Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Geochemical Exploration 78–79 (2003) 501–507
JOURNAL OF GEOCHEMICAL EXPLORATION
www.elsevier.com/locate/jgeoexp

Abstract

Hot dolomites in a Variscan foreland belt: hydrothermal flow in the Cantabrian Zone (NW Spain)

M. Gasparrini[a,1], R.J. Bakker[b], Th. Bechstädt[a,1], M. Boni[c,*]

[a] Geological-Palaeontological Institute, INF 234, 69120 Heidelberg, Germany
[b] Mineralogical Institute, Montan-University Leoben, Austria
[c] Dipartimento Geofisica and Vulcanologia, Università di Napoli "Federico II" Via Mezzocannone 8, I-80134 Napoli, Italy

Abstract

The Cantabrian Zone (CZ) in NW Spain represents the foreland belt of the Variscan Iberian Massif. It consists of a Precambrian basement covered by Palaeozoic sediments. These underwent intense thin-skinned tectonics, diagenetic to epizonal thermal events, and several episodes of fluid flow causing large-scale hydrothermal dolomitization. Aim of this research is to trace the carbonate diagenesis in the Carboniferous Barcaliente and Valdeteja Formations in the Bodón Unit, and to define type and origin of the dolomitizing fluids. Employed methods include petrography, cathodoluminescence (CL), XRD, stable isotopes and fluid inclusion (FI) microthermometry/Raman spectrometry. The dolomitizing fluid was possibly hot (100 to 150 °C), saline, Mg-rich modified seawater, operating in a burial environment.

It is assumed that the dolomitization occurred during late- to post-Variscan extensional phases. Main pathways for the fluids were the Variscan thrust and fault planes, as well as stratification/lamination joints of the host limestones. One of the main tectonic lineaments, the Leon Line, played an effective role for fluid circulation, as reflected by the highest temperatures and often almost complete dolomitization close to this fault. Extensional tectonics may have promoted a gravity driven flow of fluids, which circulated deeply down, underwent heating and depletion in ^{18}O and dolomitized the primary carbonates.

Keywords: Dolomite; Hydrothermal; Fluid flow; Northern Spain

1. Introduction

Post-Variscan hydrothermal dolomites are well known from several regions of Europe (Spain, Italy, Belgium, Germany, Ireland, Czech Republic, etc.). Dolomitization affected large areas of Palaeozoic (Cambrian to Carboniferous) carbonates, mostly situated in the external zones of the Variscan orogen. These dolomites share many characteristics, like mineralogy and geochemistry, pervasive replacement patterns, high salinity and temperature fluid inclusions, progressive depletion in ^{18}O from their source limestones and radiogenic Sr values. However, due to the variable age and the different diagenetic stages of precursor limestones in each of the districts considered, the resulting geochemical signatures of the epigenetic dolomites are quite distinct. It has been assumed, that a late-Variscan possibly long-lasting

---

* Corresponding author. Tel.: +39-81-2535068; fax: +39-81-2535070.

E-mail addresses: marta.gasparrini@urz.uni-heidelberg.de (M. Gasparrini), boni@unina.it (M. Boni).

[1] Fax: +49-6221545503.

0375-6742/03/$ - see front matter © 2003 Elsevier Science B.V. All rights reserved.
doi:10.1016/S0375-6742(03)00115-8

hydrothermal event, which coincided with post-thrusting extensional tectonics and crustal thinning, was responsible for the widespread dolomitization process (Boni et al., 2002).

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 thrusted in late Carboniferous time due to the Variscan orogeny, resulting in several thin-skinned thrust units (Fig. 1) (Pérez-Estaún et al., 1988). 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 dolomitization. The affected lithotypes bear significant secondary porosity and minor, non economic base metal deposits.

Aim of current research is to reconstruct the different episodes of dolomite emplacement and to define type and origin of the dolomitizing fluids in the most affected Bodón thrust unit (Fig. 1). Employed methods included so far petrography, cathodoluminescence (CL), XRD, O- and C-stable isotope geochemistry and fluid inclusion (FI) microthermometry, coupled with Raman spectrometry.

