

**AAPG HEDBERG CONFERENCE**

***“Deformation History, Fluid Flow Reconstruction and Reservoir Appraisal in Foreland Fold and Thrust Belts”***

**May 14-18, 2002, Palermo – Mondello (Sicily, Italy)**

**Hydrothermal massive dolomitization in the Cantabrian Zone (NW Spain): a Permian to Triassic event promoted by extensional tectonics?**

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**Introduction**

The Cantabrian Zone (CZ) in NW Spain represents the foreland belt of the Variscan Iberian Massif and is made up of a Precambrian basement covered by Palaeozoic sediments. The succession was folded and thrust in late Carboniferous time due to the Variscan orogeny, resulting in several thrust units (Fig. 1) (Perez-Estaún et al., 1988). Renewed compression during the Alpidic period lead to further uplift (Pulgar et al., 1999).

The Palaeozoic rocks underwent intense tectonics, diagenetic to epizonal thermal events, and several episodes of fluid flow. A spectacular product of epigenetic fluid circulation in this area is a very large scale, hydrothermal dolomite, bearing significant secondary porosity and minor, non economic base metal deposits.

The aim of this study is to reconstruct the different episodes of carbonate emplacement and to define type and origin of the dolomitizing fluids in the most affected thrust unit: the Bodón Unit (Fig. 1).

Employed methods include so far petrography, cathodoluminescence (CL), XRD, O- and C- stable isotopes, and fluid inclusion (FI) microthermometry coupled with Raman spectrometry.

**Study area and dolomite distribution**

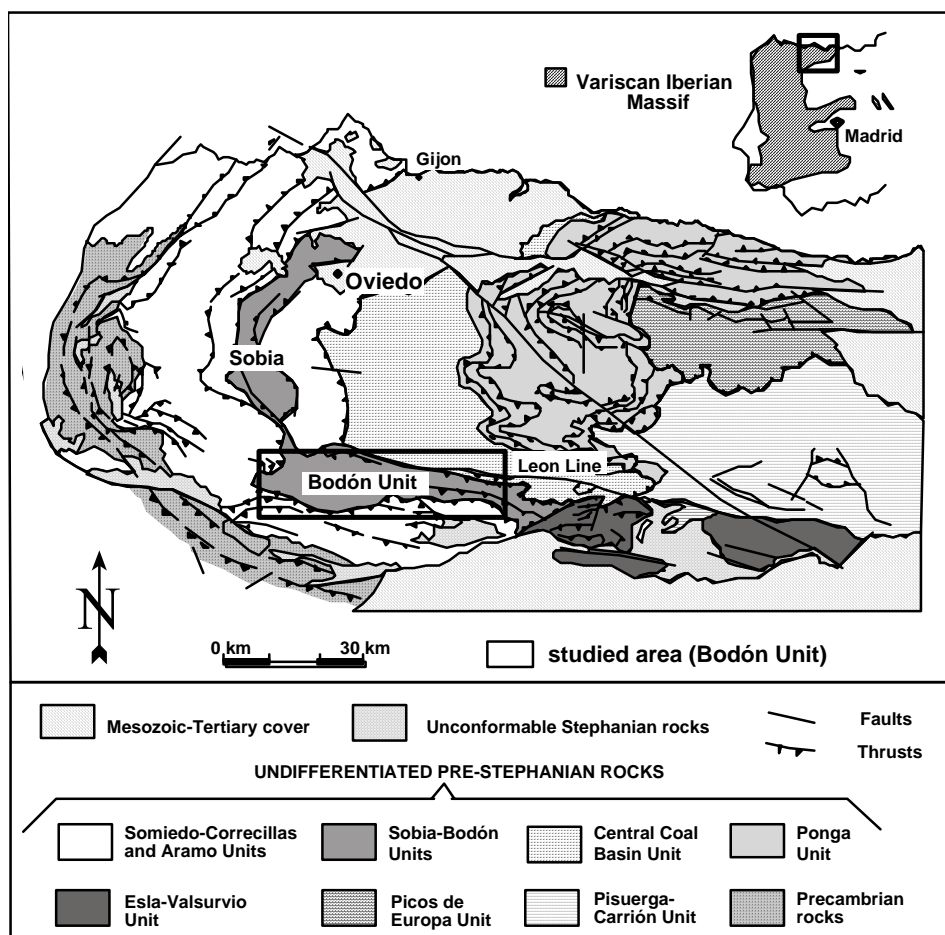
The study area is the E-W oriented Bodón thrust unit, located in the southern part of the CZ (Fig. 1). It consists of a pre-Variscan (Cambrian to Lower Carboniferous) and a syn-Variscan (Lower Carboniferous to Upper Westphalian) succession, with post-Variscan deposits either lacking or completely eroded. Mesozoic and Cenozoic sediments, discordantly overlying the Palaeozoic successions, occur in the south, in the north and much further to the east. In the north, the Bodón Unit is separated from the Central Coal Basin Unit by the Leon Line: an E-W oriented regional fault system, which was active from the Variscan to the Alpidic time, and alternated strike-slip and vertical movements. In the south, the Bodón Unit is overthrust by the Somiedo-Correcillas Unit (Marcos, 1968).

