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Oxygen, carbon and strontium isotope records of Ediacaran carbonates in Central Iberia (Spain)

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Abstract

Carbon, oxygen and strontium isotope ratios were determined in the uppermost Neoproterozoic carbonate rocks at Pastores (SW Salamanca, Central Iberia). The low $\delta^{18}O$ V-SMOW values (15–19‰) indicate an alteration of the whole stratigraphic series. However, the alteration process does not seem to have affected most of the $\delta^{13}C$ and $^{87}Sr/^{86}Sr$ data. These data reveal that only one particular level of the carbonate section shows simultaneous relative increases in Mn/Sr and $^{87}Sr/^{86}Sr$ ratios, decreases in the $\delta^{18}O$ and $\delta^{13}C$ values, and covariations between $^{87}Sr/^{86}Sr$ and the other parameters. Despite this, most of the carbonate section lacks these covariations and its $\delta^{13}C$ (−4.6 to −0.5‰) and $^{87}Sr/^{86}Sr$ (0.70845–0.70853) ratios probably reflect the seawater isotopic features at the time of sedimentation. The data for C and Sr isotopes at the Pastores carbonate section and the presence of *Cloudina* in platform carbonates together with an overlying major sub-Cambrian unconformity following a relative sea level fall are features comparable to those frequently shown by Proterozoic–Cambrian boundary series across the world. Thus, our results consistently support the notion that the carbonates at Pastores are equivalent to other carbonates deposited close to the Ediacaran/Cambrian boundary.

Keywords: Ediacaran; Spain; Carbonate; C isotope; Sr isotope; Correlation

1. Introduction

The late Neoproterozoic–Early Cambrian was a period of global extension, with the formation of rifts, ocean basins and passive margins. Such major geotectonic events affect ocean circulation patterns, the sites of upwelling and nutrient supply, and the rates of organic matter burial and recycling. All these factors are known to affect the isotopic composition of seawater (Tucker, 1989) and chemostratigraphic data must be used to establish high resolution stratigraphy (Knoll et al., 1986; Tucker, 1986a; Brasier et al., 1990; Kirschvink et al., 1991; Magaritz et al., 1991; Smith et al., 1994; Derry et al., 1994). Correlation studies are based on the acceptance that variations of isotopic composition in carbonates reflect those of seawater through time. Detailed studies of $\delta^{13}C$ data in whole-rocks versus micritic cements have shown that both are comparable in a number of Upper Proterozoic sequences (Fairchild and Spiro, 1987; Kaufman et al., 1991; Derry et al., 1992). These results indicate that diagenetic fluids did not significantly alter whole-rock carbon isotope ratios. However, correlations based only on carbon isotopes can be problematic and this has been demonstrated for Neoproterozoic sequences (see Kennedy et al., 1998; Misi and Veizer, 1998). More efficient has been the combined use of carbon and strontium isotopes (Derry et al., 1992;

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Kaufman et al., 1993, 1996, 1997; Burns et al., 1994; Brasier et al., 1996; Kennedy et al., 1998; Veizer et al., 1999; Jacobsen and Kaufman, 1999; Walter et al., 2000; Pyle et al., 2004), which has led to the proposal of $\delta^{13}C$ and $^{87}Sr/^{86}Sr$ secular curves for seawater (see the review by Melezhik et al., 2001b).

In Central Iberia outcrops of terminal Proterozoic carbonates are not abundant, are not very thick, and are frequently affected by regional metamorphism and granite intrusions. In this study, a carbonate section was selected for the study of oxygen, carbon and strontium isotopes in a zone where the sedimentology of the section and sequence stratigraphy of the Upper Neoproterozoic and Lower Cambrian siliciclastic succession have been defined previously (Valladares, 1995; Valladares et al., 2000). The oxygen, carbon and strontium isotope results, together with major and trace element data, suggest some alteration of the carbonate rocks. However, most of carbon and strontium isotope data are consistent with those found for the carbonates from other terminal Proterozoic series across the world. The section studied here is the first terminal Proterozoic carbonate series in Europe in which isotopic studies have been reported**.** In this work carbon- and strontium isotope chemostratigraphy, sequence stratigraphy and the scarce biostratigraphy of the carbonates in Central Iberia allow these strata to be correlated with other, thicker Ediacaran successions worldwide, whose chemostratigraphy and biostratigraphic and dating constraints are well established.

2. Geological setting

Over the past few years detailed stratigraphic studies of the Precambrian–Cambrian succession in Central Iberia (Fig. 1) have been published (Valladares et al., 2000, 2002) and hence only a summary of the most relevant aspects is given below. According to the above authors, the Precambrian–Cambrian succession consists of 12 lithostratigraphic units (I–XII) organized in two depositional sequences separated by a type-1 unconformity (Fig. 2A). The lower depositional sequence (units I–IV) is of late Vendian age, based on the occurrence of trace fossils and acritarchs in the units I–III and the occurrence of *Cloudina* in the unit IV. Based on the occurrence of ichnofossils, the upper depositional sequence is probably of Early Cambrian age (units V–XII).

