Upper Cambrian carbonate sequences of the Argentine Precordillera and the Steptoean C-Isotope positive excursion (SPICE)

A.N. Sial [a,*], S. Peralta [b], V.P. Ferreira [a], A.J. Toselli [c], F.G. Aceñolaza [c], M.A. Parada [d], C. Gaucher [e], R.N. Alonso [f], M.M. Pimentel [g]

[a] *NEG-LABISE, Departamento de Geologia, UFPE, C.P. 7852, Recife, PE, 50670-000, Brazil*
[b] *Instituto de Geología, Universidad Nacional de San Juan-CONICET, 5400 Argentina*
[c] *INSUGEO, Miguel Lillo 205, S.M. Tucuman, 4000 Argentina*
[d] *Departamento de Geología, Universidad de Chile, Santiago, Chile*
[e] *Departamento de Paleontologia, Facultad de Ciencias, Iguá, 4225, 11400 Montevideo, Uruguay*
[f] *Departamento de Geología, Universidad Nacional de Salta, Argentina*
[g] *Instituto de Geociências, Universidade de Brasilia, Brasilia, D.F., 70.910-900, Brasil*

Abstract

Carbon and Sr-isotope profiles in Upper Cambrian platformal carbonate Formations in the Precordillera, western Argentina (Zonda, La Flecha and La Silla Formations), were constructed for three representative sections: (a) Quebrada de la Flecha, Eastern Precordillera, (b) Cerro La Silla, Central Precordillera and (c) Quebrada de La Angostura, northern part of the Central Precordillera.

At Quebrada de La Angostura, upper part of the La Flecha Formation, $\delta^{13}C_{carb}$ varies continuously up-section from −2.0 to +5.6‰ (PDB) and records the SPICE anomaly (+5‰) reported for the first time in South America. The peak of this excursion is characterized by intercalated 2 m thick beds of black shale with marl and limestone that record the onset of a sea-level change.

The Steptoean Zonda Formation dolomites at the Quebrada de la Flecha exhibit a total $\delta^{13}C$ range from −2.7 to +0.6‰ with discrete positive anomaly about 200 m from the transition to the overlying Sunwaptan La Flecha Formation. Pronounced C-isotope anomaly (−5.6‰) is observed in the La Flecha Formation at about 300 m below the transition to the La Silla Formation.

At the Cerro La Silla section, the Zonda Formation exhibit $\delta^{13}C$ values of ∼−1‰, increasing slightly at the transition to the La Flecha Formation (−1 to 0‰). The transition of the La Flecha to the La Silla Formations is characterized by alternation of black shales and dolomitic limestone with a discrete positive C-isotope excursion, probably corresponding to the SPICE.

At the Quebrada de La Flecha, $^{87}Sr/^{86}Sr$ for the Zonda Formation varies from 0.70924 to 0.70955 and for the La Flecha Formation from 0.70908 to 0.70942. At Cerro La Silla this ratio varies from 0.70914 to 0.70923 for the La Flecha Formation, and from 0.70898 to 0.70980 for the La Silla Formation. At the Quebrada de La Angostura, ratios for the La Flecha carbonates range from 0.70918 to 0.70993. The overall variation of $^{87}Sr/^{86}Sr$ is consistent with globally reported Upper Cambrian seawater values at ca. 500 Ma.

The unambiguous record of SPICE in the La Flecha Formation at the Quebrada de La Angostura supports a Steptoean age for its deposition and allows precise local, regional, and global stratigraphic correlation. The pronounced negative C-isotope excursion recorded in the La Flecha Formation carbonates at the Quebrada de La Flecha is likely equivalent to that registered in Sunwaptan carbonates of North America and Australia, and might be tied to a global event, as a valuable tool in stratigraphic correlation (SNICE, acronym for Sunwaptan negative isotope carbon excursion).

Keywords: Upper Cambrian; C and Sr isotopes; SPICE; SNICE; Argentina

* Corresponding author. Tel.: +55 81 2126 8243; fax: +55 81 2126 8242.
E-mail addresses: sial@ufpe.br (A.N. Sial), speralta@unsj-cuim.edu.ar (S. Peralta), valderez@ufpe.br (V.P. Ferreira), ajtoselli@infovia.com.ar (A.J. Toselli), maparada@cec.uchile.cl (M.A. Parada), gaucher@chasque.apc.org (C. Gaucher), rnalonso@sinectis.com.ar (R.N. Alonso), marcio@unb.br (M.M. Pimentel).