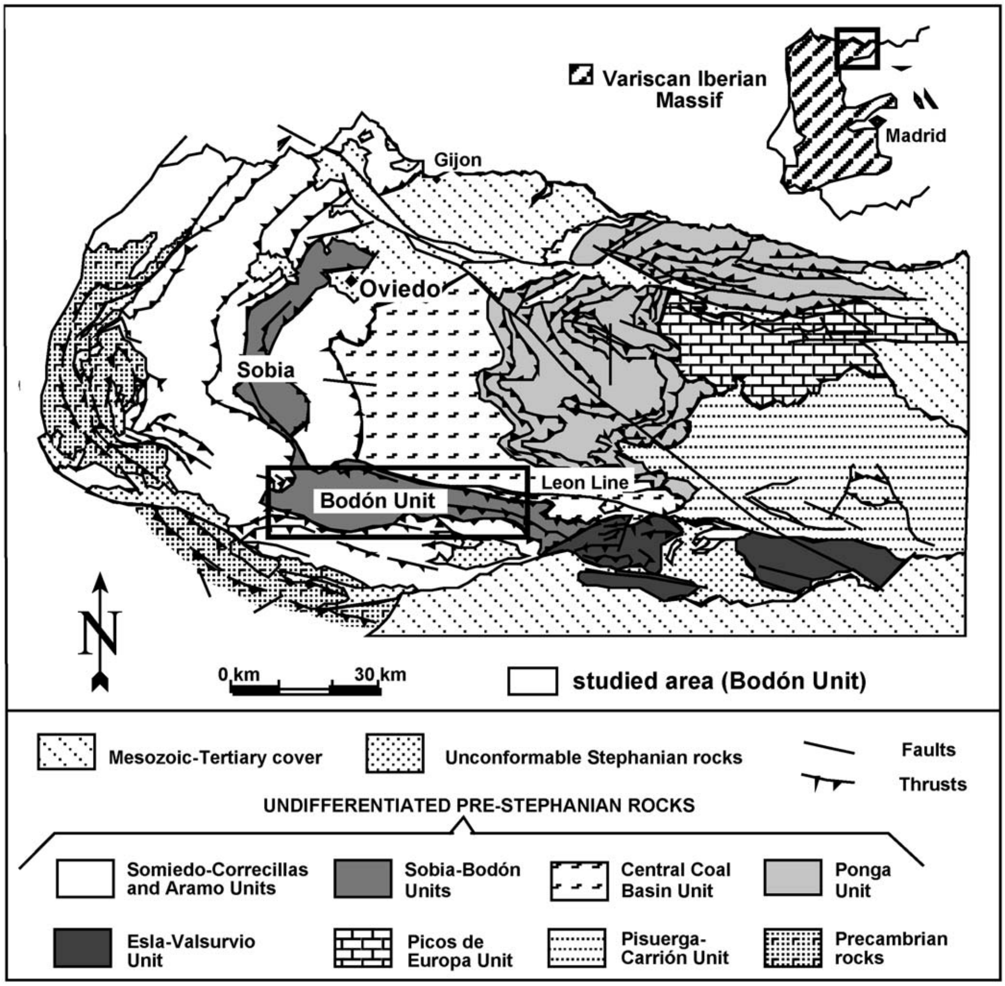

Fig. 1. Tectonic sketch map of the CZ, showing the studied area (Bodón Unit) and the location of the Leon Line (after Perez-Estaún et al., 1988).

2. Geological setting

2.1. Study area and dolomite distribution

The study area is the E–W-oriented Bodón Unit, located in the southern part of the CZ (Fig. 1). This nappe 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. 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 underwent strike-slip and vertical movements. In the south, the Bodón Unit is overthrusted 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 Formations. The Barcaliente Formation (Namurian A–B), 200 to 350 m in thickness, consists of a dark grey, well-bedded and laminated bituminous limestone. The Valdeteja Formation (Namurian B–Westphalian A), 0 to 1000 m in thickness, is composed of 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 central portion of the Bodón Unit, in the proximity of the Leon Line. Towards the eastern and western parts of the unit, several 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.