The epigenetic dolomitization is rare in the sediments of the pre-Variscan succession. In these rocks the dolomite bodies never exceed a few tens of cubic meters and are always related to tectonic lineaments: Cambrian rocks containing larger volumes of dolomite, occur in fact directly above the Correcillas Thrust.

The most dolomitized sediments belong to the early syn-Variscan succession, represented by the Barcaliente and Valdeteja Fms. The Barcaliente Fm. (Namurian A - Namurian B), 200 to 350 m in thickness, is a dark grey, well bedded and laminated bituminous limestone. The Valdeteja Fm. (Namurian B - Westphalian A), 0 to 1000 m in thickness, is a light grey, massive limestone, often containing bioconstructions.

In these two formations, dolomitization varies from complete to absent. The most widespread dolomitization occurs in the middle part of the Bodón Unit, in proximity to the Leon Line. Towards the eastern and western parts of the unit, remnants of undolomitized carbonates become gradually more frequent.

In the sediments of the late syn-Variscan and post-Variscan successions, no similar dolomite has been reported yet.



**Fig. 1:** Tectonic sketch map of the CZ, showing the studied area (Bodón Unit) and the location of the Leon Line (after Perez-Estaún et al., 1988).

Phase	Isotope study		Fluid Inclusion study				
	$\delta^{18}\text{O}$ ‰PDB	$\delta^{13}\text{C}$ ‰PDB	Type	Fluid	Te (°C)	Tm (°C)	Th (°C)
<b>Cal 1</b>	-6,4 to -11,0 (8)	2,1 to 4,5 (8)	Secondary	-	-	-	-
<b>Dol A</b>	-3,0 to -10,4 mode at -7,5 (41)	3,2 to 5,4 (41)	Primary, 2-phases size: <5µm F=0.83 to 0.93	G= water vapour L= H <sub>2</sub> O + salts	< -34	Tm [ice] -34 to -36,5 (25)	100 to 140 mode at 130 (25)
<b>Dol B</b>	-4,2 to -10,5 mode at -9,0 (32)	3,0 to 5,3 (32)	Primary 2-phases size: up to 15µm F=0,85 to 0,95	G= water vapour L= H <sub>2</sub> O+MgCl <sub>2</sub> + +NaCl+CaCl <sub>2</sub>	-52±1	Tm [MH] -43,5 to -45,5 Tm (ice) -36,5 to -33,0	100 to 155 mode at 145 (97)
<b>Cal 2</b>	-8,0 to -15,2 mode at -11 (20)	-2,4 to 2,1 (20)	Primary 2-phases size: up to 25µm F=0.87 to 0.97	G= water vapour L= NaCl+H <sub>2</sub> O+ +CaCl <sub>2</sub>	-36 to -45	Tm [ice] -20,1 to -28,2 Tm [HH] -16,3 to -18,5	100 to 130 mode at 120 (43)

**Fig. 2:** Results of the stable isotope and FI study. Liquid and gas composition in FIs were detected by means of Raman spectrometry. F= degree of fill; G= gas; L= liquid; Te= eutectic temperature; Tm= melting temperature; Th= homogenization temperature; HH= NaCl•2H<sub>2</sub>O; MH= MgCl<sub>2</sub>•12H<sub>2</sub>O. In round brackets is the number of measurements.

## Field observations

Limestones of both formations of interest underwent burial and deformation prior to dolomitization, resulting in strongly inclined to overturned bedding, development of bedding parallel stylolites, and calcitic veins (Cal 1) crosscutting primary features.

Dolomite/limestone contacts are sharp, irregular in shape, and cut both stratification and sedimentary structures.

The dolomite is typically sucrosic, and often forms banded fabrics similar to those reported in literature as “zebra structures” (Wallace et al., 1994; Nielsen et al., 1998). The zebra fabrics, given by the repetition of mm-scale dark grey and white dolomite sheets (Dol A and Dol B, respectively), bear cavities linear to roundish in shape. Cavities range from less than 1 mm to several cm in length and are sometimes completely filled by a later calcite phase (Cal 2).

Orientation of the cavities and associated zebra fabrics strongly depends on the type of host rock involved. They are mostly controlled by sub-horizontal microfissures where dolomitization affected the well bedded and laminated Barcaliente Fm, whereas they are randomly distributed in the massive limestones of the Valdeteja Fm. In addition, the zebras are sometimes confined by subvertical fissures, giving them a pipe-like appearance. The development of cavities and related zebras is, therefore, controlled by stratification/lamination/microfissures.