1. Introduction

A large and global positive excursion in $\delta^{13}C$ for Late Cambrian (Steptoean stage) carbonates has been reported from

North America, Kazakstan, South China and Australia and marks the beginning of a worldwide extinction of trilobites (Saltzman et al., 1998, 2000). This Steptoean positive C-isotope excursion (~+5‰), described by the acronym SPICE (Saltzman et al., 1998) represents a major perturbation of the Cambrian carbon cycle at ~500 Ma and, as a peculiarity, a worldwide mass extinction (mainly trilobites among other faunas) coincides with the onset of the positive shift, rather than with the rising limb of the excursion. The peak of faunal diversity (Saltzman et al., 2000) correlates in North America with the peak of SPICE.

C-isotope variation curves for the Cambrian–Ordovician boundary at Black Mountain, Australia (Ripperdan et al., 1992), and at Lawson Cove, Ibex area, Utah (Ripperdan and Miller, 1995), reveal a pronounced negative C-isotope excursion (−4‰) in the uppermost Cambrian (Sunwaptan stage). The Cambrian-Ordovician boundary is characterized by synchronous changes in sea-level, conodont (*Paltodus deltifer* in Precordillera) biozones, and $\delta^{13}C$ of marine inorganic carbon (Ripperdan et al., 1992).

If the Sunwaptan negative C-isotope excursion (called SNICE in the present study) can be demonstrated as a global event, SPICE and SNICE in combination can be valuable tools for high-resolution correlation and can be used to locate primary subdivisions of the Cambrian system in unfossiliferous carbonate sequences globally (Fig. 1). Although SPICE figures in the composite carbon isotopic record for the Cambrian system in Brasier and Sukhov (1998), no reference is made to SNICE in their study.

The Sr-isotope composition of the seawater in the Cambrian Period is characterized by a continuous increase of $^{87}Sr/^{86}Sr$ that is interrupted several times by sharp rises representing important changes in Earth history (Montañez et al., 2000). The Cambrian rise in Sr values is interpreted to be a consequence of the late stages of the Pan-African/Brasiliano orogenies according to Montañez et al. (2000). Typical $^{87}Sr/^{86}Sr$ values for Late Cambrian seawater, around 500 Ma, are in the 0.7090–0.7095 interval (Burke et al., 1982). The shape of the Sr secular variation curve makes it possible, in many cases, to estimate the depositional age of Cambrian carbonates.

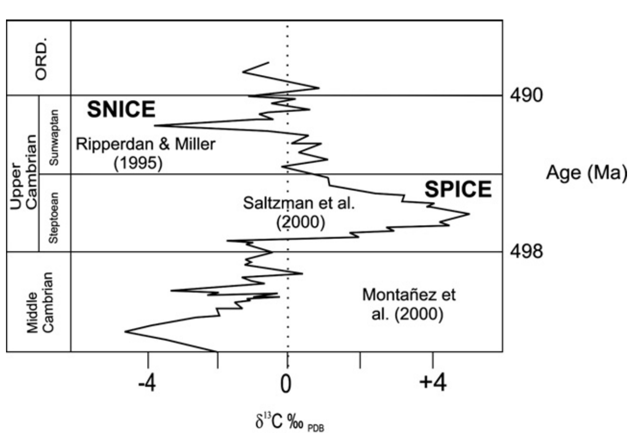

Fig. 1. Compiled $\delta^{13}C$ secular variation curve for the Upper Cambrian. For the Steptoean, the data are from Saltzman et al. (2000), and for the Sunwaptan, from Ripperdan et al. (1992), Ripperdan and Miller (1995). The data for Middle Cambrian are from Montañez et al. (2000).

A detailed carbon isotope study on Late Cambrian to Early Ordovician carbonates of the Precordillera was carried out by Buggisch et al. (2003). Although SPICE has been considered a global oceanographic event, no record of it has been found in South America. We have studied the C-, O- and Sr-isotope stratigraphy of representative Upper Cambrian sections of the Eastern and Central Precordillera at San Juan Province, Western Argentina (Fig. 2) in their type localities (Quebrada de La Flecha, Cerro La Silla and Quebrada de Zonda). Additionally, we studied the Quebrada de La Angostura section in the northern part of the Central Precordillera, in the south of the La Rioja Province. The present study aims to: (i) search for SPICE and SNICE C-isotope excursions to reinforce/demonstrate their global occurrence, (ii) use these C-isotope excursions for high resolution stratigraphy, and (iii) examine paleo-environmental conditions for Upper Cambrian-Lowermost Ordovician carbonate deposition.

