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Geochemical, and stable and radiogenic isotope records in Devonian and Early Carboniferous carbonates from Valle de Tena, central Pyrenees (Spain): evidence for their diagenetic environments

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Abstract

Mineralogical, textural and geochemical investigations were made to determine the post-depositional evolution of Devonian and Early Carboniferous carbonates from Valle de Tena. The carbonate association is made up of low-Mg calcite, which occurs as micrite, spar cements, neomorphic patches and spar filling veinlets. Non-stoichiometric dolomite and ankerite occur as cements (dolomite also as replacements) in the Middle Devonian, post-dating calcite types. All these phases pre-date tectonic stylolites, indicating compaction after stabilization of the carbonate minerals. Strontium concentrations indicate that Early Devonian and Early Carboniferous micrites initially precipitated as aragonite; Middle and Late Devonian micrites precipitated as high-Mg calcites. Both precursors were diagenetically stabilized to low-Mg calcites through interaction with meteoric waters in phreatic environments. Trace elements in dolomite and ankerite indicate precipitation from Sr-enriched meteoric water. All studied carbonates, except Middle Devonian limestones, precipitated in reducing environments, which favoured incorporation of Fe and Mn. Late calcite generations precipitated from more saline waters than micrites. Light $\delta^{18}O$ values in micrites suggest alteration mainly in meteoric-phreatic environments. The dolomites and ankerites precipitated from more ^{18}O-depleted fluids than the calcites, suggesting a greater contribution from meteoric waters. Variations in $\delta^{13}C$ of micrites represent primary secular trends, according to published $\delta^{13}C$ variations. The $\delta^{13}C$ oscillations within each succession probably relate to sea-level oscillations. Strontium isotopes also point to a meteoric origin of diagenetic fluids. Model calculations suggest that O and Sr isotopes equilibrated between calcites and fluid at relatively low water/rock ratios, whereas C isotopic signatures are inherited from limestones.

Introduction

The diagenetic stabilization of primary marine carbonates is usually accompanied by textural and chemical changes. Generally, the increase in the degree of post-depositional alteration in the diagenetically precipitated low-Mg calcite results in an increase in textural maturity as well as in a decrease of elements having a distribution coefficient lower than unity (Sr^{2+}, Na^{+}) and an increase in elements with a coefficient higher than unity (Fe^{2+}, Mn^{2+}) (Brand & Veizer 1980, 1981, Veizer 1983a, b). In addition, mineralogical stabilization being a wet dissolution-reprecipitation process (Bathurst 1975), each dissolution-reprecipitation step involves equilibration with diagenetic water not only for minor and trace elements but also for O, C and Sr isotopes (Matthews 1974, Allan & Matthews 1977, Land 1980, Popp et al. 1986, Veizer et al. 1986, Wadleigh et al. 1990, Gao & Land 1991, Veizer 1992). The objective of this study is to demonstrate how the combined study of textural, chemical, and stable and radiogenic isotope analyses provides insights for estimating the degree of diagenetic alteration of ancient carbonates.

Chemical and isotope analyses of Devonian and Early Carboniferous rocks from Valle de Tena, Span-

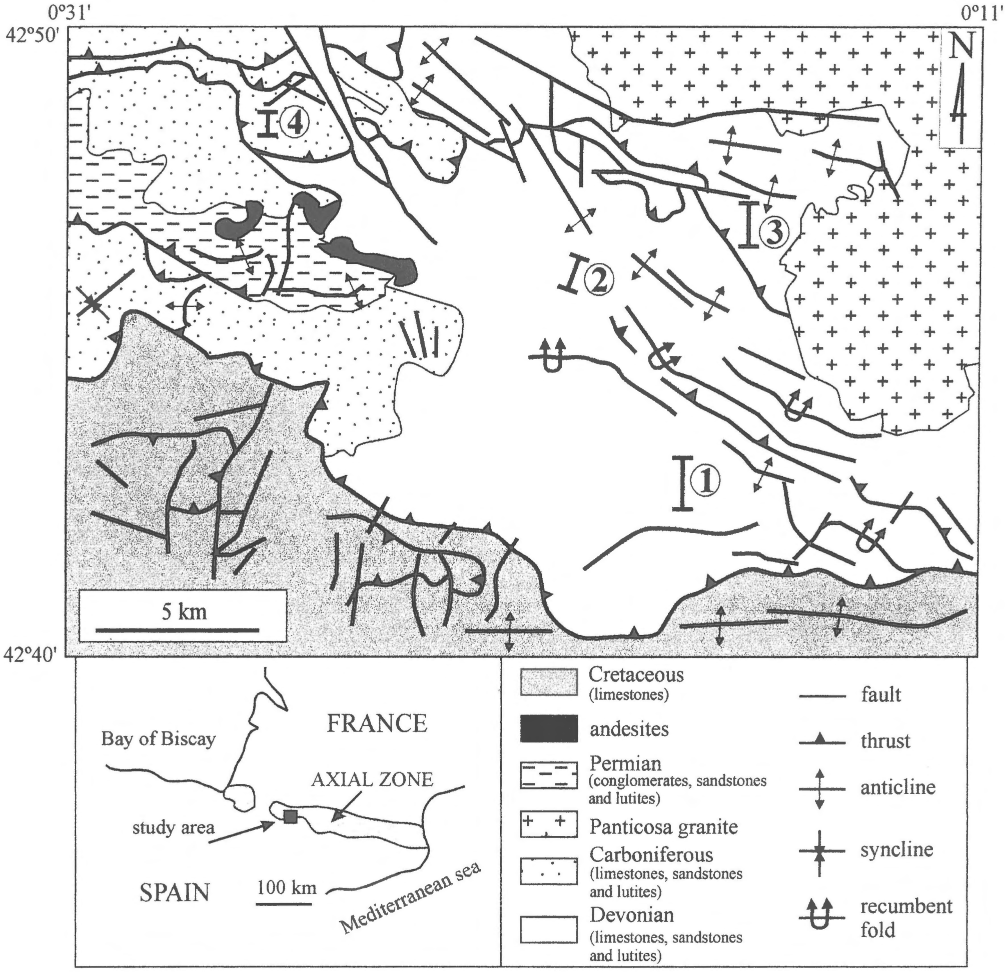

Figure 1. Geological sketchmap of the Valle de Tena, showing the location of the sampled Early Devonian (1), Middle Devonian (2), Late Devonian (3) and Early Carboniferous (4) sequences shown in Figure 2.

ish central Pyrenees, are presented. Studies of the post-depositional evolution of the Palaeozoic sedimentary to metasedimentary units of the Pyrenees are rare. Subías et al. (1990) reported the first systematic mineralogical investigation of the study area (Figure 1). They focused on the clay mineralogy of the Devonian and Early Carboniferous pelitic and semi-pelitic rocks. We concluded from their data that the largest impact recorded by the rocks was that of burial diagenesis. The post-depositional processes affecting the carbonates of the study area were not investigated by Subías et al. (1990). Therefore, we undertook combined mineralogical, textural and geochemical (trace elements and C, O and Sr isotopes) studies of these carbonates with the aim to provide new insight into their diagenesis. In addition, these new data give information on the nature of the fluids involved in the process.

Regional geological setting

Valle de Tena is located in the northernmost section of Huesca province (Figure 1). The study area lies in the Axial Pyrenean Zone and belongs to the southwestern end of the Gavarnie nappe. The structural pattern of the study area is a product of polyphase tectonics caused by the Hercynian and Alpine orogenies. Wensink (1962), Mirouse (1966), Ríos et al. (1983) and Bixel et al. (1985) have described the geology of this area in detail.

The area is composed of sedimentary and igneous rocks, with the former comprising Palaeozoic and Cretaceous lithological units. The importance of the Hercynian metamorphism of the Palaeozoic rocks in the Pyrenees varies from place to place. Although some high-temperature, low-pressure metamorphic domes exists in the eastern Pyrenees, maybe related to a high-heat flow environment (Zwart 1986), metamorphism clearly reached lower and lower grades westward. In the study area, the post-depositional evolution reached the anchizone as deduced from the clay mineralogy of pelitic rocks (Subías et al. 1990).