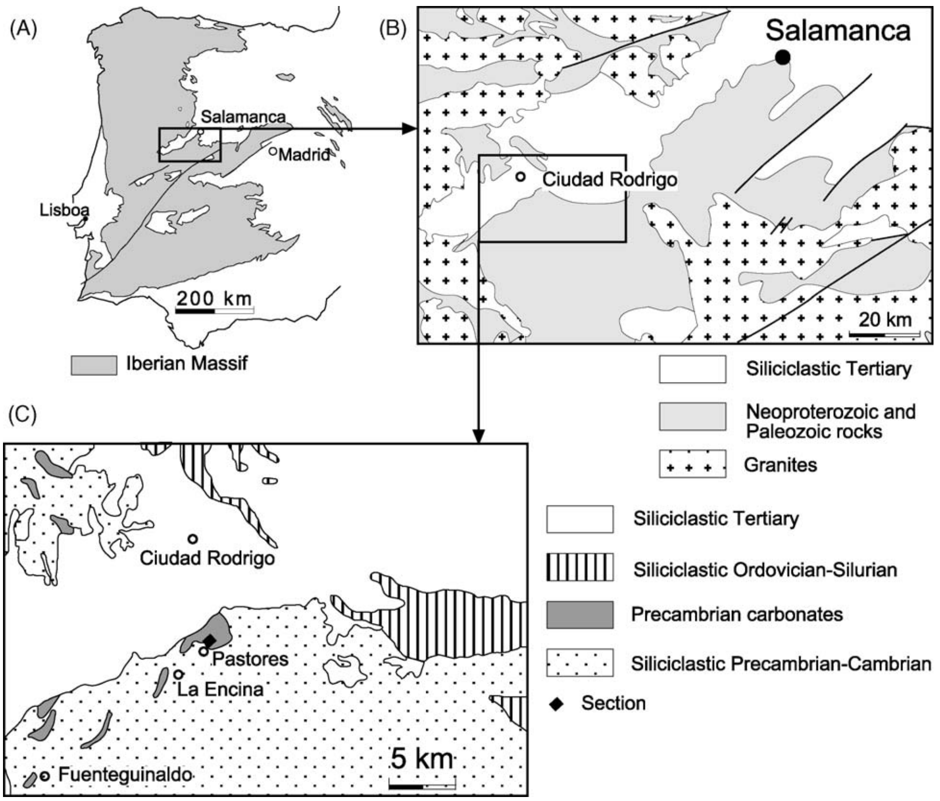

Fig. 1. (A) Iberian Massif. (Insets B and C) General and local geological maps of the region studied.

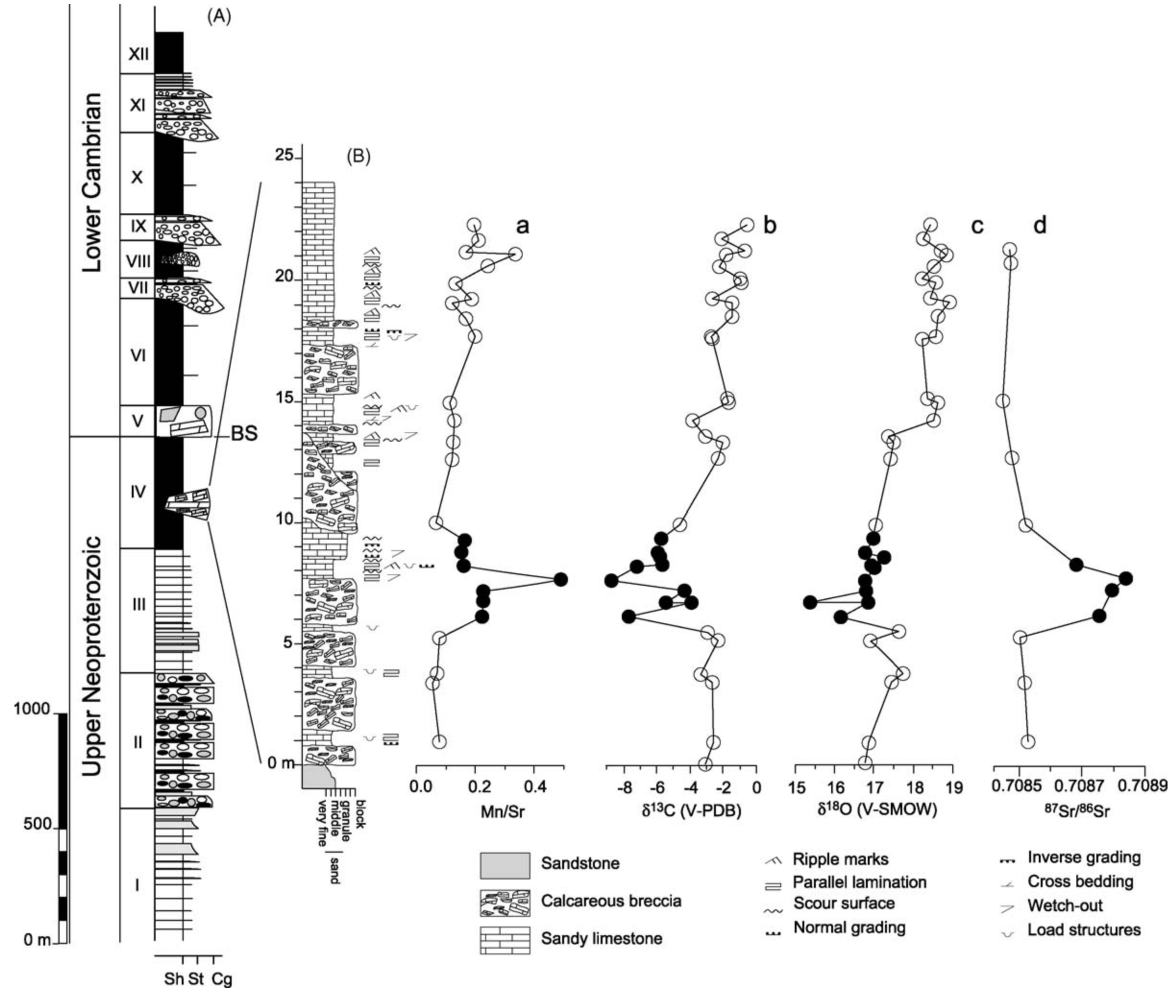

Fig. 2. Stratigraphic variation in Mn/Sr and isotope ratios in carbonates from the Pastores section. (A) General stratigraphic series in the region studied (after Valladares et al., 2000, simplified). BS: boundary sequence (see text). Sh, St and Cg: shale, sandstone and conglomerate, respectively. (B) Pastores section: (filled circles) altered samples; (open circles) unaltered or only slightly altered samples; see text.