2. Geologic setting

The Precordillera of La Rioja, San Juan and Mendoza Geological Province is part of a more extensive tectonostratigraphic unit called the Cuyania Terrane (Ramos et al., 1986), which is considered allochthonous by several authors (Ramos et al., 1984, 1986; Benedetto, 1993; Astini et al., 1995, 1996; Thomas and Astini, 1996; among others), and as para-autochthonous by others (Baldis et al., 1989; Aceñolaza and Toselli, 1999; Aceñolaza et al., 2002; Finney et al., 2002, 2003). The Precordillera extends from the southern part of the La Rioja Province, through the San Juan Province, up to the Rio Mendoza area (northern Mendoza Province), striking N–S between the Andes Cordillera to the west and Pampean Range to the east. According to Ortiz and Zambrano (1981) and Baldis et al. (1982), three morpho-structural units are recognized in the Precordillera: (a) The Eastern Precordillera, extending only in the San Juan Province, showing thick-skinned deformation with westward vergence; (b) The Central Precordillera, extending from the La Rioja, through San Juan, up to the Mendoza Province, characterized by thin-skinned deformation showing eastward vergence, and (c) the Western Precordillera, characterized by a general eastward vergence.

Cambrian to Lower-Middle Ordovician platformal carbonate successions occur exclusively in the eastern and central Precordillera, and are absent as autochthonous deposits in the western Precordillera, where they appear only as resedimented deposits (Bordonaro, 2003a,b). Mixed and siliciclastic Upper Ordovician deposits are widely distributed in the Precordillera, whereas Silurian to Lower Devonian siliciclastic deposits are important components in the Middle Paleozoic stratigraphic framework of the Eastern and Central Precordillera, but not in the Western Precordillera where their occurrence has not been confirmed. From a tectono-sedimentary point of view, the Cambrian to Devonian successions are part of the Famatinan tectonic cycle (Aceñolaza and Toselli, 1988), which is bounded at the top by the Chanic tectonic phase.

In the Early Paleozoic Precordillera basin (San Juan Province), a continuous sequence of carbonates with regressive