3. 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 centimeters in length and are sometimes completely filled by a later calcite phases.

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 Formation, whereas they are randomly distributed in the massive limestones of the Valdeteja Formation. 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.

4. Petrography

A common paragenesis of the dolomite phases could be established for the whole area. Pre-dolomitization calcite veins (CV), cutting Carboniferous limestones, have non-luminescent to dark orange CL. Dol A is replacive in origin and consists of a mosaic of fine- to medium-sized interlocked crystals. It shows a uniform dull red and unzoned CL, with some bright red spots representing remnants of the preceding limestone. Coarser crystals show a slightly undulose extinction, typical of saddle dolomite (Radke and Mathis, 1980). Subhedral and anhedral crystals coexist together. Nevertheless anhedral, closely packed crystals with lobate or curved intercrystalline boundaries are most common. According to the classification on the dolomite textures proposed by Sibley and Gregg (1987), this phase can be classified as non-planar.

As in the above-described replacive dolomite phases, the crystals of Dol B are interlocked, but coarser and clearer since impurity coatings are less frequent. None of the host limestone features is recognisable in this phase. The crystal sizes of Dol B increase towards the last crystal generation, close to the cavities. The contact between replacive and void-filling dolomites never corresponds to a reaction border. Dol B void-filling crystals are quite coarse and display planar-s textures (xenotopic-c texture after Sibley and Gregg, 1987). Their shape ranges through increasing face curvature from rhombohedral with straight boundaries, to symmetrical saddle forms. Dol B has the same dull red CL as Dol A, although it lacks limestone remnants. In addition, the outmost rim of the crystals 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% $CaCO_3$ with mode at 49%).

The cavity filling carbonate (Cal 1) is a xenotopic blocky calcite with variable size. Cal 2 is probably a much younger phase.

5. Analytical results

Concerning the stable isotope analyses of the carbonates in the study area, $\delta^{13}C$ values for the unaffected Carboniferous limestones are in agreement with those reported for Carboniferous seawater, whereas the large spread of $\delta^{18}O$ values point to a highly variable degree of diagenetic alteration. In fact, the original $\delta^{18}O$ data for the Carboniferous limestones in Spain, reported by Grossman (1994), range from 0.83 ‰ to −2.51 ‰ PDB, while the $\delta^{13}C$ values vary between 5.17 ‰ and 6.13 ‰ PDB.

The calcite in the pre-dolomitization veins (CV) is buffered from the enclosing limestone because of