Units I–IV comprise up to 2300 m of conglomerates, sandstones and sandstone–shale alternations (units I–III), together with mainly black shales (unit IV) deposited by debris flows, high and low concentration turbidity currents, submarine slides and settling in-slope and base-of-slope environments. These units probably correspond to lowstand systems tracts (units I–III) and transgressive and highstand systems tracts (unit IV).

Unit V is a calcareous megabreccia, with blocks derived from the lower units (IV and III), some of which show signatures of subaerial exposure before emplacement in the megabreccia. The boundary between units IV and V is strongly erosive and is interpreted as a type-1 sequence boundary (see Fig. 2A) because the data for unit V suggest that the platform emerged following a relative fall in sea level, which probably dropped below the platform slope break.

Units V–XII comprise up to 2800 m of megabreccia with predominantly limestone clasts at their base, black shales and shale-sandstone alternations, with local intercalations of sandstones and conglomerates, that were mainly deposited by slides, debris flows, turbidite currents and settling. This upper depositional sequence ends at the top with sandstones and limestones deposited in shallow environments, i.e., platform and tidal flat.

There are no radiometric dates available for the late Neoproterozoic succession in Central Iberia. Simple trace fossils such as *Nimbia occlusa*, *Gordia marina*, *Neonereites* aff. *uniserialis* and *Torronwangea rosei* occur in the three units underlying unit IV, which includes the Pastores carbonates. The skeletal fossil

Cloudina is abundant in situ in platform dolomites within unit IV and in limestone boulders of unit V (Vidal et al., 1994). The first appearance datum of the *Monomorphichnus lineatus*-*Phycodes pedum* assemblage, which appears to delineate the Precambrian–Cambrian boundary in Iberia (Gámez-Vintaned and Liñán, 1996) and small specimens of *Psammichnites* ichnosp are observed from the base of the stratigraphic unit immediately above unit V, while anabaritids, halkieriids, sponges, small shelly fossils (aff. *Aldanella*), hyoliths and others appear higher up in the succession (Palacios et al., 1999). According to this paleontological record the age of units I–IV is late Vendian (Vidal et al., 1994; Gámez-Vintaned and Liñán, 1996), while unit V and successive units have been dated as Early Cambrian (Palacios et al., 1999).

The chemical and isotopic (Sm–Nd) results on siliciclastic rocks separate the Upper Neoproterozoic from the Lower Cambrian sediments, reveal their recycled nature, and suggest that the sedimentary succession reflects the inverted stratigraphy of its source (Ugidos et al., 1997a,b, 2003b). Element redistribution in the siliciclastic material of the lowermost Cambrian units (Ugidos et al., 2003a) suggests reworking and redeposition of the uppermost Neoproterozoic sediments and is consistent with the sea level fall referred to above.

3. The Pastores section

In the vicinity of Ciudad Rodrigo (Fig. 1B and C), within the upper half of unit IV, consisting of up to 500 m of black shales with some phosphate nodules, there is an intercalation of mixed rocks (siliciclastic-carbonate) that defines a lenticular geometry, up to 3 km long and 260 m thick (Valladares, 1995). The carbonate section studied in the present work outcrops close to the village of Pastores (Fig. 1C). Although this section is only 24 m thick, it was chosen because it has not been affected by contact metamorphism, as is the case for certain other carbonate outcrops in the area (e.g., in Fuenteguinaldo; Fig. 1). This section consists of alternations of limestone breccias and stratified sandstone–limestone couplets (Fig. 2B) several metres thick. The breccias are clast-supported, with disorganized clasts that sometimes protrude out of the beds and form both channelled and tabular beds up to 3.5 m thick. The stratified sandstone–limestone couplets are up to 20 cm thick with parallel and ripple lamination, a low angle planar cross-lamination or pebbles forming inversely graded beds. Throughout the entire unit IV, slumps, slide-scars, fluid-escape and flame structures and pseudonodules are common. Sedimentation of the black shales resulted from settling on a slope with high organic productivity and low oxygen concentration seawater. The deposition of the alternations of limestone breccias and sandstone–limestone couplets resulted from debris flows and high concentration turbidity currents derived from the adjacent platform margin and/or from the slope above a mixed slope apron environment (Valladares, 1995).

The lower and upper boundaries of the four lower breccia levels (Fig. 2B) are gradual transitions between the corresponding sandstone–limestone couplets and breccia (Valladares and Rodríguez-Alonso, 1988; Valladares, 1995). Following their deposition, the calcareous beds were partially lithified while the siliciclastic beds of the couplets remained unconsolidated. Thus, brecciation occurred later through load processes and fluidization. The cemented calcareous beds behaved in a brittle manner, creating the breccia clasts, and the unconsolidated siliciclastic beds reacted plastically, producing load and flame structures and thus forming the matrix of these breccias (Valladares and Rodríguez-Alonso, 1988). The rest of the breccias above 9.7 m (Fig. 2B) have an erosive lower surface and an upper irregular, or more rarely erosive surface. The carbonate rocks have been suggested to represent highstand shedding of this carbonate from the platform (Valladares et al., 2000, 2002).