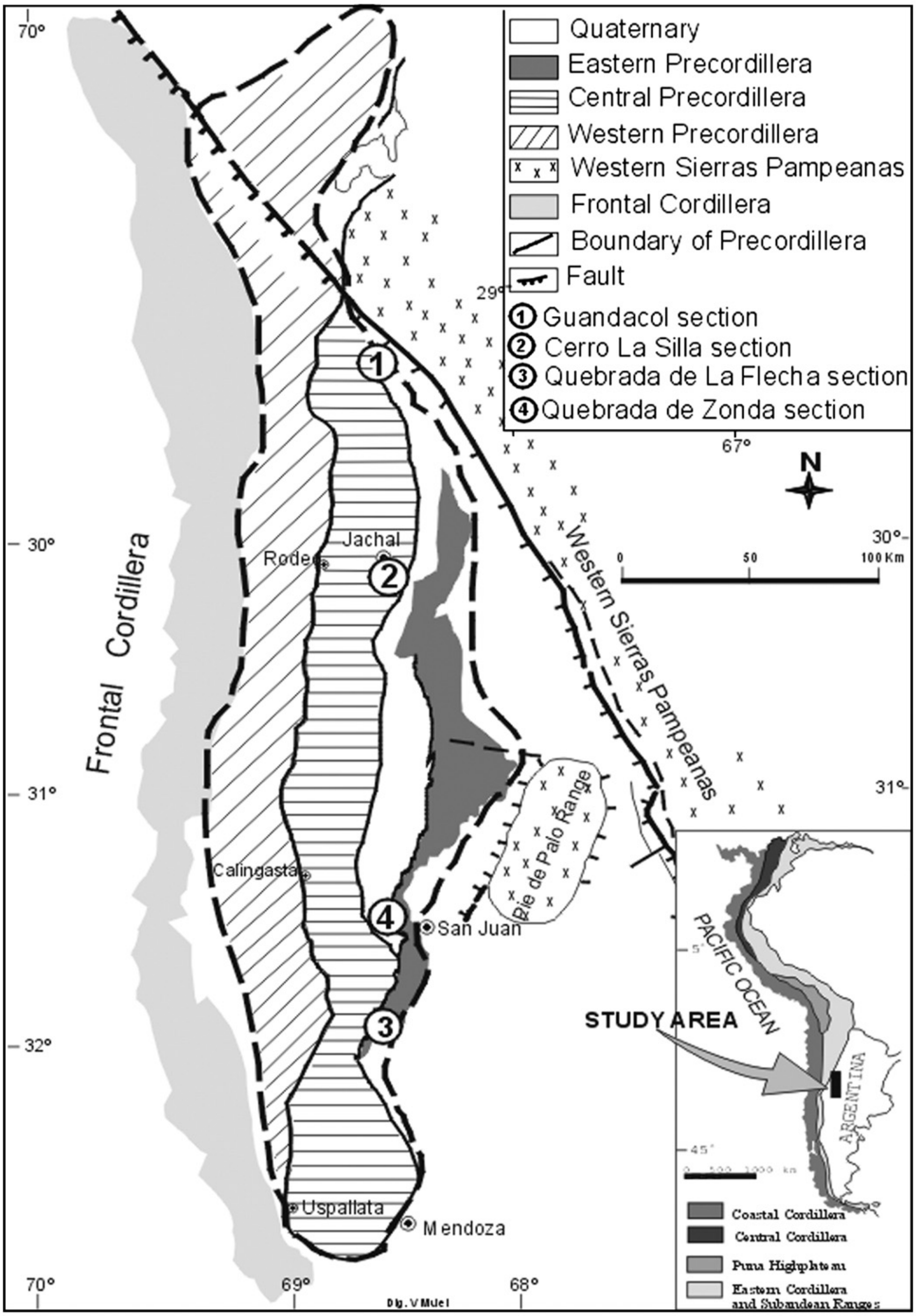

Fig. 2. Location of the studied stratigraphic sections: (a) Quebrada de la Flecha in the eastern Precordillera; (b) Cerro La Silla, Central Precordillera (c) Quebrada de La Angostura, 200 km north of San Juan, La Rioja province (maps were compiled and modified from Baldis et al. (1984).

characteristics developed from the Lower Cambrian (*Ollenelus* zone) to the base of the Ordovician, at which point a transgressive stage started (Baldis et al., 1984). An updated scheme for the Cambrian stratigraphic record of the Argentine Precordillera, grouping stratigraphic sucessions into an inner platform, outer slope and mixed zones (Fig. 3), was given by Bordonaro (2003a,b).

2.1. Lower to Middle Cambrian

In the Eastern Precordillera, the La Laja Formation is the oldest unit of the carbonate platformal succession and consists of several large-scale sedimentary sequences that have two main components, a siliciclastic interval and a calcareous one (Keller, 1999). The lower boundary is poorly known due to tectonic