Prior to compressional paroxysm during the Late Carboniferous, a major extension phase occurred during the Early Carboniferous. Carreras & Capellá (1994) reviewed different models explaining the Hercynian structure of the Pyrenees. Some of these models involve important crustal extension: i) as rifting (Wickham & Oxburg 1985), or ii) as gravitational collapse (Van den Eeckhout & Zwart 1988). Arthaud & Matte (1977) proposed that the main Hercynian structures resulted from a late Hercynian dextral shear along a major wrench fault. Gleizes et al. (1997) demonstrated the syn-orogenic character of Hercynian plutons of the Pyrenees; the Pyrenees acted as a large dextral ductile zone during the Hercynian deformation. In the study area, igneous rocks are represented by the Panticosa granite (290 Ma; Debon 1980) which intruded into the Devonian and Carboniferous sedimentary pile. Subsequently, late Hercynian extensional tectonics promoted the opening of Stephano-Permian basins in the study area, which favoured the deposition of a continental red-bed succession with intercalations of thick calc-alkaline to alkaline volcanic sequences. The Hercynian structure remained relatively unaffected in between the Alpine N–S faults.

Stratigraphy, facies and depositional environments

The oldest sedimentary rocks in the Valle de Tena area are Silurian and consist of black phyllites and minor limestones. These rocks acted as a lubricant layer and caused much of the heterogeneous and discontinuous nature of the younger sequences during the Hercynian structural development of the investigated area. In this paper, we have focused on Devonian and Early Carboniferous successions containing abundant carbonate rocks. The younger Late Carboniferous sequence consists of detrital rocks. Figure 2 shows a synthetic stratigraphic section of the investigated succession, with the location of the studied samples.

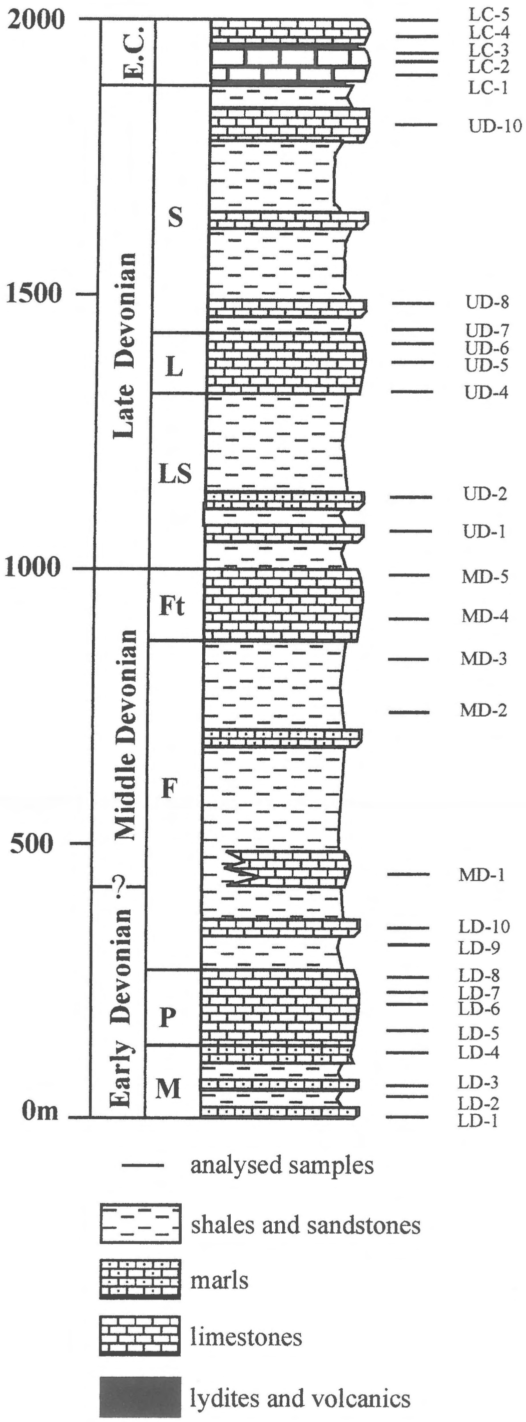

Figure 2. Stratigraphic framework of the sampled Devonian and Early Carboniferous succession in the Valle de Tena. Abbreviations: E.C.: Early Carboniferous; S: Sia facies; L: Larrue facies; LS: La Sarra facies; Ft: Foratata facies; F: Formigal facies; P: Pacino facies; M: Mandilar facies.

The Early Devonian can be subdivided into at least two different lithofacies and includes a 100-m-thick alternation of calcareous shales and marls (samples LD-1 to LD-4), the Mandilar facies of Valero (1974). This is separated, by an erosional gap, from an approx. 150-m-thick carbonate sequence (LD-5 to LD-8): the Pacino facies (Valero 1974) which completes the Early Devonian sequence. Both facies were deposited under open shallow-marine conditions (Galera 1987).

The Formigal facies (Subías et al. 1990) consists of ca. 600 m of alternating shales and greywackes (LD-9, MD-2 and MD-3). Near its base it includes a subordinate calcareous (LD-10), and a multicoloured calcareous sequence (MD-1). The age of the basal part of this succession is uncertain (Early or Middle Devonian). The fauna assemblage in the multicoloured limestones and in the upper part of the Formigal facies indicates a Late Emsian to Eifelian age (Bixel et al. 1985, Ríos et al. 1989). The Formigal facies was mainly deposited in a sublittoral environment; the multicoloured limestones probably originated in a back-reef environment (Galera 1987).

The Foratata facies contains a reefal assemblage (Dalloni 1910, Wensink 1962, Mirouse 1966, Ríos et al. 1989). It consists of ca. 150 m of layered limestones (MD-4) grading upsection into massive limestones (MD-5). The latter contain silicified concretions containing fossils, mainly tetracorals. The age based on these corals is Late Eifelian to Givetian (Joseph & Tsien 1975).

The Late Devonian succession begins with the so-called 'pélito-grauwackeus' complex of Perret et al. (1972) and continues with up to 300-m-thick shales interbedded with calcareous to shaly-sandy rocks (UD-1 to UD-2). This is followed by the 100-m-thick Larrue facies which consists of nodular limestones (UD-4) overlain by laminated micrites (UD-5 to UD-7), with a conodont fauna of Givetian to Frasnian age (Perret et al. 1972). Galera (1987) proposed that these sediments were deposited in protected areas between reefs. The overlying 600-m-thick Sia facies consists of an alternation of shales and sandstones, with flaser structures and ripple marks, interrupted by rare calcareous layers (UD-8 and UD-10). It is considered to be of Frasnian age (Joseph et al. 1980) and was deposited in a sublittoral environment (Llense 1978). The uppermost part of the Devonian contains calcareous sediments of the Famennian 'griotte' facies (Boyer et al. 1974).

The extensional tectonics at the end of the Devonian resulted in erosion of the Middle to Late Devonian strata in the western part of the study area (Galera 1987).

A few meters of nodular limestones and lydites, often associated with phosphatic nodules, form the base of the Carboniferous sequence. It is of Late Tournaisian to Late Visean age (Boyer et al. 1974). This is overlain by a carbonate-dominated succession of Visean to Namurian age (Mirouse et al. 1983, Ríos et al. 1989), which is composed of grey nodular limestones that evolve upsection into grey thin bedded limestones (LC-1 to LC-3). Thin layers of pyroclastic material also occur. The sequence was deposited in a pelagic environment (Joseph et al. 1984, Ebner 1991). Laminated algal and fetid black limestones (LC-4 and LC-5) overlie the grey limestones, with an intraformational breccia in between. The top of the sequence is a karstic palaeorelief.

Sample preparation and experimental methods

Twenty-eight samples of carbonates were collected away from granitic and contact-metamorphic rocks in order to avoid alteration products (Figure 1).