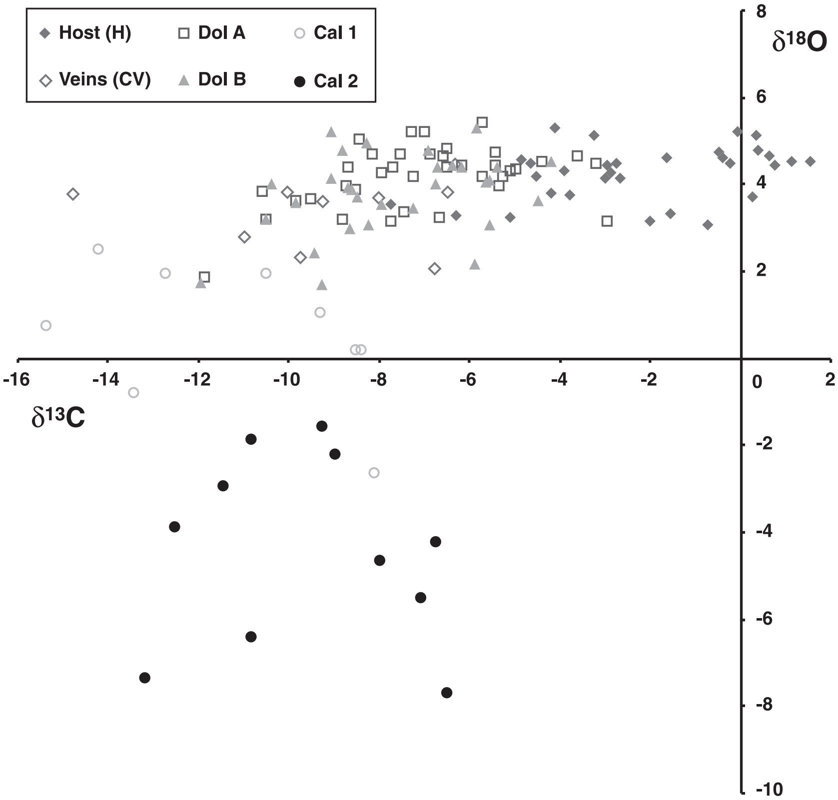

Fig. 2. $\delta^{13}C$ vs. $\delta^{18}O$ (PDB) scatter plots of hydrothermal dolomites (Dol A and Dol B) and Calcite 1; in the diagram are reported also the values of the neighbouring undolomitized limestones (Host) and of the pre-dolomitization veins (CV).