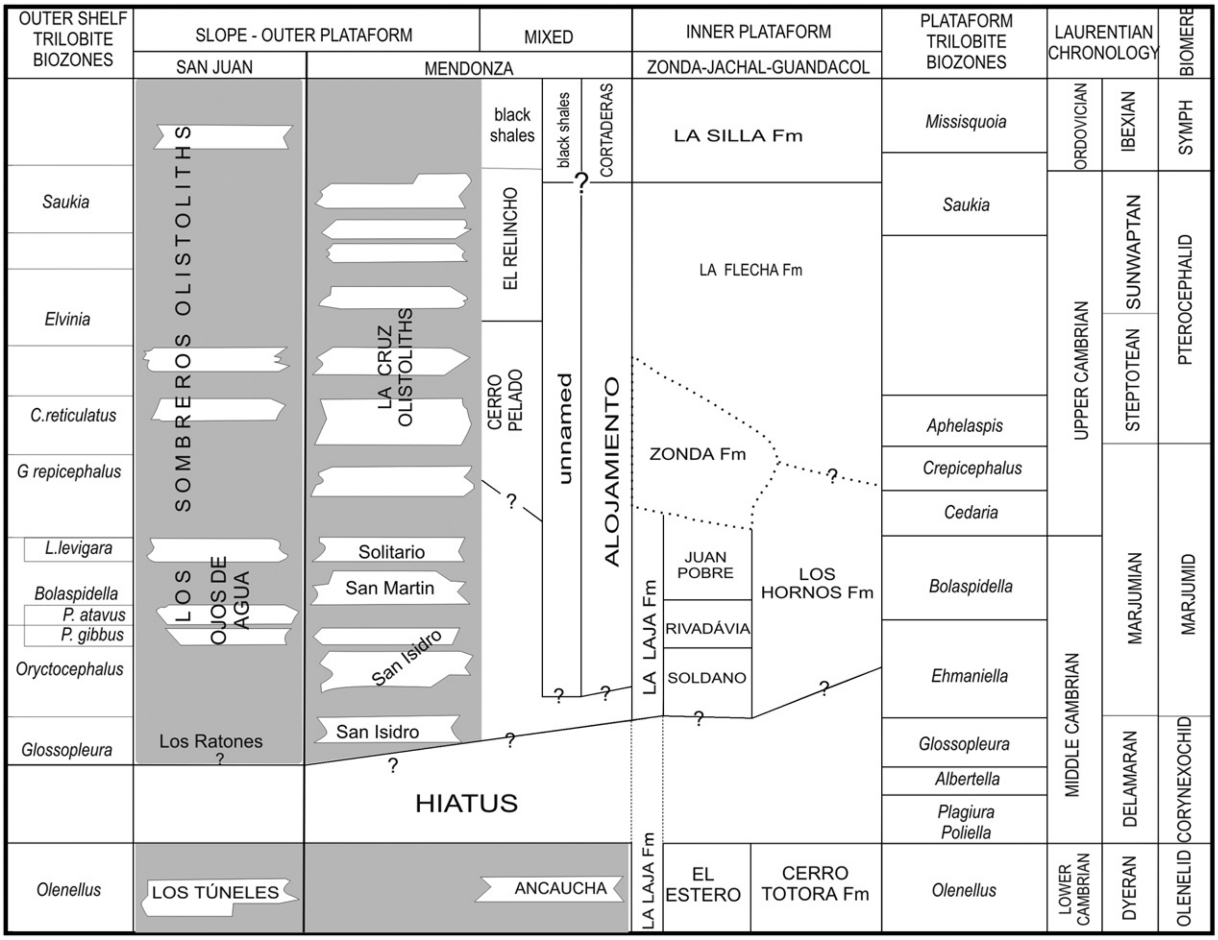

Fig. 3. Cambrian stratigraphic record of the Argentine Precordillera, grouping stratigraphic successions into an inner platform, slope-outer and mixed zone. The names of olistoliths correspond on the localities where they are found. Laurentia chronology (modified from Bordonaro, 2003a).

disturbance and its upper boundary is drawn at the transition between limestones and dolomites of the Zonda Formation (Bordonaro, 1980). In the Quebrada de Zonda section, four members are recognized in the La Laja Formation with a total thickness of about 1400 m. These are the El Estero Member, Early Cambrian in age (*Olenellus* Zone), composed of sandstone, shale, marl and grainstone; the Soldano Member, Late Middle Cambrian in age (*Ehmaniella* Zone), composed of limestone, mudstone and marl; the Bernadino Rivadavia Member (upper *Ehmaniella*-lower *Bolaspidella* Zones), Upper Middle Cambrian in age, consists of homogeneous black limestone; and the Juan Pobre Member, Upper Middle Cambrian (*Bolaspidella* Zone) in age, composed of interbedded oolitic and black limestones. The lower boundary of the El Estero Member is not exposed due to faulting, and contains only trace fossils but no diagnostic shelly fauna.

2.2. Upper Cambrian

The Cerro La Silla section, located 150 km to the north of the San Juan Town (Fig. 2), represents a significant outcrop of Cambrian rocks in the Central Precordillera. This section includes a thick Late Cambrian to Early Ordovician westward-dipping carbonate sequence, which comprises the Zonda, La Flecha, La Silla and San Juan Formations. Elsewhere, the latter is unconformably overlain by siliciclastic Upper Ordovician or Silurian deposits (Fig. 4a).

The La Flecha Formation is almost totally composed of small-scale, shallowing upward cycles (1–5 m) and exhibits a great variety of domal stromatolites and cryptalgal laminites (Fig. 4b), together with subtidal to supratidal lithotypes as well as oolite beds (Keller, 1999; Keller et al., 1994). A large amount of chert and chalcedony replaced locally the biogenic structures assigned to *Thalassinoides* isp (Fig. 4c). This ichnogenera is referred to feeding structures of living decapod crustacea, and is representative of intertidal to the upper part of the subtidal zone in the marine environment (Ekdale et al., 1984). The shallowing upward cycles are peritidal in origin and consist of small-scale, stacked successions (Baldis et al., 1981; Keller et al., 1994).

The Cerro La Silla is the type locality for the Silla Formation where this formation is 350 m thick and ranges in age from the Uppermost Cambrian to the Earliest Tremadoc (Keller et al., 1994). This Formation is predominantly calcareous with dolomite mainly in sparse biolaminated horizons. The succession is composed of an alternation of peloidal grainstones, intraclast grainstones and mudstones with abundant bioturbation. Distribution of facies seems to be random and no cycle or sedimentary rhythm could be demonstrated to date (Keller,