The X-ray diffraction (XRD) powder method, using Philips Pw1710 equipment, Cu Kα radiation and automatic slit, was used to determine the mineralogical composition of the bulk samples. For the quantitative estimation of concentrations, the intensity factors of Schultz (1964) and Barahona (1974) were used.

Electron microprobe analyses (EPMA) of the micrites, neomorphic patches and veinlets and of some dolomite and ankerite were carried out on a CAMECA microprobe at the University of Granada, Spain. An operating voltage of 20 kV and an aperture current of 15 nA were used. The detection limit was 0.1 wt%.

The samples for isotopic analyses were obtained by using a dental drill. The C and O isotopic compositions of selected samples were determined at the 'Servicio General de Análisis de Isótopos Estables', University of Salamanca, Spain. The extraction of CO_2 from carbonates was performed following standard techniques (McCrea 1950, Craig 1957) and was done for ankerite with 100% H_3PO_4 at 25 °C in a glass extraction line, and for calcite at 90 °C using an ISOCARB device. When calcite and dolomite were present in the sample a fractional extraction technique was employed, such that the whole rock powder was dissolved in the acid at 25 °C, and aliquots of CO_2 were taken at different intervals, considering the in

Table 1. Mineralogical composition (wt%) of Valle de Tena samples shown in Figure 2, determined by XRD. Abbreviations: cte: calcite; dol: dolomite; ank: ankerite; fto: feldspars; Q: quartz; phy: phyllosilicates; E.: Early; L.: Late; M.: Middle; Carb.: Carboniferous; Dev.: Devonian; *: < 5 wt%.

Age	Sample	cte	dol	ank	fto	Q	phy
E. Carb.	LC-5	97				*	
	LC-4	97				*	
	LC-3	93				7	
	LC-2	97				*	*
	LC-1	96				*	
L. Dev.	UD-10	85			6	*	7
	UD-8	90				5	5
	UD-7	11	6		7	35	41
	UD-6	85				12	*
	UD-5	88				9	*
	UD-4	94				*	*
	UD-2	39			*	38	21
	UD-1	81				8	11
M. Dev.	MD-5	99				*	*
	MD-4	98	*			*	*
	MD-3	*		38		38	23
	MD-2	*		43	*	30	23
	MD-1	73	10			11	6
E. Dev.	LD-10	86	*		*	9	*
	LD-9	41	6		*	21	30
	LD-8	84				16	
	LD-7	85	*			11	
	LD-6	90	*			*	5
	LD-5	87	*		*	6	*
	LD-4	49	10		*	19	22
	LD-3	55	*		*	24	19
	LD-2	37	*		5	31	23
	LD-1	62	*		*	19	13

dications of Walters et al. (1972). The quality of the results was monitored by means of repeated analyses of carbonate laboratory standards. The average precisions were ± 0.02‰ ($\delta^{13}C$) and ± 0.12‰ ($\delta^{18}O$).

The Sr isotopic compositions of nine samples were determined at the Département de Minéralogie, University of Geneva (Switzerland). HCl 1N was used to dissolve powdered carbonate samples. Strontium was isolated by conventional cation-exchange techniques and analysed with a 7 collector Finningan Mat 262 thermal ionization mass spectrometer. The samples were loaded on a double Re filament. The reproducibility of the duplicate samples was always better than 0.00005 (2σ). The average value of the NBS 987 standard during the course of this study was 0.710242 ± 0.000005 (2σ).

Results and discussion

Carbonate mineralogy and textures

The mineralogical composition of the selected samples, determined by XRD, is presented in Table 1. The bulk samples consist of calcite, dolomite, quartz and phyllosilicates, mainly muscovite and chlorite. The non-carbonate fraction, quartz and phyllosilicates, has been used to distinguish the carbonate rocks in terms of pure (limestones) and impure (marls). Although dolomite has been found at various stratigraphic levels in the Devonian, it mainly occurs near the base of that succession.

The *Early Devonian* carbonate rocks can be grouped into two lithological types: marls and limestones. The former type is made up of micrite to microspar calcite with quartz, phyllosilicates, lithoclasts, bioclasts and minor organic matter. Fe-oxide-bearing micrite peloids occur occasionally. Spar calcite cements the textural constituents, locally as neomorphic patches. Two types of dolomite replacing calcite are distinguished: idiomorphic and xenotopic crystals. Braided dissolution seams often affect the carbonate constituents, where clay minerals and organic matter are concentrated together with poikilitic sparry calcite. Late calcite generations are filling both fractures and cavities. These calcites exhibit equant mosaic and poikilitic fabrics. Evidence for silica neomorphism was found in fractures and dissolution seams.

The Early Devonian lime-mudstones contain ooids, bioclasts and/or fenestrae. Neomorphism is evidenced by the presence of sparry calcite patches. In addition, these mudstones show late calcite generations, as is the case in marly samples.

The *Middle Devonian* limestones show the same fabrics as the Early Devonian carbonates (micrite, spar patches and sparry calcite filling veinlets). In contrast to the latter carbonates, the dolomitization is stronger. Dolomite occurs as sparry crystals arranged in a xenotopic mosaic. Arenitic layers located at the top of Formigal facies contain skeletal quartz, mica grains and partly ankeritized bioclasts cemented by ankerite. Idiomorphic ankerite crystals are often observed within the cement.

The *Late Devonian* carbonate rocks (marls and limestones) show the same textures as those of the

Table 2. Electron microprobe analyses expressed in weight percentage (left) and mole percentage (right) of the three calcite types and of ankerite (ank) and dolomite (dol) from the Valle de Tena section. Abbreviations as in Table 1. N: number of measurements.