From a petrographic point of view, the limestones of the Pastores section are very homogeneous and mainly consist of equigranular crystals (<0.2 mm) of iron-rich pseudospar, disseminated organic matter and some siliciclastic minerals. In some samples rare skeletal ghosts are found, although no depositional textures are preserved. Here sampling points have been selected on the basis of petrographic homogeneity, and 35 samples were collected from the whole of the carbonate section. Moreover, four clasts from the breccia above 9.7 m of the Pastores section, one carbonate clast from unit V in La Encina (Fig. 1) and seven samples from a limestone outcrop (unit IV) within a metamorphic thermal aureole at Fuenteguinaldo (Fig. 1) were collected for $\delta^{18}O$ and $\delta^{13}C$ analyses. These latter samples show metamorphic associations such as calcite-dolomite, calcite-epidote and quartz-muscovite-chlorite-biotite. All the other rocks analyzed lack these metamorphic associations and detrital components mostly consist of variable quantities of quartz and clays.

4. Analytical techniques

Thick sections of homogeneous carbonate samples were micro-drilled and aliquots were separated for analytical purposes. Pre-analytical treatment followed the

Table 1
Chemical and isotope composition of acid-soluble components of carbonate rocks of Pastores series

Sample	Height	CaO (%)	Mg (%)	FeO (%)	Mn (ppm)	Sr (ppm)	Mn/Sr	1/Sr ($\times 10^3$)	1/(Sr/Ca)	δ^{13}C (V-PDB)	δ^{18}O (V-SMOW)	^{87}Sr/^{86}Sr
P-1	22.20	44.29	0.71	0.22	201	1108	0.182	0.90	286	−0.5	18.5	
P-2	21.60	44.51	0.61	0.21	217	1108	0.196	0.90	287	−2.1	18.3	
P-3	21.10	37.22	0.68	0.32	155	1015	0.153	0.99	262	−0.7	18.7	0.70847
SM-15A	21.00	50.16	0.62	0.24	302	981	0.308	1.02	365	−1.8	18.9	
P-4	20.50	40.98	0.67	0.38	248	1108	0.224	0.90	264	−2.2	18.5	0.70848
SM-14A	20.00									−1.0	18.2	
P-5	19.80	40.97	0.67	0.36	155	1260	0.123	0.79	232	−0.9	18.6	
P-6	19.20	29.53	1.07	0.47	163	939	0.173	1.07	225	−2.7	18.5	
SM-13A	19.00	33.83	0.54	0.24	132	1218	0.108	0.82	199	−1.5	18.9	
P-7	18.40	53.76	0.96	0.36	209	1336	0.157	0.75	288	−1.5	18.7	
P-8	17.60	35.36	0.59	0.26	147	812	0.181	1.23	311	−2.7	18.6	
SM-12A	17.50									−2.7	18.2	
SM-11A	15.10									−1.7	18.4	
P-9	14.90	29.16	0.73	0.30	116	1122	0.104	0.89	186	−1.7	18.7	0.70845
P-10	14.15	42.49	0.68	0.18	116	1006	0.115	0.99	302	−3.9	18.5	
SM-10A	13.50									−3.1	17.4	
P-11	13.30	41.03	0.72	0.17	101	854	0.118	1.17	343	−2.1	17.5	
P-12	12.60	42.46	0.69	0.16	101	905	0.111	1.11	335	−2.3	17.5	0.70848
P-13	9.95	46.41	0.72	0.23	77	1251	0.062	0.80	265	−4.6	17.1	0.70852
P-14	9.30	45.55	0.68	0.27	155	998	0.155	1.00	326	−5.7	17.0	
P-15	8.75	47.14	0.62	0.25	147	1074	0.137	0.93	314	−6.0	16.8	
SM-5A	8.60									−5.8	17.3	
P-16	8.25	48.03	0.72	0.31	147	1032	0.143	0.97	333	−5.6	17.0	0.70867
SM-4A	8.20									−7.2	17.0	
P-17	7.65	47.51	0.52	0.23	341	693	0.491	1.44	490	−8.7	16.8	0.70882
P-18	7.20	39.82	0.48	0.20	170	820	0.208	1.22	347	−4.3	16.8	0.70878
P-19	6.75	45.37	0.49	0.22	201	939	0.215	1.07	345	−5.5	15.4	
SM-3A	6.70									−4.0	16.9	
P-20	6.15	26.41	1.04	0.25	108	516	0.210	1.94	366	−7.7	16.2	0.70874
SM-2A	5.50									−2.9	17.7	
P-21	5.20	47.34	0.71	0.15	85	1226	0.069	0.82	276	−2.3	16.9	0.70850
P-22	3.75	49.90	0.79	0.19	93	1361	0.068	0.73	262	−3.3	17.8	
P-23	3.40	43.92	0.69	0.16	62	1235	0.050	0.81	254	−2.7	17.5	0.70852
P-24	1.00	46.96	0.76	0.17	70	956	0.073	1.05	351	−2.6	16.9	0.70853
SM-1A	0.10									−3.1	16.8	

Height in metres above the base of the carbonate section.