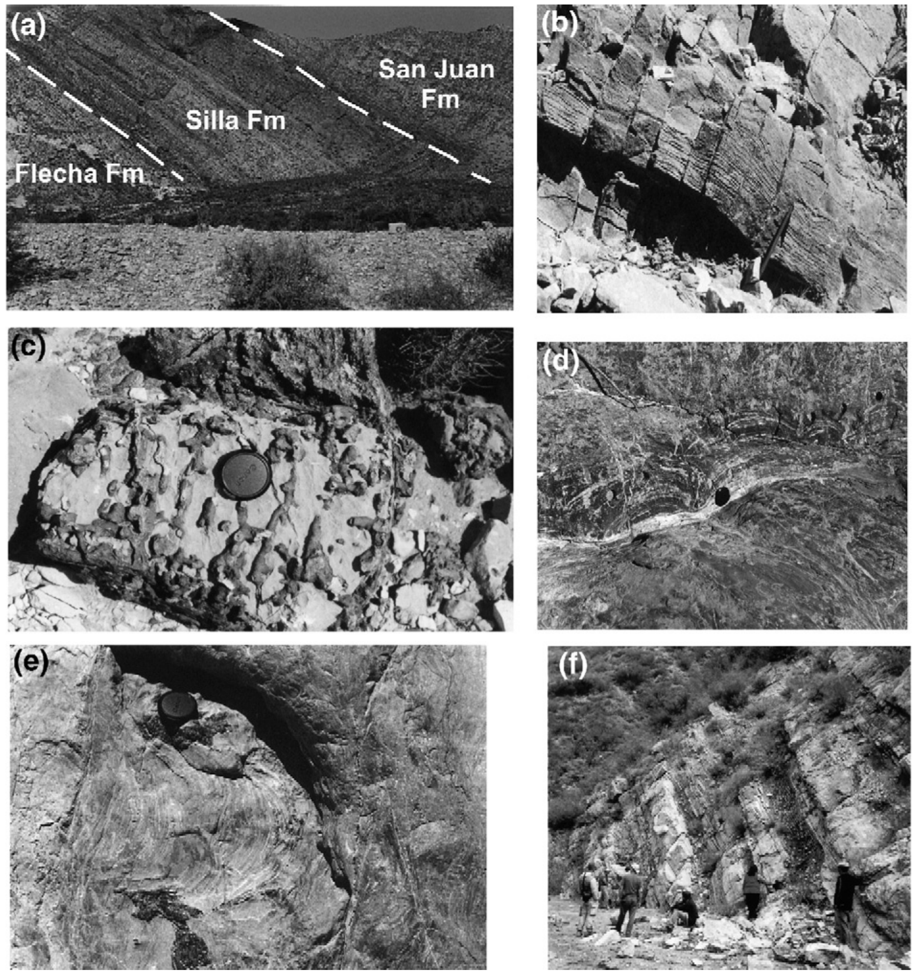

Fig. 4. (a) Exposure of the La Flecha, Silla and San Juan Formations at Cerro La Silla section, where carbonate strata dip westward. Several antithetic faults cut through La Silla Formation carbonate strata; (b) microbial mats are a common feature in both La Flecha (this photo) and La Silla Formations, at the Cerro La Silla section; (c) *Thalassinoids* isp. in basal carbonates of the La Silla Formation, Cerro La Silla. They are the record of living-feeding structures of decapod crustacea, and representative of intertidal to upper part of subtidal zone in a marine environment; (d) representative stromatolites in the Quebrada de la Flecha section (LLH-type) and (e) stromatolites at the same section showing well-developed lamination that defines an upward-widening morphology during growth (SH-type). (f) Black shales intercalated in limestones in the uppermost La Flecha Formation.

1999; Keller et al., 1994). The calcareous San Juan Formation of Late Tremadoc to Arenig age has a thickness of 350 m and its lower boundary is characterized by the occurrence of an open marine fauna (Keller et al., 1994).

The type section of the La Flecha Formation is located in the Quebrada de la Flecha, at the Eastern Precordillera, at about 90 km to the south of the San Juan town. In this section, there are several faults which, in places, preclude complete stratigraphic sampling of the Zonda Formation dolomite. From a litho- and biostratigraphic point of view a clear distinction can be made between the Zonda Formation and the La Flecha Formation in the type section. Here, *Plethopeltis* cf. *P. saratogensis* was found at the base of the formation (Keller et al., 1994) indicating a Franconian age (Ludvigsen and Westrop, 1983; Ludvigsen et al., 1989). In the middle part of the section, *Stenopilus convergens* (Raymon) appears, indicating the *Saukia* zone of the late Trempealeau (Longacre, 1970; Ludvigsen et al., 1989). On the other hand, in the La Angostura section, near Guandacol village further north, Dresbrachian trilobites appear near the base of the La Flecha Formation, which are time-equivalents to the Zonda Formation in the southern sections, such as in the type locality, at the Quebrada de la Flecha. In the La Angostura section, the top of the La Flecha Formation can be placed in the *Saukia* zone (Keller et al., 1994). In this way, a diachronous character between the La Flecha Formation and the Zonda Formation can be recognized as a result of a lateral transition (interfingering of facies) from south to north (Keller et al., 1994).

The Zonda Formation, deposited during the Steptoean stage according to Keller (1999), is mainly composed of massive dolomite with occasional stromatolites (laterally linked hemi-spheroids-LLH and, less commonly, vertically stacked up hemispheroids-SH) and thrombolites. The afore-mentioned features, typical of the La Flecha Formation at Cerro La Silla are also present in this unit at this section, with columnar stromatolites showing well-developed lamination with upward widening during growth (SH and LLH types; Fig. 4d and e). Likewise at the Cerro La Silla section, the uppermost portion of