Age	Textural type	N	wt %						Mole %					
			Ca	Mg	Fe	Mn	Sr	Na	mCa	mMg	mFe	mMn	mSr	mNa
E. Carb.	micrites		39.7	0.23	0.13	0.03	0.19	0.02	98.22	0.94	0.23	0.05	0.21	0.09
	mean range	28	39.25–39.50	0.14–0.33	0.01–0.30	0.02–0.05	0.05–0.32	0.02–0.02	97.93–98.56	0.57–1.37	0.02–0.54	0.03–0.10	0.06–0.36	0.08–0.10
	patches		39.15	0.44	0.15	0.02	0.16	0.01	97.67	1.81	0.27	0.04	0.18	0.06
	mean range	40	39.10–39.20	0.34–0.53	0.03–0.32	0.01–0.03	0.08–0.23	0.01–0.02	97.55–97.80	1.41–2.17	0.04–0.57	0.02–0.05	0.10–0.26	0.04–0.08
	veinlets		39.40	0.22	0.10	0.03	0.38	0.01	98.30	0.92	0.19	0.05	0.43	0.05
	mean range	48	38.08–39.81	0.03–0.84	0.00–0.79	0.00–0.07	0.00–1.50	0.00–0.04	95.01–99.33	0.12–3.46	0.00–1.41	0.00–0.12	0.00–1.71	0.00–0.19
L. Dev.	micrites		39.19	0.33	0.18	0.12	0.09	0.01	97.79	1.37	0.33	0.22	0.10	0.05
	mean range	26	38.92–39.53	0.18–0.55	0.11–0.24	0.04–0.25	0.03–0.21	0.01–0.02	97.10–98.64	0.73–2.25	0.20–0.43	0.07–0.46	0.03–0.24	0.03–0.07
	patches		39.02	0.27	0.53	0.23	0.07	0.01	97.35	1.11	0.95	0.42	0.08	0.05
	mean range	80	38.47–39.57	0.20–0.44	0.11–1.21	0.06–0.38	0.05–0.08	0.00–0.02	95.98–98.73	0.81–1.80	0.19–2.16	0.11–0.69	0.06–0.09	0.01–0.09
	veinlets		38.95	0.26	0.44	0.28	0.14	0.01	97.17	1.08	0.78	0.51	0.15	0.04
	mean range	27	38.12–39.79	0.03–0.64	0.15–0.81	0.13–0.42	0.04–0.31	0.00–0.03	95.11–99.28	0.12–2.61	0.27–1.45	0.23–0.76	0.04–0.36	0.00–0.11
M. Dev.	micrites		39.78	0.14	0.00	0.01	0.03	0.00	99.25	0.59	0.01	0.01	0.03	0.01
	mean range	29	39.70–39.85	0.12–0.17	0.00–0.01	0.00–0.02	0.00–0.06	0.00–0.01	99.05–99.43	0.49–0.70	0.00–0.03	0.00–0.04	0.00–0.07	0.00–0.04
	patches		39.81	0.13	0.02	0.01	0.01	0.01	99.33	0.52	0.03	0.02	0.01	0.03
	mean range	27	39.70–39.90	0.09–0.15	0.01–0.03	0.00–0.02	0.00–0.02	0.00–0.01	99.05–99.55	0.37–0.62	0.02–0.05	0.00–0.03	0.00–0.02	0.00–0.05
	veinlets		39.83	0.13	0.00	0.01	0.04	0.00	99.38	0.54	0.00	0.01	0.04	0.01
	mean range	27	39.75–39.92	0.07–0.18	0.00–0.01	0.00–0.02	0.00–0.07	0.00–0.01	99.18–99.60	0.30–0.74	0.00–0.01	0.00–004	0.00–0.08	0.00–0.03
	ank.		19.97	5.75	13.25	0.40	0.04	0.01	49.82	23.65	23.72	0.73	0.04	0.06
	mean range	13	18.30–20.71	5.39–6.14	11.80–13.89	0.32–0.75	0.00–0.09	0.00–0.04	45.66–51.67	22.17–25.26	21.13–24.87	0.59–1.36	0.00–0.09	0.00–0.18
	dol.		21.50	9.25	3.88	0.10	0.03	0.03	53.65	38.04	6.94	0.18	0.04	0.06
	mean range	13	21.09–21.93	8.69–9.83	2.89–4.88	0.08–0.10	0.00–0.05	0.02–0.04	52.62–54.72	35.74–40.43	5.17–8.74	0.15–0.18	0.00–0.06	0.09–0.17
E. Dev.	micrites		38.99	0.33	0.52	0.05	0.20	0.01	97.27	1.37	0.94	0.08	0.23	0.03
	mean range	13	38.57–39.20	0.27–0.55	0.16–0.71	0.02–0.09	0.04–0.34	0.00–0.03	96.24–97.80	1.10–2.28	0.29–1.27	0.04–0.16	0.05–0.38	0.00–0.11
	patches		39.54	0.24	0.07	0.03	0.14	0.02	98.65	0.98	0.12	0.05	0.16	0.07
	mean range	61	39.52–39.56	0.18–0.29	0.01–0.13	0.01–0.05	0.07–0.22	0.01–0.03	98.59–98.71	0.75–1.21	0.01–0.23	0.1–0.09	0.08–0.25	0.03–0.11
	veinlets		38.99	0.33	0.52	0.05	0.20	0.01	97.27	1.37	0.94	0.08	0.23	0.03
	mean range	22	38.57–39.20	0.27–0.55	0.16–0.71	0.02–0.09	0.04–0.39	0.00–0.03	96.24–97.80	1.10–2.28	0.29–1.27	0.04–0.16	0.05–0.39	0.00–0.11

Table 3. C, O and Sr isotopic compositions of micrite calcite, ankerite and dolomite from the Valle de Tena section. Abbreviations as in Table 1. N: number of measurements.

Age	Textural type	N	$\delta^{18}O_{PDB}$(‰)	$\delta^{13}C_{PDB}$(‰)	$^{87}Sr/^{86}Sr$
E. Carb.	micrites		–13.0	+3.2	0.7095
	mean range	5	–14.0 to –11.3	+2.3 to +4.9	0.7085 to 0.7105
L. Dev.	micrites		–14.6	–0.2	0.7086
	mean range	8	–16.6 to –12.2	–2.0 to +0.0	
M. Dev.	micrites		–10.3	+1.2	0.7087
	mean range	3	–11.8 to –9.1	+0.5 to +1.9	
	ank		–14.2	–3.9	
	mean range	2	–14.3 to –14.0	–4.4 to –3.4	
	dol mean	1	–12.3	+0.0	
E. Dev.	micrites		–13.0	+1.0	0.7090
	mean range	10	–15.4 to –11.6	–2.2 to +2.7	0.7084 to 0.7097

Early and Middle Devonian: micrite, sparry calcite arranged in patches and spar filling veinlets also occur. Dolomite was detected in one sample only (UD-7).

The *Early Carboniferous* succession is made up of lime-mudstones containing bioclasts which are often microsparitized. Occasionally, these bioclasts show fibrous-radial calcite crystals, which seem to indicate a replacement of early aragonite. In addition, micritic peloids and fenestral fabrics, the latter filled by crypto to microcrystalline quartz, microspar and pyrite, can be recognized at the base of the sequence. Calcitic patches indicate neomorphism. Algal lamination was recognized in the top part of this succession. The Early Carboniferous limestones show dissolution seams, veinlets filled with sparry calcite arranged in a xenotopic mosaic, and stylolites crosscutting the veinlets.

Carbonate geochemistry

The geochemical data (mean and range values) are shown per succession and per textural type in Tables 2 and 3. The former table contains the microprobe data set, expressed in percentage by both weight and mole, whereas Table 3 lists the isotope results. The $\delta^{18}O$ and $\delta^{13}C$ values mentioned in the text are expressed in $‰_{PDB}$ except where indicated otherwise ($‰_{SMOW}$).

Early Devonian carbonates

All analysed calcite types are low-Mg calcites. The $CaCO_3$ content varies from 97 to 99 mole% and $MgCO_3$ from 1 to 2 mole%. Strontium contents vary from 0.1 to 0.4 wt%, the fine-grained calcites being Sr-depleted relative to the coarse-grained ones. The Fe concentration ranges between 0.16 and 0.71 wt%; the highest Fe contents occur in calcites from the marly samples.

Micrites from marls have $\delta^{18}O$ values ranging from –12.8 to –11.6‰, whereas those from limestones are slightly more ^{18}O-depleted: from –15.4 to –11.8‰. The $\delta^{13}C$ values also vary with lithology, ranging from –2.2 to +1.9‰ for marls, and from –1.2 to +2.7‰ for limestones. The $^{87}Sr/^{86}Sr$ ratios are also lithology-dependent: calcites from marls are more radiogenic (0.7097) than those from limestones (0.7084 to 0.7090).

Most micrites from Early Devonian samples have Sr contents well above the predicted and measured Sr concentration for marine calcite, which is 0.12 wt% (Turekian & Kulp 1956, Kinsman 1969, Veizer 1983a). These Sr-rich compositions suggest that the original mineralogy was aragonite containing about 0.8 ± 0.2 wt% Sr, typical of present-day aragonitic muds (Bathurst 1975). This assumption is also supported by petrographic evidence (e.g. fibrous-radial calcite crystals). Since the distribution coefficient for Sr is smaller than unity, diagenetic stabilization to low-Mg calcite lowered the initial Sr content. The Fe and Mn contents are relatively high in comparison with marine calcite (< 0.0001 mole%; Veizer 1983a, b). This reflects that the distribution coefficients for Mn and Fe are greater than unity. The influence of meteoric waters and the existence of a reducing diagenetic environment favour these elements to be incorporated in the carbonate lattice. In addition, the presence of fine-grained clastics, acting as Fe and Mn donors,

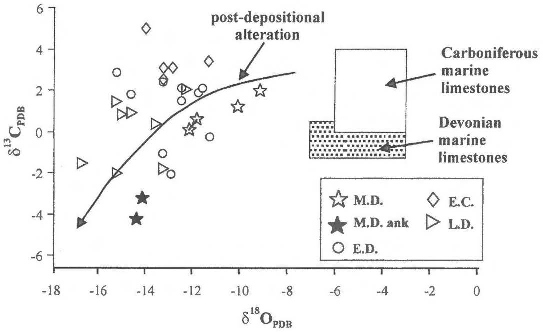

Figure 3. Scatter diagram of δ^{13}C and δ^{18}O for Valle de Tena micrites showing post-depositional alteration trend. Abbreviations: E.D.: Early Devonian; M.D.: Middle Devonian; M.D. ank: Middle Devonian ankerites; L.D.: Late Devonian; E.C.: Early Carboniferous. Rectangles indicate global isotope compositions of Devonian and Carboniferous marine limestones. Two Middle Devonian plots (stars connected by line) represent calcite (upper) and associated dolomite (lower) of sample MD-1.

probably explains that the Fe and Mn contents of micrite are higher in marls than in limestones.