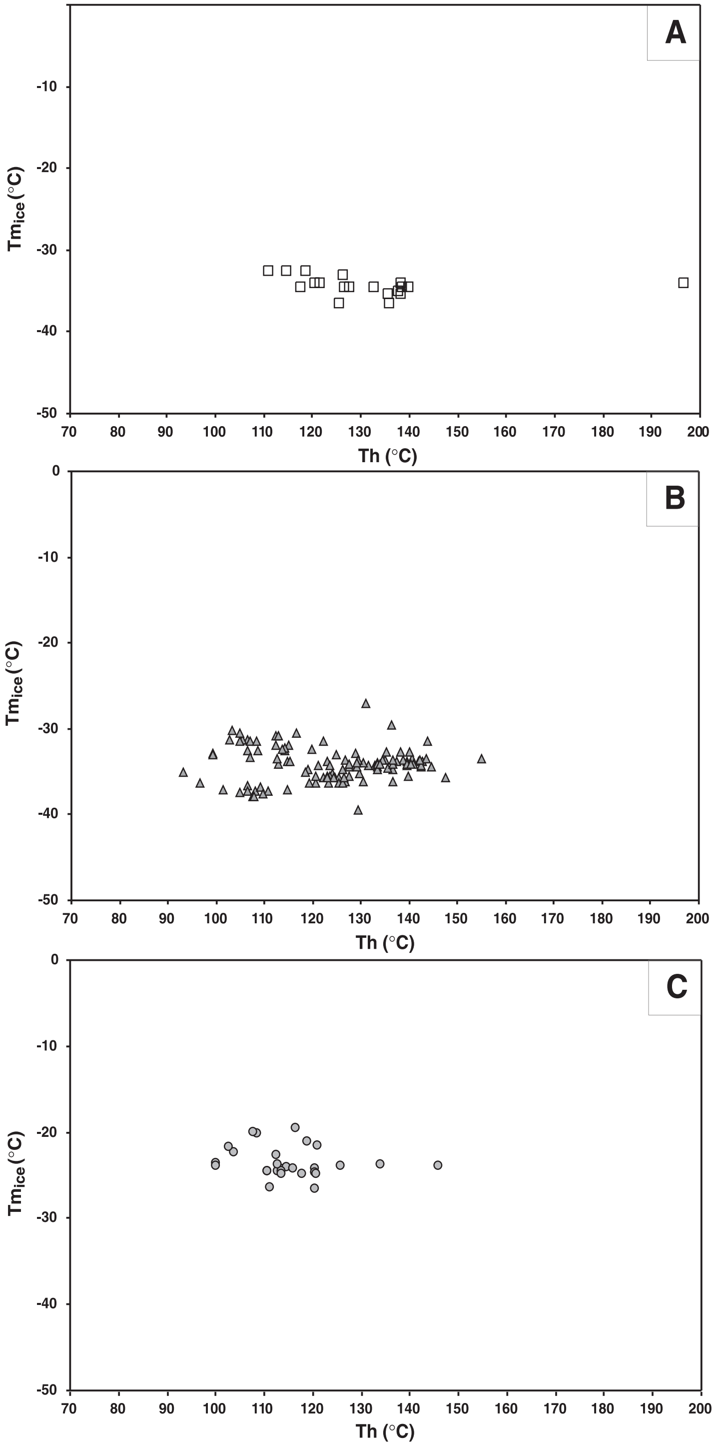

Fig. 3. Results of the fluid inclusions study: Th (°C) versus Tm$_{ice}$ (°C) for Dol A (A), Dol B (B) and Cal 1 (C).

similarities in CL and $\delta^{13}C$ signature, whereas its $\delta^{18}O$ values point to a burial diagenetic origin. The $\delta^{18}O$ values of the hydrothermal dolomites, though much lighter respective to their precursor limestones, show a very large spread and are often overlapping the whole field of Carboniferous early diagenetic carbonates. $\delta^{13}C$ data are similar to those of the limestones. Results of the stable isotope studies for all carbonate phases, both calcites and dolomites, are reported in Fig. 2.

The fluid inclusion data for Dol A, Dol B and Cal 1 are reported in Fig. 3. All the measured FIs are primary and have an aqueous composition (aqueous liquid + water bubble as indicated by Raman Spectroscopy measurements at room temperature). FIs for all phases are characterised by low eutectic temperature, and it is indicated the presence of more than one salt dissolved in the aqueous solution. The final melting temperatures are in the ice field ($Tm_{ice} = Tm_{final}$). Raman spectroscopy combined with low temperature microthermometry revealed a presence of ice, $MgCl_2$-hydrate (MH) and NaCl-hydrate (HH) in the frozen FIs of Dol B.

The salinity of the FIs was calculated in the binary system $H_2O-MgCl_2$ (Dubois and Marignac, 1997) by means of the program AQSO3, and expressed as eq. wt.% $MgCl_2$.

For those FIs which have their final melting at temperatures lower than Te of this system (− 33 °C), the used equation of state was extended into the stability field of ice and $MgCl_2$-hydrate. FIs in both Dol A and Dol B have consistent salinity values. The salinity of FIs in Dol A varies in the narrow range between 20.5 and 21.8 eq. wt.% $MgCl_2$. FIs in Dol B have salinity in the slightly broader range of 19.0–22.6 eq. wt.% $MgCl_2$. For both types of FIs, the salinity mode value is 22 eq. wt.% $MgCl_2$.

A slight gradient in homogenization temperatures of primary FIs has been recognized for Dol B. The highest temperatures (100 to 205 °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 to 130 °C with mode at 115 °C) areas of the same 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}O. The fluid was a hot, highly saline and Mg-rich fluid, possibly modified seawater, which operated in a burial environment. Cal 1 was formed from a less effective (the calcite is not ubiquitous), very saline, Na-rich and slightly cooler fluid system. It was probably also modified seawater, which underwent slight contamination from meteoric water when the chain became exposed. This contamination might explain the lower $\delta^{13}C$ values measured for this phase. Cal 2 is derived from a completely different fluid of meteoric origin.

Preliminary $^{87}Sr/^{86}Sr$ isotope data showed slightly radiogenic values respect to Carboniferous limestones both for Dol A, Dol B and Cal 1, this pointing to a slight enrichment of radiogenic Sr trough water circulation.

6. Dolomite origin

To carry out 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 supply the high Mg content of both fluid and dolomite phases, and (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 dolomitizing 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 uncomformably overlying

Permian rocks, cropping out to the N (Sánchez 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. A high heat flow during post tectonic time, is in line with the model of Fernández-Suárez et al. (2000), who assume tectonic delamination of the Variscan belt of NW Iberia in the time span 310–285 Ma. During this interval, at about 295–290 Ma, a post-tectonic magmatic association (tonalite–granodiorite–monzogranite) was emplaced in the Cantabrian and West Asturian–Leonese zones.