procedures described by Derry et al. (1992). Major and trace elements were analyzed on the Plasma-II Perkin Elmer ICP-AES of the Salamanca University. Analytical uncertainty was ±10%. Carbon and oxygen isotopes were analyzed at the Stable Isotope Laboratory of the University of Salamanca. Extraction of CO_2 for isotopic analysis followed standard techniques. For calcite, about 0.5–1 mg of powder was reacted with 103% H_3PO_4 at 90 °C, employing an Isocarb device connected on-line to a VG-Isotech Sira-II^{TM} mass spectrometer. Precision was monitored by repeated analysis of internal and international (NBS-19) carbonate standards under identical analytical conditions. During the time of analysis the average precision obtained was ±0.08‰ for $\delta^{13}C$ and ±0.18‰ for $\delta^{18}O$ (1σ; $n = 35$). Isotope results are given relative the V-PDB ($\delta^{13}C$) and V-SMOW ($\delta^{18}O$) scales. Strontium isotope analyses were performed at SUERC (East Kilbride, UK). For Sr isotopes, samples were leached in 1N ammonium acetate prior to digestion in 1M acetic acid. Sr was separated using standard ion exchange techniques. Total procedure blanks are <300 pg. Sr was loaded on single Ta filaments with 1N phosphoric acid. Sr isotope compositions were measured on a VG Sector 54–30 mass spectrometer in dynamic multi-collection mode and corrected for instrumental mass fractionation using an exponential law and $^{87}Sr/^{86}Sr = 0.1194$. NIST SRM987 gave 0.710243 ± 20 (2S.E., $n = 88$).

5. Geochemical data and results

The chemical (Ca, Mg, Sr, Mn, Fe) and carbon and oxygen isotopic data on 35 samples from the Pastores series are shown in Table 1. From the 35 samples, 12 were chosen for strontium isotope analyses. In general terms, the carbonate series studied showed narrow ranges of most element contents and isotope ratios. The data on $\delta^{18}O$ and $\delta^{13}C$ for the samples from the other outcrops are shown in Table 2.

The low $\delta^{18}O$ values (15.4–18.9‰ relative to V-SMOW) found for the whole Pastores section suggest that alteration affected the complete series, indicating substantial post-depositional oxygen isotopic mobility. Tucker (1986b) has shown that some Proterozoic limestones with very low $\delta^{18}O$ values (13–20‰) were originally composed of aragonite, which was replaced at depth during burial diagenesis, the $\delta^{18}O$ spread reflecting mobility during neomorphism (Buick et al., 1995). The possibility of burial diagenesis for the Pastores carbonates is consistent with this, given their depositional environment.

Table 2
Isotope data of the carbonate clasts and metamorphosed limestones

Sample	$\delta^{13}C$ (V-PDB)	$\delta^{18}O$ (V-SMOW)
SM-16A[a]	−3.8	21.8
SM-17A[a]	−2.7	20.9
SM-18A[a]	−3.8	20.4
SM-19A[a]	−4.1	17.4
SM-20A[a]	−6.4	16.1
SM-21A[a]	−2.2	15.4
SM-22A[a]	−3.7	15.6
SM-6A[b]	−2.4	17.4
SM-7A[b]	−3.0	18.0
SM-8A[b]	−3.2	17.2
SM-9A[b]	−2.1	17.2
SS-1A[c]	−2.2	17.8

[a] Metamorphosed limestones from the Fuenteguinaldo outcrop.
[b] Carbonate clasts from the Pastores section.
[c] Carbonate clast from the La Encina outcrop.

The $\delta^{13}C$ values are not very low (most are higher than −4.6‰) and are similar to primary values recorded in other terminal Proterozoic carbonates. This is also the case of the $^{87}Sr/^{86}Sr$ (0.70845–0.70882) ratios (see Jacobsen and Kaufman, 1999; Melezhik et al., 2001a,b). The low Mg/Ca ratios exclude dolomitization processes and the relatively low abundance of Mn (61–341 ppm) and low Mn/Sr ratios (0.050–0.491) suggest that alteration processes other than those involving oxygen would not have affected the Pastores carbonates. The possibility that the carbon and strontium isotope data might be considered as primary or weakly altered is discussed below in light of all the geochemical data and stratigraphic variations in geochemistry.

For isotope data to be applicable for stratigraphic correlation studies it is necessary to check whether they are primary or whether they reflect one or more secondary processes in the carbonates. In principle, evidence for secondary processes (in the present case recrystallization, see above) means that carbonate samples are not good candidates for isotopic correlation studies. However, each particular case must be considered carefully, given that primary isotopic features may be slightly modified or partially preserved even under amphibolite-facies metamorphic conditions (Melezhik et al., 2001a).

Modelling by different authors (Nabeleck, 1987; Banner and Hanson, 1990; Jacobsen and Kaufman, 1999) has demonstrated that the alteration of isotope ratios mainly depends on the compositions of the original sediment and fluid, the water-rock ratio, distribution coefficients, etc (see above authors). From these studies, some generalizations have been made that can be