Late spar low-Mg calcite is relatively depleted in Sr, Fe and Mn, suggesting a greater contribution of Sr-poor meteoric waters and more oxidizing diagenetic conditions. The last fracture-filling calcite generation (veinlets of Table 2) shows high Sr, Fe and Mn contents, indicating that the precipitating fluids were meteoric saline waters probably resulting from leaching of Sr-bearing phases (primary carbonates?) and reducing conditions.

The Early Devonian micrites show clearly more negative δ^{18}O values than those reported from Devonian marine calcite and from their modern counterparts (Popp et al. 1986, Veizer et al. 1986, Wickham & Taylor 1990, Soler 1990, Delgado 1993, Figure 3). This isotopic shift toward more ^{18}O-depleted compositions could be related to several factors such as: a) changes of seawater δ^{18}O over geological time, b) changes of ocean temperature, and c) increasing post-depositional alteration with age. In the latter case, low δ^{18}O values could reflect either an isotopic exchange with isotopically lighter meteoric waters, or a progressive increase of burial temperature or both. Assuming the δ^{18}O mean value for Devonian marine calcites being –5.5‰ (Popp et al. 1986, Veizer et al. 1986) and a seawater temperature of 25 °C (Karhu & Epstein 1986), the oxygen isotope composition of Devonian seawater would be ca. –3.5‰ $_{\mathrm{SMOW}}$ (fractionation equation of Friedman & O'Neil 1977).

The interpretation of stable isotope data requires knowledge of the original compositions of marine calcites. The most ^{18}O-rich carbonates in a suite of samples from the same formation or of the same age are more likely to have retained their original isotopic composition, since if secondary processes would have affected them, their δ^{18}O values are almost always lowered. Consequently, if the diagenetic fluids were of marine origin, the highest δ^{18}O value can be used to determine the maximum burial temperature. Taking this into account and assuming a surface temperature of 25 °C and a palaeogeothermal gradient of 30 °C km^{-1}, the heaviest δ^{18}O value for our Early Devonian micritic calcites (–11.6‰) would correspond to an equilibrium precipitation with marine pore waters at a temperature of approx. 60 °C, equivalent to a burial depth of about 1.2 km. However, petrographic and geochemical evidence indicates that the diagenetic fluids were affected by meteoric waters, and that the calcites were stabilized at smaller depths in a shallow phreatic diagenetic environment. The variability of δ^{18}O data can reflect minor changes in the isotopic composition of pore waters, probably due to variations in meteoric water composition, and/or in the diagenetic stabilization depth (Figure 4(a)).

The δ^{13}C values of the Early Devonian calcites are similar to those of Devonian marine calcite (+1.0 ± 1.0‰, Figure 3; Popp et al. 1986, Veizer et al. 1986). Since the C isotope composition is rock-buffered in the diagenetic system (Banner & Hanson 1990), the δ^{13}C value of pure carbonate is usually little changed from its initial value by diagenetic alteration. Consequently the determined values probably reflect primary marine values. However, some values as ^{13}C-depleted as δ^{13}C –2.1‰, possibly reflect an organic carbon contribution to precipitating fluids. The relatively lower δ^{13}C values shown by marly samples, containing abundant organic matter, can be related to the contribution of organic carbon from the decay of organic matter to diagenetic pore waters.

The Sr isotope signature of the Early Devonian micritic calcites is more radiogenic than corresponding values for coeval seawater (0.7084; Burke et al. 1982, Veizer 1992; Figure 6). Furthermore, these calcites are ^{87}Sr-enriched as compared to Devonian limestones from the central Pyrenees (0.7083–0.7084) reported by Delgado (1993). This more radiogenic Sr isotope signature can probably be due to interaction with ^{87}Sr-bearing meteoric waters involved in reactions with clastic Rb-bearing silicates. It is noteworthy that the calcites from the marls exhibit higher ^{87}Sr/^{86}Sr ratios than the calcites from the limestones, suggesting a much more pronounced contribution of

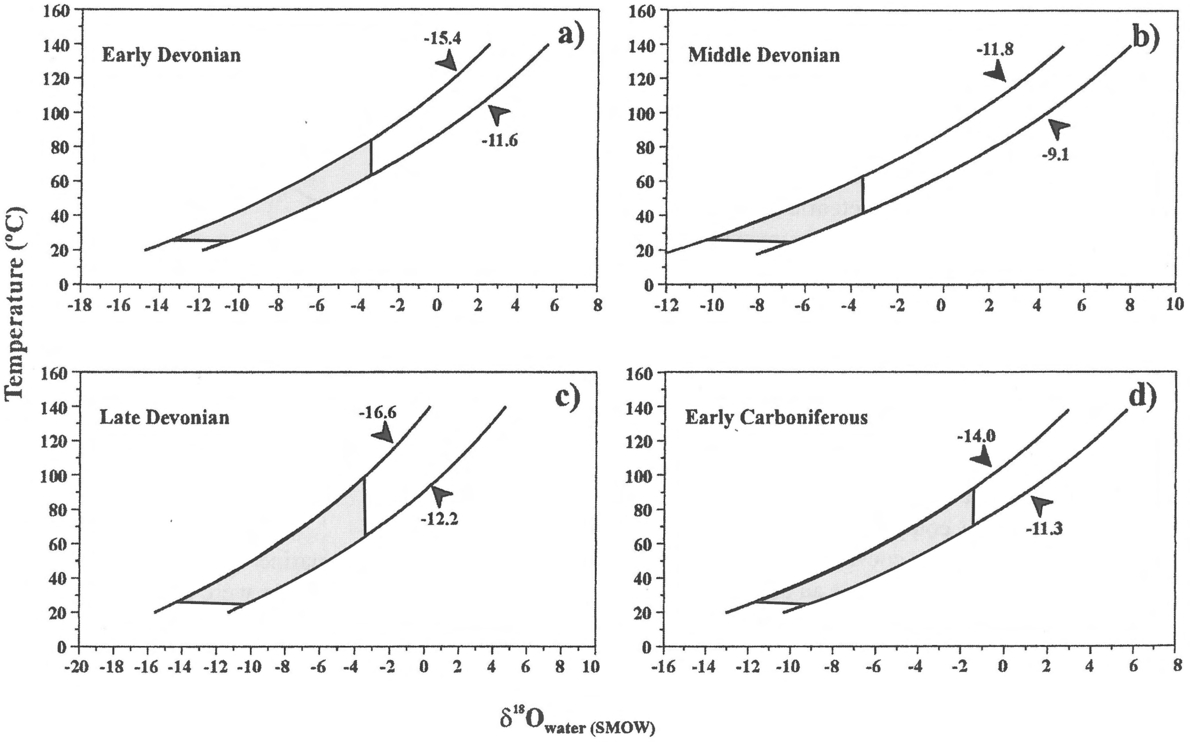

Figure 4a-d. Relationships between range of $\delta^{18}O$ of calcite (arrows, Table 3), $\delta^{18}O$ of water, and temperature, according to 10^3 lnα $_{\text{calcite-water}}$ = 2.78 (10^6T^{-2}) – 2.89 (Friedman & O'Neil 1977). Grey shading areas indicate equilibrium precipitation of calcite with seawater. For values of limiting curves see text.