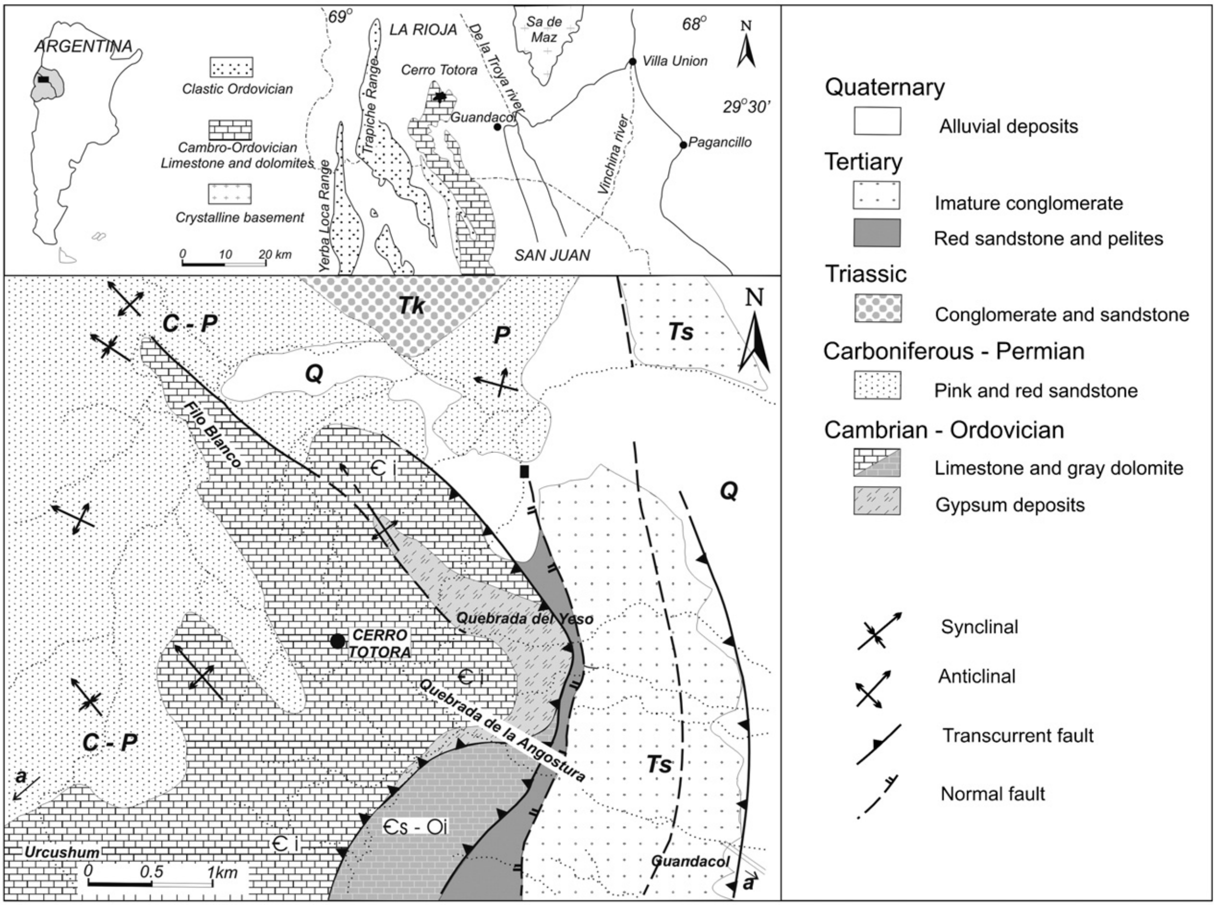

Fig. 5. Map indicating the location of the Quebrada de La Angostura, to the west of Guandacol Village, about 200 km north of San Juan town, western Argentina and the geology of the Precordillera in the La Rioja province. The Early Cambrian Cerro Totora Formation (gypsum intercalated with carbonates) was thrust over sediments of the La Flecha Formation. The La Silla Formation, in turn, overthrusts Tertiary sediments.

this Formation is characterized by the presence of massive dolomite, about 100 m thick. The La Flecha Formation at this section was deposited in the Sunwaptan stage according to Keller (1999) and the La Silla Formation is characterized by limestone beds that were deposited progressively at deeper levels up-section, almost entirely at the Uppermost Cambrian-Lowermost Ordovician boundary.