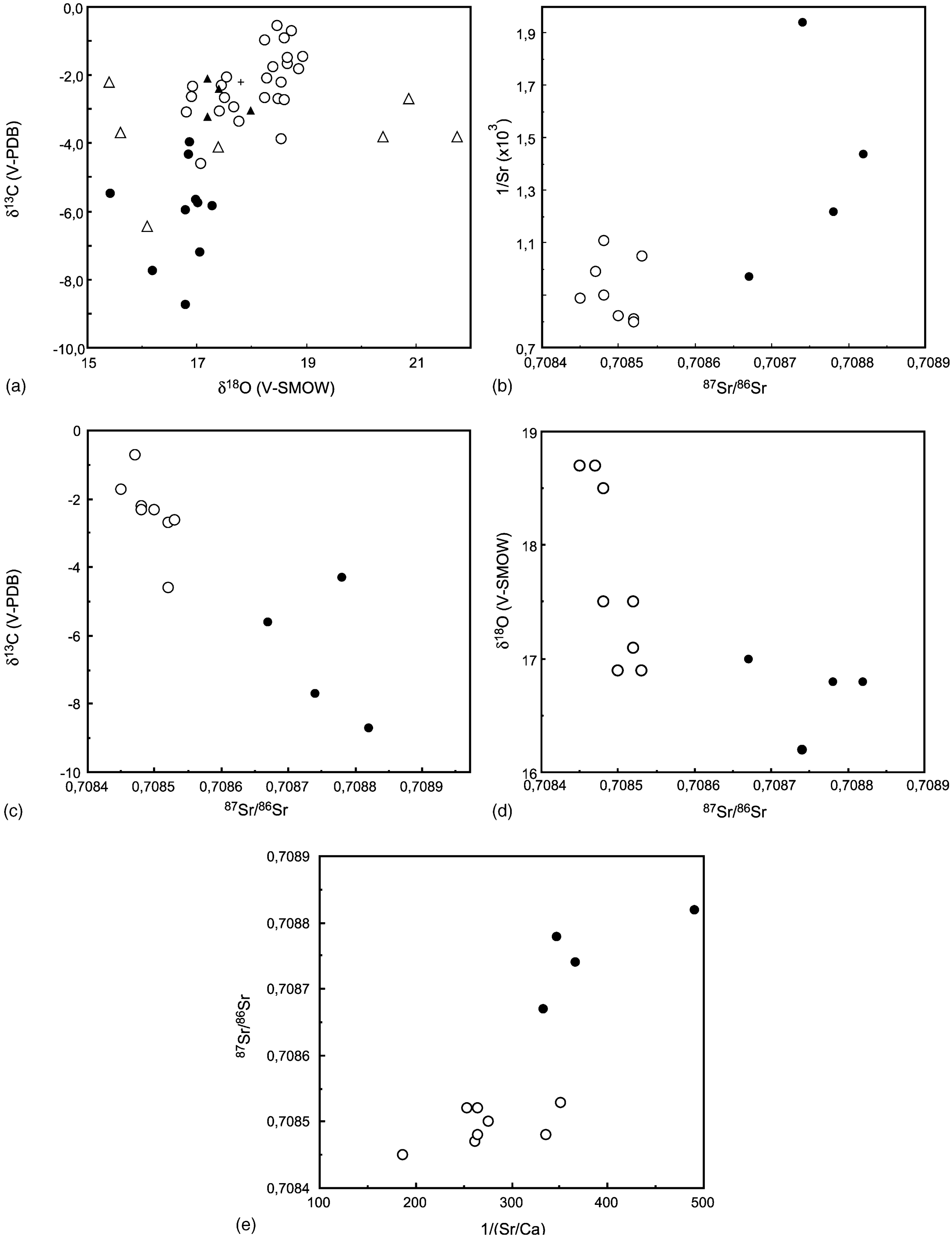

Fig. 3. Isotope ratio diagrams of carbonates of the Pastores section: (filled circles) samples from 6 to 9.7 m; (open circles) all the other samples. In diagram a, (filled triangles) limestone clasts from the Pastores section; (cross) limestone clast from unit V in the La Encina outcrop; (open triangles) metamorphosed limestones from the Fuenteguinaldo outcrop; see text.

applied directly to detect secondary processes and to define to what extent their effects are significant. Thus, it is expected that alteration may result in: (a) a resetting of the isotope systems. This does not necessarily happen simultaneously or to an equivalent extent in all systems. Equilibrium for one system may be reached during alteration while in other systems isotope changes may be absent or unimportant; (b) a decrease in Sr contents and a related increase in the $^{87}Sr/^{86}Sr$ ratio; (c) negative $^{87}Sr/^{86}Sr$–$\delta^{18}O$ and positive $\delta^{18}O$–$\delta^{13}C$ covariations and L-shaped trends are also expected; (d) an increase in Mn abundance and Mn/Sr ratio as a consequence of recrystallization of calcite by fresh water. The values of the Mn/Sr ratio have been successfully used to demonstrate possible alteration processes and, consequently, to inform sample selection. However, there is no consensus as to what Mn/Sr represents a reliable cut-off. Therefore, in some cases relatively high ($Mn/Sr > 1.5$, Bartley et al., 2001) or low values ($Mn/Sr > 0.6$, Derry et al., 1994; $Mn/Sr > 0.2$, Melezhik et al., 2001a) have been used to exclude the corresponding samples for isotope studies. Accordingly, in each case, the chemical results must be considered in the light of other data (Melezhik et al., 2001b). The specific geochemical features of each carbonate succession must be taken into account in the evaluation of possible alteration processes (Derry et al., 1994; Bartley et al., 2001).