^{87}Sr-bearing waters to their precipitating fluids. The radiogenic Sr was probably acquired from reactions with clastic Rb-rich feldspar and micas. The contributions of clay minerals were probably minor since their exchangeable Sr is mostly surface-bound and hence similar to that of the environment (Chaudhuri & Clauer 1992).

Middle Devonian carbonates

All the analysed calcite types are low-Mg calcite, with 99 mole% $CaCO_3$. Concentrations of Sr, Fe and Mn vary similarly to mg: micrites and fracture-filling sparites show minor amounts of these elements, whereas patches contain 0.01, 0.02 and 0.01 wt%, respectively. $\delta^{18}O$ values of micrite range between –11.8 and –9.1‰, $\delta^{13}C$ values between +0.5 and +1.9‰, and their $^{87}Sr/^{86}Sr$ ratio is 0.7087.

Dolomites at the bottom of this sequence are calcian and ferroan. Their $CaCO_3$ content is always close to 54 mole%, whereas their $MgCO_3$ content varies from 36 to 40 mole%, and their $FeCO_3$ content from 5 to 9 mole%. Their Sr concentration is low, from 0.00 to 0.05 wt%, and the average Mn content is 0.1 wt%. Their $\delta^{18}O$ and $\delta^{13}C$ values are –12.3 and 0.0‰, respectively, being very similar to those of the associated micrite ($\delta^{18}O$ = –11.8‰, $\delta^{13}C$ = +0.5‰).

Ankerites cementing sandy levels, have a mean composition corresponding to $Ca_{1.02}Mg_{0.48}Fe_{0.48}-Mn_{0.02}(CO_3)_2$ and show low Sr concentrations (0.00–0.08 wt%). Their $\delta^{18}O$ values range from –14.3 to –14.0‰ and their $\delta^{13}C$ values from –4.4 to –3.4‰.

Micritic calcites have the lowest Sr contents determined in the analysed micrites, being even more Sr-depleted than marine calcites, suggesting that high-Mg marine calcites were their primary precursor. On the other hand, the low Fe and Mn concentrations indicate precipitation under high Eh conditions. The latter conditions also continued during the deposition of vein and fracture-filling spar calcite, which took place under near-surface conditions. The intermediate calcite generation, neomorphic sparry patches, was precipitated from relatively more saline meteoric pore waters, which probably gained elements from dissolution of Sr-rich carbonates. They were stabilized at greater depths under more reducing conditions, as indicated by their higher Fe and Mn concentrations.

The heaviest $\delta^{18}O$ value of micrites is –9.1‰, which would correspond to calcite precipitated in isotopic equilibrium with marine water at a temperature of ca. 44 °C, equivalent to a burial depth of ca. 600 m for the geothermal gradient already mentioned for the Early Devonian (Figure 4(b)). However, petrographic and geochemical data reflect meteoric alteration and, therefore, the stabilization temperature must have been lower. The $\delta^{13}C$ values are slightly higher than those of coeval marine calcite (Popp et al. 1986, Veizer et al. 1986; Figure 3), probably indicating that they were precipitated in more ^{13}C-enriched marine waters during periods of high organic productivity. Since the diagenetic environment for C isotopes is rock-buffered (Banner & Hanson 1990), the C isotope signature is primary and unaffected during diagenetic stabilization. The Sr isotope composition, with a $^{87}Sr/^{86}Sr$ ratio more radiogenic than coeval seawater (Figure 6; Burke et al. 1982, Veizer 1992), is an additional argument to support the contribution of meteoric water to the diagenetic stabilization of these micrites.

The xenotopic texture of dolomites at the bottom of the Middle Devonian can result either from neomorphism and/or from non-mimetic replacement under high-temperature conditions (Gregg & Sibley 1984). The analysed dolomites show Ca/Mg molar ratios higher than 1.3, and are therefore non-stoichiometric, and they have elevated Fe, Mn and Sr concentrations. Recrystallized dolomites commonly exhibit a high degree of Ca/Mg stoichiometry (Sperber et al. 1984). The extent to which excess Ca can be replaced by mg is limited by the water/rock ratio during recrystallization, it being possible that lattice constraints on dolomite stability at low water/rock ratios can promote the precipitation of these dolomites (Searls 1994). The high Sr content suggests a relatively closed system with interstitial saline waters comparable to seawater (Land 1980), whereas the ferrous iron content (up to 9.0 mole% $FeCO_3$) suggests reducing conditions and a high availability of this ion probably related to the associated shales. The $\delta^{18}O$ values of coexisting dolomite and calcite (–12.3 and –11.8‰, respectively; Table 3) indicate that they are not cogenetic since if they were, dolomite should have been isotopically heavier (ca. 3‰) than calcite (Land 1980). The negative O isotope composition of dolomite can suggest either that O was precipitated from ^{18}O-depleted meteoric waters or that dolomitizing fluids were warmer than those from which calcite was precipitated, or both. Assuming a reference $\delta^{18}O$ value of Devonian seawater of –3.5‰ SMOW (Popp et al. 1986, Veizer et al. 1986) and a marine origin for dolomitizing fluids, the studied dolomites were precipitated at temperatures of approx. 85 °C (fractionation equation of Land 1983), corresponding to a burial depth of about 2 km. However, the petrographic and geochemical evidence does not support a burial-diagenetic environment. Therefore, the temperature of precipitation would have been lower and a meteoric supply would have to be required to form dolomitizing fluids. These fluids were possibly interstitial saline waters, which replaced calcites at temperatures below 85 °C in a phreatic diagenetic environment. The sources of Mg and other ions would have been, at least partially, fluids expelled from compaction of the associated shales.

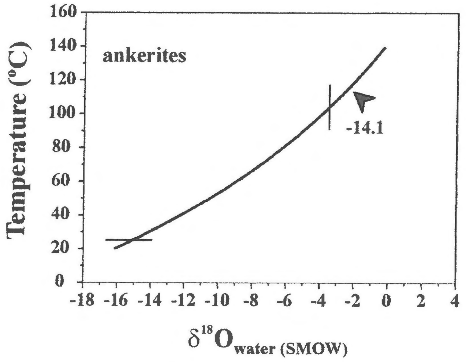

Figure 5. Relationship between mean $\delta^{18}O$ of ankerite, $\delta^{18}O$ of water, and temperature, according to: $10^3 \ln\alpha_{\text{ankerite–water}} = 2.78 (10^6 T^{-2}) + 0.32$ (Dutton & Land 1985). Straight lines indicate equilibrium precipitation of ankerite with seawater.

Ankerite cement in sandy levels shows Sr concentrations up to 0.08 wt%, suggesting precipitation from interstitial saline waters similar to seawater in a reducing environment with a high availability of Fe and Mn. These waters probably obtained Sr from dissolution of younger carbonates. The O isotope composition of ankerite (ca. –14‰) would correspond to precipitation in isotopic equilibrium with seawater at temperatures of about 105°C (fractionation equation of Dutton & Land 1985), equivalent to 2.5 km. of burial depth (Figure 5). This temperature appears too high to be consistent with that calculated for the underlying dolomite. Consequently, ankerite had to precipitate from fluids that were more depleted in ^{18}O and more influenced by meteoric waters that the fluids which precipitated dolomite. In addition, $\delta^{13}C$ values, lighter than those of dolomite, reflect a greater contribution of organic carbon, probably derived from decaying organic matter.

Late Devonian carbonates

Although all calcite types are low-Mg calcites, their average mole% $CaCO_3$ decreases from micrites (98%) to neomorphic sparite and to fracture-filling sparite (97%). Concurrently, the Sr concentration increases from 0.09 to 0.14 wt% and the 'Fe + Mn' content from 0.30 to 0.72 wt%. The $\delta^{18}O$ values of micrite range from –16.6 to –12.2‰, with oscillations through the sequence without a definite trend. The $\delta^{13}C$ values exhibit similar oscillations, varying from –2.0 to +0.0‰. The $^{87}Sr/^{86}Sr$ ratio from a level near the top of the sequence is 0.7086.