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 times, was active in large parts of Europe. This extensional tectonics may have promoted a gravity-driven flow of the brines, which circulated deeply down, underwent heating and depletion in the ^{18}O, were slightly enriched in radiogenic Sr 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 Formations, in comparison to the underlying less permeable, more lithified Devonian carbonates.

References

Boni, M., Bechstädt, Th., Gasparrini, M., 2002. Post-Variscan hot dolomites in Europe: a "Crustal scale Hydrothermal Palaeofield"? 16th International Sedimentological Congress Johannesburg, July 2002, Abstract, p. 1.

Brinkmann, R., Lögters, H., 1968. Diapirs in western Pyrenees and foreland, Spain. In: Braunstein, J., O'Brien, G.D. (Eds.), Diapirism and Diapirs. Memoir Am. Assoc. Petrol. Geol. Bull., vol. 8, pp. 275–292.

Dubois, M., Marignac, C., 1997. The H_2O–NaCl–$MgCl_2$ ternary phase diagram with special application to fluid inclusion studies. Economic Geology 92, 114–119.

Fernández-Suárez, J., Dunning, G.R., Jenner, G.R., Gutiérrez-Alonso, G., 2000. Variscan collisional magmatism and deformation in NW Iberia: constraints from U–Pb geochronology of granitoids. Journal of the Geological Society (London) 157, 565–576.

García-López, S., Bastida, F., Brime, C., Aller, J., Valín, M.L., Sanz-López, J., Méndez, C.A., Menéndez-Álvarez, J.R., 1999. Los episodios metamórficos de la Zona Cantábrica y su contexto estructural. Trabajos de Geologia, 177–187.

Gómez-Fernández, F., Both, R.A., Mangas, J., Arribas, A., 2000. Metallogenesis of Zn–Pb carbonate-hosted mineralization in the southwestern region of the Picos de Europa (Central Northern Spain) Province: geologic, fluid inclusion, and stable isotope studies. Economic Geology 95, 19–40.

Grossman, E.L., 1994. The carbon and oxygen isotope record during the evolution of Pangea: Carboniferous to Triassic. Geological Society of America, Special Paper 288, 207–228.

Marcos, A., 1968. La tectónica de la unidad de la Sobia-Bodón. Trabajos de Geologia 2, 59–87.

Nielsen, P., Swennen, R., Muchez, Ph., Keppens, E., 1998. Origin of the Dinantian zebra dolomites south of the Brabant–Wales Massif, Belgium. Sedimentology 45, 727–743.

Pérez-Estaún, A., Bastida, F., Alonso, J.L., Marquínez, J., Aller, J., Alvarez-Marrón, J., Marcos, A., Pulgar, J.A., 1988. A thin-skinned tectonics model for an arcuate fold and thrust belt: the Cantabrian Zone (Variscan Ibero–Armorican Arc). Tectonics 7, 517–537.

Radke, B.H., Mathis, R.L., 1980. On the formation and occurrence of saddle dolomite. Journal of Sedimentary Petrology 50, 1149–1168.

Sánchez de la Torre, L., Águeda Villar, J.A., Colmenero, J.R., Manjón, M., 1977. La serie Permotriássica en la región de Villaviciosa (Asturias). Cuadernos de Geología Ibérica 4, 329–337.

Sibley, D.F., Gregg, J.M., 1987. Classification of dolomite rock texture. Journal of Sedimentary Petrology 57, 967–975.

Wallace, M.W., Both, R.A., Morales-Ruano, S., Fenoll Hach-Ali, P., Lees, T., 1994. Zebra textures from carbonate-hosted sulfide deposits: sheet cavity networks produced by fracture and solution enlargement. Economic Geology 89, 1183–1191.