In Fig. 2, chemical and isotopic data are plotted versus height in metres above the base of the series. In the stratigraphic interval between 6 and 9.7 m positive excursions of Mn/Sr and $^{87}Sr/^{86}Sr$ ratios (Fig. 2A and D) coincide with negative excursions of $\delta^{13}C$ and $\delta^{18}O$ (Fig. 2B and C). These are the most striking features of the stratigraphic section, suggesting alteration of carbonates. In Fig. 3a, it is apparent that the $\delta^{18}O$ and $\delta^{13}C$ data from the altered interval and from all the other samples define two fields rather than a linear covariation related to a simple alteration event. More plausibly, a process affecting the oxygen system in the whole series would have continued under different conditions between 6 and 9.7 m and would have enhanced the strontium isotope ratio and the low $\delta^{18}O$ and $\delta^{13}C$ values only in this interval. Disparity between isotopic systems is common in Proterozoic carbonates (Kaufman and Knoll, 1995) and can be explained in terms of the notion that the fluids involved in isotopic exchange had low C–O ratios (Marshall, 1992; Wickham and Peters, 1993) or the water-rock ratios were low (Banner and Hanson, 1990; Jacobsen and Kaufman, 1999). In both cases, partial or even total retention of the primary $\delta^{13}C$ composition is favoured. In most cases, recrystallization and dolomitization of carbonate sediments caused no or only slight changes in the $\delta^{13}C$ values, since the carbon was derived from the original carbonate (Tucker, 1989). The present case seems to be a representative example of $\delta^{13}C$ retention in most samples. In Fig. 3a, the plots of limestone clasts from the Pastores section above 9.7 m, a clast from unit V, and most samples of the metamorphosed carbonates show $\delta^{13}C$ values similar, or slightly modified, to those above 9.7 m and below 6 m. However, the $\delta^{18}O$ data show a wide range of values for the carbonates within the thermal aureole.

As noted above, in Fig. 3a two fields for samples from 6 to 9.7 m and all the other samples are defined. The samples from the former group show a clear covariation in the $^{87}Sr/^{86}Sr$–1/Sr and $^{87}Sr/^{86}Sr$–$\delta^{13}C$ (Fig. 3b and c) diagrams, suggestive of alteration, but this is not the case for the other samples. The same is suggested by the alteration trends defined in the $^{87}Sr/^{86}Sr$–$\delta^{18}O$ and $^{87}Sr/^{86}Sr$–1/(Sr/Ca) diagrams (Fig. 3d and e). The extreme isotope values of these trends indicate pristine and altered end members. Other diagrams (not included) point to the absence of covariation between Mg/Ca and the parameters Mn/Sr, $\delta^{18}O$, $\delta^{13}C$, and $^{87}Sr/^{86}Sr$ which consistently suggests that dolomitization did not affect the carbonate series. According to the above generalizations, all these features demonstrate that alteration would have caused relatively important chemical (Sr, Mn) and isotopic (C, Sr) changes only in the 6–9.7 m sub-section of the carbonate series. Relatively high water-rock ratios would have been required for carbonate minerals to equilibrate with fluid $\delta^{13}C$ or $^{87}Sr/^{86}Sr$ values (Banner and Hanson, 1990; Jacobsen and Kaufman, 1999). Thus, the resetting of Sr isotopes, together with lowering of $\delta^{18}O$ and $\delta^{13}C$ values in the 6–9.7 m level, developed under conditions different from those affecting the whole series. This is also suggested by the relative increase in Mn contents and the Mn/Sr ratio in that level. Thus, the $^{87}Sr/^{86}Sr$ (0.70845–0.70853) and $\delta^{13}C$ (>−4.6‰) values shown by the carbonates below 6 m and above 9.7 m of the series studied are probably primary or slightly modified, given that no increases in the Mn/Sr ratio or correlations suggestive of alteration are observed there.

6. Discussion and conclusions

As described above relatively thick carbonate beds became disrupted and carbonate breccias resulted in situ in the Pastores section. Differences in the lithification of the calcareous and siliciclastic beds favoured a brittle and a plastic behaviour, respectively, of these beds, and brecciation resulted from load processes and fluidization, as suggested by load and flame structures in the breccias.

Fluidization probably also favoured an upward migration of diagenetic fluids and a higher water/rock ratio in some levels, and hence a modification of the oxygen, carbon and strontium isotope ratios. At the 9.7 m height of the section an erosive surface is observed and above this surface the breccias did not develop in situ by fluidization; instead the clasts correspond to transported fragments of carbonate beds. Apparently, alteration of the isotopic ratios coincides with evidence for fluidization at the corresponding level. Thus, the lower values of $\delta^{18}O$ shown by the carbonates in the 6–9.7 m level resulted from overprinting of a specific process over a previous general diagenetic event that mainly modified the depositional $\delta^{18}O$ values. Study of the causes of this first alteration is beyond the scope of this work. The problem of primary versus secondary values of $\delta^{18}O$ in ancient oceans is hotly debated but in general terms it is accepted that ^{18}O depletion results from diagenetic processes (e.g. Land and Lynch, 1996). Alternatively, fluids related to igneous events in the late Neoproterozoic could change the primary $\delta^{18}O$ values. Evidence for volcanism has been reported in the region studied (Rodríguez-Alonso et al., 2004) and a crystallization age of 546 ± 3 Ma for the protolith of an orthogneiss about 100 km east of the Pastores section has also been proposed (Zeck et al., 2004). However, it is not known whether other intrusions of similar age affected the sediments in the Pastores area. Thus, any relationship between igneous activity, related fluids and diagenetic alteration of $\delta^{18}O$ in the carbonates studied remains speculative, although possible.