The low Sr content of the micrites suggests an original marine high-Mg calcite precursor, except for those micrites with a Sr content of 0.21 wt%, whose precursor was probably aragonite. The effect of diagenetic remobilization is shown by the loss of Sr and the gain of Fe and Mn, which are more enriched in limestones stabilized under more reducing conditions. The Fe and Mn contents are higher than those of marine calcite (Veizer et al. 1980), suggesting a meteoric contribution to the diagenetic fluids which is also supported by isotopic evidence. So, the contribution of meteoric water to the precipitating fluids was possibly more pronounced for spar calcites, and their diagenetic environment was also more reducing. These meteoric waters probably were more Sr-enriched than normal ones from the dissolution of relatively Sr-rich phases such as younger primary carbonates.

The Late Devonian limestones display more negative O isotope compositions than those of the underlying Middle Devonian (Figure 3). Their precipitating fluids had a greater contribution of ^{18}O-depleted meteoric water since their burial depth was necessarily shallower. Therefore, assuming that Palaeozoic meteoric waters were ^{18}O-depleted by about –7‰ relative to seawater, as is the case for present-day meteoric waters and seawater from the same latitude (López-Vera & Araguas 1986), the isotopic equilibrium temperature between Late Devonian micrites (heaviest value of –12.2‰) and such meteoric waters would have been about 25°C, which would correspond to near-surface depths. In contrast, if pore waters had been of marine origin, the precipitation temperature for these calcites would have been about 65°C, corresponding to a burial depth of 1.3 km. This is not supported by stratigraphic evidence: the thickness of the sedimentary pile overlying the Late Devonian is ca. 900 m only (Ríos et al. 1989). Therefore, it appears more reasonable to consider a meteoric contribution to the diagenetic fluids. Petrographic and geochemical evidence also supports this. Obviously, if Palaeozoic meteoric waters were less ^{18}O-depleted than supposed, the burial depths would have been smaller. Anyway, it appears reasonable to consider that diagenetic stabilization took place in a more or less shallow phreatic environment.

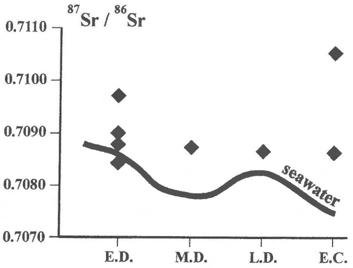

Figure 6. $^{87}Sr/^{86}Sr$ values for the Valle de Tena sequence. $^{87}Sr/^{86}Sr$ seawater curve for Devonian and Carboniferous (Burke et al. 1982) is shown for reference. Abbreviations as in Figure 3.

The more radiogenic character of the analysed micrite relative to coeval marine calcite (Figure 6) corroborates the contribution of meteoric waters. In contrast, $\delta^{13}C$ values seem to reflect a primary signature since, as already said, C isotopes are rock-buffered in diagenetic calcites (Banner & Hanson 1990). The registered oscillation in $^{13}C/^{12}C$ ratios through the Late Devonian sequence is probably related to variations in the organic carbon/bicarbonate carbon balance that result from short-term $\delta^{13}C$ changes in seawater. These changes are probably related to sea-level oscillations and their control on the rate of organic-matter oxidation in the ocean (Magaritz & Stemmerik 1989, Compton et al. 1990).

Early Carboniferous carbonates

Micrites and spar calcites consist of low-Mg calcite with an average 98 mole% $CaCO_3$. The micrites display Sr contents which vary from 0.05 to 0.32 wt%, increasing upward in the sequence, whereas Fe and Mn concentrations vary inversely. Spar calcite within bioclasts shows low Sr, Fe and Mn contents and fracture-filling spar calcite is relatively Fe and Sr-enriched, with mean contents of 0.1 and 0.38 wt%, respectively. The micritic matrix shows negative $\delta^{18}O$ values, ranging from –14.0 to –11.3‰, and positive $\delta^{13}C$ values, from +2.3 to +4.9‰, and its $^{87}Sr/^{86}Sr$ ratios vary between 0.7085 and 0.7105.

The upward increasing trend of Sr concentrations in the Early Carboniferous micrites suggests either a change in the primary carbonate mineralogy from high-Mg calcite to aragonite, or a change in the water/rock ratio of the diagenetic system affecting the originally aragonitic precursor. The upward decreasing trend in Fe and Mn contents reflects stabilization under progressively shallower conditions, at increasing Eh conditions. The more reducing diagenetic environment and higher Fe availability at the bottom of the Early Carboniferous sequence is also supported by the presence of pyrite. Spar calcite filling fractures displays a high Sr content (0.38 wt%) that suggests its precipitation from saline Sr-rich fluids derived from dissolution of such phases as celestite or aragonite. In addition, a precipitation in a near-surface environment with high Eh conditions can be deduced from its Fe and Mn contents.

The $\delta^{18}O$ values of the analysed micrites (mean = –13.0‰) are much more negative than those of Carboniferous marine calcites (–2 to –1‰; Popp et al. 1986, Veizer et al. 1986). This ^{18}O depletion can be the result of equilibrium precipitation with seawater at temperatures of 90 to 95°C (Figure 4(d)). This would correspond to burial depths of about 2.1 km. The maximum palaeothickness of sediments overlying the Early Carboniferous carbonates in the Valle de Tena, before the Hercynian orogeny, is about 900 m of a conformable Namurian marine sandy series (Bichot 1986). Therefore, the maximum burial temperature for the Early Carboniferous carbonates would have been about 55°C, and the corresponding $\delta^{18}O$ value of marine carbonate would be –7.4‰. The additional ^{18}O-depletion down to –13.0‰ must be attributable to the contribution of ^{18}O-depleted meteoric waters to the precipitating fluids. The $\delta^{18}O$ values of these diagenetic fluids, as calculated from the maximum burial depth temperature, are –5.0‰ $_{\mathrm{SMOW}}$, which corresponds to a mixture of 35% seawater ($\delta^{18}O \approx 0.0$ $_{\mathrm{SMOW}}$) and 65% meteoric water ($\delta^{18}O \approx -8.0$‰ $_{\mathrm{SMOW}}$, see above). Changes in the relative proportions of the combined waters and/or in the stabilization depths can be responsible for the variations registered in the $\delta^{18}O$ of micrites through the Early Carboniferous sequence. In addition to petrographic and geochemical evidence, the contribution of meteoric waters to the diagenetic fluids from which calcites were stabilized, is also supported by their Sr isotope compositions, which are clearly more radiogenic than coeval seawater (0.7075–0.7082; Burke et al. 1982, Veizer 1992; Figure 6). Meteoric waters probably gained their radiogenic Sr from reactions with Rb-bearing clastics. Calcites are more radiogenic downward in the Early Carboniferous sequence (from 0.7085 to 0.7105). This, along with higher Fe and Mn contents and low Sr contents, reflects a greater contribution of meteoric water.

The $\delta^{13}C$ values of micrite exhibit an upward trend to more positive values, from +2.3 to +4.9‰. Most of these values are within the range reported for Carboniferous marine calcites (2.0 ± 2.0‰; Popp et al. 1986, Veizer et al. 1986) and seem to reflect the original marine signature. This trend can be attributed to short-term variations related to sea-level oscillations and rates of organic-matter oxidation (Compton et al. 1990, Magaritz & Holser 1990). On the other hand, their more positive $\delta^{13}C$ values relative to those of the studied Devonian calcites are consistent with the well-established long-term secular $\delta^{13}C$ seawater variation, which resulted from higher global sedimentation and organic productivity rates that account for the storage and preservation of ocean-deposited organic matter (Veizer et al. 1980, Derry et al. 1992).

Quantitative models

The isotopic trends of the studied micrites were simulated by considering a single water–rock interaction model.

