ para las muestras de la sección de Arroyo.

during three hours. Fractional extractions were practised in order to separately obtain the $\delta^{13}C$ and $\delta^{18}O$ values for calcite and dolomite respectively. The used spectrometer was a VG SIRA II.

Isotopic results and discussion

The Fig 2 shows the stratigraphic profile at Quecedo, besides the vertical evolution of C and O isotopic values for dolomite and calcite. The Figs 3, 4 and 5 are the $\delta^{13}C$ vs $\delta^{18}O$ plots corresponding to Quecedo, Tejada and Arroyo sections. The plots of Quecedo and Tejada clearly illustrate two different families of values for dolomite and calcite. The Arroyo plot (Fig 5), however, reflects a more disperse distribution, which will be explained later on. Whereas dolomite values are relatively heavy (mean values: Tejada: $\delta^{13}C=1.7‰$ PDB, $\delta^{18}O=1.4‰$ PDB; Quecedo: $\delta^{13}C=1.7‰$ PDB , $\delta^{18}O=0.0‰$ PDB; Arroyo: $\delta^{13}C=1.1‰$ PDB, $\delta^{18}O=0.9‰$ PDB), the calcite ones are moderately negative: (mean values: Tejada: $\delta^{13}C=-1.6‰$ PDB, $\delta^{18}O=-2.5‰$ PDB; Quecedo: $\delta^{13}C=-3.5‰$ PDB, $\delta^{18}O=-4.6‰$ PDB; Arroyo: $\delta^{13}C=-2.4‰$ PDB, $\delta^{18}O=-3.5‰$ PDB). Dolomite isotopic values of Quecedo and Tejada samples are close to those classically attributed by Holail *et al.* (1988) to mixing-water dolomites, but the Arroyo plot (Fig 5) reveals a second family of more negative values, suggesting a possible mixing of fresh water and evaporitic brines as described by Meyers *et al.* (1997) for the upper Miocene carbonates in Nijar (Spain). This could be reinforced by the fact of a minor subsidence and thickness of the Landraves Formation at this section. In fact, the isotopic results here do not differ with those obtained for early Mg-calcite cements in Pleistocene rocks by Vollbracht and Meischner (1996). $\delta^{13}C$ negative values for the same dolomite samples in Arroyo point out very shallow diagenetic domains, such as caliche zones and lagoon borders. This would be a symptom of vadose diagenesis combining evaporitic and mixed waters, as Gill *et al.* (1995) proposed for the Pliocene carbonates of St. Croix in the Caribbean sea. The isotopically heaviest dolomite must have precipitated from fluids enriched in ^{18}O, probably as a result of evaporation. In any case, the isotopic interpretations in dolomites should be very careful, because of both the $\delta^{18}O$ from carbonate precursors and its modification during the stabilization of early dolomite are unknown (Kupecz and Land, 1994; Vahrenkamp and Swart, 1994).

On the other hand, calcite values are more easily interpretable as precipitated in meteoric domains in the same way as Matthews (1974) proposed for the Barbados meteoric cements and Saller (1984) for those found in Enewetak atoll. The predominance of negative values for $\delta^{13}C$ in blocky and poikilotopic calcite cements can be explained as the result of precipitation in restricted paleoenvironments. In fact, Whittaker and Mountjoy (1997) assume that $\delta^{13}C$ values between +1‰PDB y -5‰PDB are indicative of restricted diagenetic conditions in the phreatic zone. The heavier values of some calcite points at Arroyo plot (Fig 5) are not in disagreement with early marine cements similar to those described by James and Choquette (1983).

Conclusions

The dolomitization processes that affected the Landraves Formation carbonates were continuous and very homogeneous both laterally and vertically. Isotopic results, together with field and textural observations we realized in previous papers, reveal that dolomitization was early in origin, developed intercrystalline and moldic porosities and took place in a context of mixing marine evaporative and fresh waters. Later calcitization occurred by generalized percolation of meteoric waters from upper to lower due to an important rupture surface now marked by Oligocene continental conglomerates. The marine formations deposited just upon the unconformity surface probably exerted a chemical control on the diagenesis affecting the underlying sediments, but are actually lost into the stratigraphic record. Calcitization was responsible for a general cementation by blocky and poikilotopic calcite that partially occluded the previous porosity. Finally, some very late phases of calcite and dolomite appear related to tectonic fractures and veins.