The sequence stratigraphy of Central Iberia has several trends of possible global importance. The Ediacaran System (Knoll et al., 2004) is bounded at the top by the Precambrian–Cambrian boundary, a major unconformity in most sections worldwide. The age of this boundary (ca. 543 Ma) is based on U–Pb zircon dates from Siberia (Bowring et al., 1993), Namibia (Grotzinger et al., 1995) and Oman (Brasier et al., 2000; Amthor et al., 2003). The sequence boundary at the top of unit IV is a type-1 unconformity expressed as an irregular and erosive surface (Valladares et al., 2000). This unconformity is overlain by unit V, a megabreccia with some calcareous blocks with *Cloudina* and other blocks showing evidence of subaerial exposure (paleokarst), prior their emplacement in the megabreccia. Above this megabreccia appear trace fossils and small shelly fossils (see above) of Early Cambrian age. Therefore, the sequence boundary is the sub-Cambrian unconformity and corresponds to a major unconformity worldwide (Narbonne et al., 1994; Christie-Blick et al., 1995; Saylor et al., 1995; Kaufman et al., 1996; Pelechaty et al., 1996; Calver and Lindsay, 1998; Bartley et al., 1998; Jiang et al., 2002; Saylor, 2003; Pyle et al., 2004), suggesting a possible eustatic origin. The duration and magnitude of the sub-Cambrian unconformity vary, between sections, but its age appears to be the same within the precision afforded by biostratigraphy and chemostratigraphic correlations.

Platform dolomites with in situ *Cloudina* in unit IV have been correlated with deep-water carbonates of the Pastores section (Valladares et al., 2000). Globally, the calcified metazoan *Cloudina* occurs only below the sub-Cambrian unconformity, while small shelly fossils and complex trace fossils first appear above the unconformity. *Cloudina* is present in Oman (Ara Group, Grant, 1990), Namibia (Nama Group, Germs, 1983) and Canada (Miette Group, Hofmann and Mountjoy, 2001). The range of *Cloudina* in Namibia has been established by U–Pb zircon ages from 550 to 543 Ma (Grotzinger et al., 1995) and also confirmed by U–Pb zircon ages of 544.5 ± 3 Ma (Brasier et al., 2000) and 542.6 ± 0.3 Ma (Amthor et al., 2003) in Oman. The extinction of *Cloudina* occurred globally at the Precambrian–Cambrian boundary (Amthor et al., 2003).

The geochemical results from the Upper Neoproterozoic siliciclastic rocks in extensive areas (tens of square km) of Central and West Iberia demonstrate the very homogeneous and recycled nature of these materials, mainly derived from Pan African orogens in N. Gondwana (Ugidos et al., 1997a,b, 2003b; Valladares et al., 2000, 2002). Thus, the relatively high $^{87}Sr/^{86}Sr$ ratio of the Pastores carbonates consistently reflects this continental input. Unfortunately, the outcropping carbonate series studied here is not thick enough to be compared directly with those from other areas where the isotopic logs are hundreds of metres thick. Thus, some doubts may arise regarding the validity of the isotopic data in this study for use in comparisons with those found in other worldwide sections and for correlation purposes. The low $\delta^{18}O$ values even in carbonates above and below the altered level indicate that the complete series has been modified diagenetically. However, this alteration does not necessarily imply that other isotopic systems have also been significantly altered, as discussed above. The diagrams in Fig. 3 strongly support the idea that, except in the 6–9.7 m level, the carbonates show chemical and isotopic features suggestive of no, or only a weak alteration of the $\delta^{13}C$ and $^{87}Sr/^{86}Sr$ values.

The carbon- and strontium-isotopic ratios in the Pastores carbonates above and below the altered 6–9.7 m level show $^{87}Sr/^{86}Sr$ values of 0.70845–0.70853 and negative $\delta^{13}C$ values between −4.6 and −0.5‰. Just below the Proterozoic–Cambrian boundary carbon-isotopic data from Ediacaran carbonates show a sharp

δ^{13}C decline of more than 7‰, which marks the stratigraphic breakpoint between faunas in which Ediacaran organisms were the main components and those dominated by Cambrian-style animals in Mongolia (Brasier et al., 1996), Iran (Kimura et al., 1997), Oman (Burns and Matter, 1993), Canada (Kaufman et al., 1997), the Siberian Platform (Brasier et al., 1996; Kaufman et al., 1996; Bartley et al., 1998), Morocco (Tucker, 1986a), southwest China (Lambert et al., 1987; Shen and Schidlowski, 2000) and the southwestern USA (Corsetti and Hagadorn, 2000). An ash bed in a carbonate unit from the Ara Group of Oman that records this abrupt negative excursion of δ^{13}C, has been dated by U–Pb zircon at 542 ± 0.3 Ma (Amthor et al., 2003). The extinction of *Cloudina* occurred globally at the Precambrian–Cambrian boundary, coinciding with a global biogeochemical event marked by the negative carbon isotope excursion (Amthor et al., 2003; Pyle et al., 2004). This excursion is not present, due to erosion or non-deposition in Namibia (Kaufman et al., 1991; Saylor et al., 1998), Australia (Walter et al., 2000) and possibly India (Jiang et al., 2002), coinciding with the sub-Cambrian sequence boundary. Sr isotopic data from Ediacaran carbonates show a marked rise in the ^{87}Sr/^{86}Sr ratio at 590 Ma from 0.7066 up to 0.7085 at the Precambrian–Cambrian boundary in samples with *Cloudina* of the Nama Group in Namibia, the Windermere Supergroup of northwest Canada and Mongolia (Kaufman et al., 1993, 1997; Derry et al., 1994; Brasier et al., 1996), while values of 0.7091 have been reported for the Ara Group in Oman (Burns et al., 1994) associated with *Cloudina* and the negative excursion of δ^{13}C at 542 ± 0.3 Ma.

It may be concluded that the integrated stratigraphy of the carbonates in unit IV of Central Iberia can be consistently correlated to worldwide carbonate successions of the terminal Ediacaran by the sub-Cambrian unconformity, the presence of *Cloudina* and similar C and Sr chemostratigraphy. Taking into account the dating results of Namibia and Oman, the age of unit IV would be close to 543 Ma.

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