Our calculations were made assuming a fluid with the following composition: $\delta^{18}O = -8$‰ $_{\mathrm{SMOW}}$, $\delta^{13}C = -8$‰$_{\mathrm{PDB}}$ and $^{87}Sr/^{86}Sr = 0.715$. A $\delta^{18}O$ value of –8‰$_{\mathrm{SMOW}}$ is in agreement with the above mentioned evolution of O isotopic compositions of Palaeozoic meteoric waters (López-Vera & Araguas 1986), and a $\delta^{13}C$ value of –8‰ is well within the range of values found by Sucheki & Land (1983) for diagenetic waters. Our calculations were carried out using highly radiogenic Sr ($^{87}Sr/^{86}Sr = 0.715$) to account for the highly ^{87}Sr-enriched signature of some of the studied carbonate samples. This is in line with both the presence of Rb-bearing rocks in the study area (Table 1 of Subías et al. 1998) and the $^{87}Sr/^{86}Sr$ ratios found in several localities world-wide (Banner et al. 1988 and reference therein).

The fluid temperature of 60°C was selected based on the assumption that fluid–rock interaction takes place at a maximum depth of 1.2 km under a 3 °C per 100 m gradient and that the fluid is close to thermal equilibrium with the host rocks. Since, as stated by Banner & Hanson (1990), it is not necessary to know the precise distribution coefficient, a conservative distribution coefficient estimate for Sr of 0.05 was used in our calculations. For O isotopes, we used the relationship: $\Delta_{\mathrm{calcite-H_2O}} = 2.78 \times 10^6/T^2 - 2.89$ (Friedman &

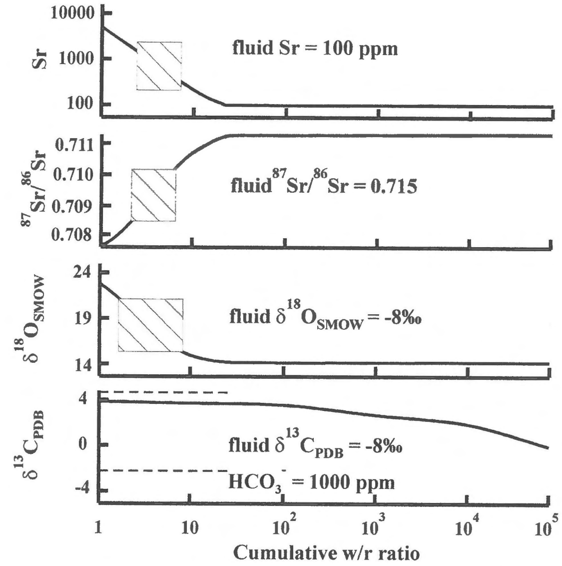

Figure 7. Variations in Sr content and in isotopic composition of Sr, O and C during open-system diagenetic alteration of a limestone as a function of cumulative water/rock (w/r) ratio. Equations and procedures of the model are detailed in Banner & Hanson (1990). Striped areas represent compositional range of the studied carbonate rocks from the Valle de Tena.

O'Neil 1977). For C isotopes, we used: $\Delta_{\text{calcite}-CO_2} = -0.388 \times 10^9/T^3 + 3.198 \times 10^6/T^2 - 8.814 \times 10^3/T - 32.738$, calculated from the equilibrium fractionation factors given in Ohmoto & Goldhaber (1997).

The above parameters allow us to reproduce the enrichment in ^{87}Sr and the impoverishment in ^{18}O compared to the initial rock composition, with $\delta^{13}C$ values being in the range of those corresponding to seawater of the Devonian and Carboniferous epochs (Figures 3, 5). The results of our model that simulate isotopic exchange during water/rock interaction, illustrate important differences in the relative ratios at which different systems are altered during carbonate diagenesis (Figure 7). Regarding the O and Sr isotopes, a low water/rock interaction ratio could account for the observed compositional range. In contrast, the quantitative modelling of the change of $\delta^{13}C$ values supports that the micrites inherited their C-isotopic signatures from marine calcites and that the recrystallization did not affect these values. In fact, these values could only be equilibrated with C in the fluid at an unreasonable higher water/rock ratio during diagenetic recrystallization (Figure 7).

The results of the quantitative modelling confirm the interpretations made in the previous sections on the basis of stable isotope geochemistry, and show that the $\delta^{18}O$ signal agrees with the Sr-isotope record. Consequently, it can be assumed that the host-rock composition evolves during the fluid–rock interaction and becomes enriched in ^{87}Sr and depleted in ^{18}O and Sr at water/rock ratios < 10. For a closed system, higher water/rock ratios are required to attain the same isotopic compositions relative to open-system calculations.

Concluding remarks

By combining geological, mineralogical, petrographic and geochemical information, the following conclusions can be made.

- Stratigraphic evidence indicates several uplift episodes in the Valle de Tena area during Devonian and Early Carboniferous times. Therefore, meteoric waters are likely to have been flushed into the Devonian and Carboniferous sediments, so that these sediments would remain, at least partially, in a meteoric-water environment throughout their burial history.
- The main carbonate phases are low-Mg calcite. Textural calcite types are micrite, spar cement, neomorphic patches and equant spar filling veinlets. In addition, nonstoichiometric dolomite and ankerite occurring as cements illustrate later diagenetic events in the Middle Devonian sequence. A final compaction took place after stabilization of the different carbonate phases since stylolites crosscut even the veinlets.
- Strontium concentrations clearly indicate that the Early Devonian and Early Carboniferous micritic calcites were precipitated initially as aragonite, whereas the precursor of the Middle and Late Devonian micrites was high-Mg marine calcite. The aragonite/calcite ratio may be influenced by several factors such as salinity (Morse & MacKenzie 1990). The observed variations in Sr contents might suggest that the Early Devonian and Early Carboniferous carbonates precipitated from warmer seawaters than the Middle and Late Devonian carbonates.
- All micritic calcites were diagenetically stabilized to low-Mg calcites through interaction with meteoric waters. This is consistent with the textural analyses. The Eh conditions under which each of the carbonates precipitated can be inferred from geochemical data: all the studied carbonates, except the Middle Devonian limestones, precipit-

ated in a reducing environment that favoured the incorporation of Fe and Mn into the carbonate lattices. The Sr signatures indicate that ankerites and dolomites precipitated from later meteoric saline waters than the investigated calcite types. The trace-element geochemistry strongly supports the precipitation of the late calcite generations under reducing conditions from waters that were more saline for late calcite generations than for micrite.

- The geological, petrographic and chemical data suggest that the micrites were stabilized by interaction with meteoric waters. This is in agreement with $\delta^{18}O$ values which are more negative than those corresponding to Devonian and Carboniferous marine calcites. Nevertheless, the $\delta^{18}O$ values of the Middle Devonian micrites suggest a less important interaction with meteoric waters than the rest of the studied sequence. This diagenetic alteration took probably place in phreatic diagenetic environments, at variable depths ranging from 1.3 km for the Middle Devonian to 0.6 km for the Late Devonian. The Middle Devonian dolomites and ankerites precipitated from more ^{18}O-depleted fluids than the calcites, suggesting that they were formed later from diagenetic solutions with a higher contribution of meteoric waters.
- The $\delta^{13}C$ values of Palaeozoic micrites in general mainly reflect primary marine values, and the differences between Devonian and Carboniferous calcites are, therefore, consistent with the well-established long-term secular $\delta^{13}C$ variation of seawater. In addition, the $\delta^{13}C$ shifts registered within each succession can be attributable to variations in the organic carbon/bicarbonate carbon balance resulting from short-term $\delta^{13}C$ changes in seawater. These changes are probably related to sea-level oscillations controlling the rate of organic-matter oxidation in the ocean.
- The Sr isotopic compositions of the Valle de Tena carbonates are more radiogenic than those of Devonian and Carboniferous marine counterparts reported in the literature, suggesting a meteoric origin for their diagenetic fluids, influenced by the interaction with Rb-rich silicate phases.
- The regional marked ^{87}Sr enrichment and the decrease in $\delta^{18}O$ and Sr values in the studied carbonate rocks can be reproduced satisfactorily by a low water/rock interaction ratio ($w/r < 10$) with a fluid whose composition is compatible with that of meteoric waters.

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