Quecedo (‰PDB)			
Calcite		Dolomite	
$\delta^{13}C$	$\delta^{18}O$	$\delta^{13}C$	$\delta^{18}O$
-4,7	-4,4	0,6	-0,6
-3,8	-5,4	1,8	0,6
-3,8	-5,7	2,4	0,4
-1,9	-5,0	2,3	0,6
-3,6	-4,5	0,8	-1,0
-5,9	-6,3	1,6	-0,3
-4,0	-5,1	1,1	-0,2
-5,0	-5,1	2,1	0,6
-2,9	-5,7	2,1	-1,1
-1,5	-2,7	2,6	0,4
-1,6	-0,6	1,8	1,0
Whole Rock			
$\delta^{13}C$	$\delta^{18}O$		
-6,0	-7,7		
-6,9	-6,8		
-6,8	-5,3		
Arroyo (‰PDB)			
Calcite		Dolomite	
$\delta^{13}C$	$\delta^{18}O$	$\delta^{13}C$	$\delta^{18}O$
-4,7	-7,0	1,5	-0,3
-4,6	-6,1	-1,9	0,0
-5,1	-6,5	-2,8	-2,3
0,7	-0,6	2,4	1,4
1,4	1,2	2,8	2,3
-3,9	-5,2	2,0	2,0
1,3	0,9	2,7	2,6
-4,3	-4,6	2,1	2,0
-7,0	-6,3	-7,1	-5,9
-6,1	-7,1	-6,0	-7,0
-6,1	-7,7	-6,1	-7,6
-5,3	-8,9	-5,3	-8,4
Tejada (‰PDB)			
Calcite		Dolomite	
$\delta^{13}C$	$\delta^{18}O$	$\delta^{13}C$	$\delta^{18}O$
-1,2	-2,3	1,6	0,8
-1,2	-2,4	1,6	0,9
-1,0	-1,9	2,0	1,4
-2,5	-3,8	1,2	0,6
-2,1	-2,4	1,3	1,3
-4,7	-4,8	1,3	1,3
-1,0	-0,9	1,9	2,0
-0,1	-0,4	1,7	1,8
-2,2	-0,4	2,1	2,1
-4,8	-7,5	1,6	1,2
-1,5	-2,1	2,4	2,2
-7,3	-6,9	-7,3	-6,6
-4,9	0,0	-4,8	1,3
Valdenoceda (‰PDB)			
Calcite		Dolomite	
$\delta^{13}C$	$\delta^{18}O$	$\delta^{13}C$	$\delta^{18}O$
-0,6	-1,5	2,1	1,6
0,8	0,6	2,1	2,0
1,7	2,0	2,2	2,5
-0,3	-0,6	1,5	1,3
-8,3	-8,2	-7,7	-7,5
Quintana (‰PDB)			
Calcite		Dolomite	
$\delta^{13}C$	$\delta^{18}O$	$\delta^{13}C$	$\delta^{18}O$
-6,4	-5,6	1,6	1,6
0,7	-0,2	2,4	1,7
2,0	1,7	2,8	2,4
0,6	0,0	2,3	1,4
-6,6	-5,5	-6,5	-4,6
-1,8	-2,2	0,6	0,2

Table 1.- $\delta^{13}C$ and $\delta^{18}O$ values for samples from the five studied sections.

Tabla 1.- Valores de $\delta^{13}C$ y $\delta^{18}O$ para las muestras de las cinco secciones estudiadas.

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References

Floquet, M. (1991): *Mém. Géol. Univ. Dijon*, 14: 925 p.

Floquet, M. (1992): *International Symposium Sequence Stratigraphy of Mesozoic-Cenozoic European Basins. Field-trip Guidebook.* 130 p.

García Garmilla, F. (1979): *Tesis de Licenciatura.* Univ. País Vasco. 73 p.

García Garmilla, F. y Elorza, J. (1998): *15th International Sedimentological Congress.* Alicante (Spain).

Gill, I.P.; Moore, Jr. C.H. and Aharon, P. (1995): *Jour. Sedim. Research,* A65 (4): 591-604.

Holail, H; Lohmann, K.C. y Sanderson, I. (1988): In: *Sedimentology and Geochemistry of Dolostones, SEPM, Spec. Publ.*, 43: 191-207.

James, N.P. and Choquette, P.W. (1983): *Geoscience Canada*, 10: 162-179.

Kupecz, J.A. and Land, L.S. (1994): In: *Dolomites. A Volume in Honour of Dolomieu. IAS Spec. Publ.*, 21: 255-279.

Matthews, R.K. (1974): In *Reefs in Time and Space, SEPM Spec. Publ.*, 18: 234-256.

McCrea, J.M. (1950): *Jour. Chem. Phys.*, 18: 849-857.

Meyers, W.J., Lu, F.H. and Zachariah, J.K. (1997): *Jour. Sedim. Research*, 67 (5): 898-912.

Pluchery, E. (1995): *Thèse Université de Bourgogne*, 327pp.

Ramírez del Pozo, J. (1971): *Mem. Inst. Geol. Min. Esp.* Madrid. 3 vols.

Rioja, M.A., García Garmilla, F. y Elorza, J. (1996): *Geogaceta* , 20 (3): 647-650.

Saller, A.H. (1984): *Geology*, 12: 217-220.

Vahrenkamp, V.C. and Swart, P.K. (1994): In: *Dolomites. A Volume in Honour of Dolomieu. IAS Spec. Publ.*, 21: 133-153.

Vollbracht, R. and Meischner, D. (1996): *Jour. Sedim. Research*, 66 (1): 243-258.

Whittaker, S.G. and Mountjoy, E.W. (1997): *Jour. Sedim. Research*, 66 (5): 965-975.