## Analytical results and interpretation

$\delta^{13}\text{C}$  values for the unaffected limestones are in agreement with Carboniferous sea water, whereas the large spread of  $\delta^{18}\text{O}$  values point to a different degree of diagenetic alteration (compare also Grossman, 1994). Results of stable isotope and FI study for the diagenetic phases are reported in Fig. 2.

Pre-dolomitization veins are filled by fine grained, not twinned calcite (Cal 1), with non-luminescent to dark orange CL. This calcite is buffered from the enclosing limestone because of similarities in CL and  $\delta^{13}\text{C}$  signature, whereas  $\delta^{18}\text{O}$  values point to a burial diagenetic origin.

The dark grey dolomite (Dol A) is fine to medium crystalline and replacive in origin. It shows a uniform dull red and unzoned CL, with some bright red spots representing remnants of the preceding limestone.

The white dolomite (Dol B) is medium to coarse crystalline and void-filling in origin. Dol B has the same dull red CL as Dol A, although it lacks limestone remnants. In addition, the outmost rim of the crystals, close to the cavities, is mostly zoned.

Dol A and Dol B approximate the stoichiometric composition of ideal dolomite, both being Mg enriched (48.5 to 50.5 mol%  $\text{CaCO}_3$  with mode at 49%).

A slight gradient in homogenization temperatures of primary FIs has been recognized in Dol B. The highest temperatures (100 to 155°C with mode at 145°C) were measured in the middle of the Bodón Unit, whereas the lowest ones correspond to the easternmost (120 to 130°C with mode at 125°C) and westernmost (100°C to 130°C with mode at 115°C) areas of the unit. The dolomite phases derived from a common fluid, which first replaced the limestones forming Dol A, and then precipitated Dol B, in a continuous and isochemical process. The cavities must have been formed prior to Dol B, and probably during Dol A emplacement. During this evolution, the crystallization rate slowed down, resulting in crystal size increase, and the fluid became slightly warmer and more depleted in  $^{18}\text{O}$ . The fluid was possibly a hot, highly saline and Mg-rich modified seawater, which operated in a burial environment.

The late calcite (Cal 2), which occupies the last position in the mineral paragenesis, is white to transparent, very coarse crystalline, twinned and has a bright orange, rarely zoned CL. The calcite was formed from a less effective (the calcite is not ubiquitous), very saline, Na-rich and slightly cooler fluid system. It was probably modified sea water, which underwent slight contamination from meteoric water at the time of chain exposure. This contamination might explain the lower  $\delta^{13}\text{C}$  values measured for this phase.

## Dolomite origin

To reconstruct the process of dolomitization, the following factors are required: 1) a proper tectonic setting for the fluids to be put into motion, 2) an effective net of conduits for the dolomitizing fluids to flow, 3) a conspicuous source of Mg to justify the high Mg content of both fluid and dolomite phases, 4) a source of heat to explain the high minimum trapping temperatures of Dol A, Dol B and Cal 2.

It is assumed that the dolomitization was emplaced during a late- to post-Variscan extensional phase as suggested by Gómez-Fernández et al. (2000) for another tectonic unit of the CZ.

Main pathways for the fluids were probably the Variscan thrust and fault planes, as well as stratification/lamination joints. The Leon Line played an effective role for fluid circulation: this is reflected in the highest temperatures and almost complete dolomitization found in the middle part of the Bodón Unit, close to this fault.

The highly saline and Mg-rich brines might have been derived from evaporative basins. Evaporitic rocks are found in the unconformably overlying Permian and Triassic rocks, cropping out to the N (Sanchez de la Torre et al., 1977) and E of the study area (Brinkmann and Lögters, 1968)).

A candidate for the required heat might be a Permian thermal event, which led to diagenetic conditions all over the Bodón Unit and to anchizonal/epizonal conditions in the southernmost area of the Central Coal Basin (García-López et al., 1999), in contact with the Bodón Unit by means of the Leon Line. This thermal event might have maintained a high geothermal gradient in the area up to the onset of the evaporative basins.

In our opinion, the main motor, that could have set pre-concentrated brines into motion, was the extensional tectonics that, in post-Variscan, Permian and Triassic time, was active in large parts of Europe.

This extensional tectonics promoted a gravity driven flow of the brines, which circulated deeply down, underwent heating and depletion in the  $\delta^{18}\text{O}$ , and started to dolomitize the more permeable carbonate rocks close to fault lines. The emplacement of dolomitization might have been favoured by the better permeabilities of the well-bedded Barcaliente and the not fully cemented Valdeteja Fms., in comparison to the underlying less permeable, more lithified Devonian carbonates.

A later extensional phase, related to the opening of the Atlantic Ocean and the Bay of Biscay, occurred during the Late Jurassic and Early Cretaceous time. At that time, however, the origin of Mg and the source of heat appear less constrained than in Permian and Triassic time.

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