At the Quebrada de La Angostura section, near Guandacol village (La Rioja Province), about 200 km north of San Juan, the Lower Cambrian redbeds and evaporites of the Cerro Totora Formation overthrust La Flecha or La Silla Formation carbonates that, in turn, have overthrust Tertiary pelites (Astini and Vaccari, 1996; Fig. 5). Part of the lowermost portion of the La Flecha Formation is not exposed at this section. The lowermost exposures, bounded by a thrust fault, are essentially composed of intercalations of laminated limestone with massive limestone, with thrombolites and microbialites in dark beds, deposited in a very stable, low-energy environment under constant subsidence/sedimentation rate. In places, low-amplitude hummocky structures are present in this part of the section. Up-section, there are well-developed bioherms on which mudcracks are observed, and which are followed by intercalations of marls with 2 m-thick black shale beds that reveal important sea level change. Above this massive limestones exhibit *Thalassinoids* and thrombolites and have been affected by thrust faults that preclude a complete picture of the section. The well-developed SH-type stromatolites and abundant dolomites observed in the uppermost part of the La Flecha Formation at Quebrada de La Flecha and Cerro la Silla are absent at Quebrada de La Angostura.

3. C-, O- and Sr-isotope stratigraphy

3.1. Sampled sections and methods

We examined and sampled continuous sections at Quebrada de La Flecha in the Sierra Chica de Zonda, at Cerro La Silla and Quebrada de la Angostura localities. Samples were collected along traverses, perpendicular to the strike of the carbonate strata, in meter intervals.

Analyses of C and O isotopes of carbonates were performed at the stable isotope laboratory (LABISE) of the Department of Geology, Federal University of Pernambuco, Brazil. Extraction of CO_2 gas from micro-drilled powder (1 mm drill bit was used, avoiding fractures, recrystallized portions and weathered surfaces) was performed in a high vacuum line after reaction with 100% orthophosphoric acid at 25 °C for one day (three days allowed, when dolomite was present). Released CO_2 was

Table 1
Carbon, O and Sr isotopes, major and trace elements of carbonates from Quebrada de la Flecha, eastern Precordillera

	Sample	Height* (m)	$\delta^{18}O‰_{PDB}$	$\delta^{13}C‰_{PDB}$	Mg/Ca	Si ppm	Fe ppm	Mn ppm	Sr ppm	Mn/Sr	Rb ppm	$^{87}Sr/^{86}Sr$ (1σ)
Zonda Formation	QLFZ21	0	−7.0	−1.9								
	QLFZ20	10.0	−5.2	−0.2	0.42	2707	2121	78	278	0.28	<10	0.70934
	QLFZ19	20.0	−5.0	+0.6	0.42	20113	1956	50	417	0.12	<10	
	QLFZ18	29..5	−5.2	−1.0	0.46	7047	8534	543	229	2.4	<10	0.70955
	QLFZ17	38.5	−6.0	−0.6	0.45	3780	1318	24	349	0.07	<10	
	QLFZ16	43.0	−7.6	−0.5								
	QLFZ15	49.0	−6.6	−0.5	0.52	152787	2031	30	172	0.17	<10	
	QLFZ14	59.0	−6.4	−0.6	0.44	5087	1394	32	310	0.10	<10	0.70947
	QLFZ13	66.0	−5.6	−0.8	0.46	2053	2092	39	217	0.18	<10	
	QLFZ12	76.0	−5.9	−0.3								
	QLFZ11	86.0	−5.9	−0.6	0.45	45993	2779	28	261	0.10	<10	
	QLFZ10	96.0	−6.0	−1.2								0.70949
	QLFZ9	106.0	−6.2	−1.1								
	QLFZ8	118.0	−5.6	−1.6								0.70927
	QLFZ7	124.0	−5.7	−2.0	0.39	12040	1768	31	269	0.10	<10	
	QLFZ6	141.0	−6.8	−1.2								
	QLFZ5	1510	−5.2	−1.6								
	QLFZ4	161.0	−6.2	−1.4	0.31	10967	2169	41	235	0.17	<10	
	QLFZ3	171.0	−6.7	−2.7	0.46	129407	2281	29	207	0.14	<10	
	QLFZ2	181.0	−7.1	−1.4								
	QLFZ1	191.0	−7.5	−.19	0.47	108827	2451	31	228	0.14	<10	
	QLF 1	192.0	−6.7	−1.7	0.31	5056	716	55	311	0.16	tr.	0.70950
	QLF 2	222.0	−6.4	−1.3	0.45	21593	2195	19	363	0.05	<10	
	QLF2A	223.0	−10.4	−1.1	0.46	12495	1506	35	219	0.16	tr.	
	QLF2B/C	225.0	−6.2	−1.5								
	QLF 2D	226.0	−6.4	−1.8	0.36	90489	2019	30	218	0.11	tr.	
La Flecha Formation	QLF 3	245.0	−5.8	−1.8								
	QLF 4	255.0	−6.3	−1.5								
	QLF 5	265.0	−6.7	−1.6	0.41	97637	2006	41	281	0.15	tr.	0.70908
	QLF 6	275.0	−5.6	−1.9								
	QLF 7	285.0	−5.9	−2.7								
	QLF 8	295.0	−5.4	−1.9								
	QLF 9	305.0	−6.1	−1.4								
	QLF 10	315.0	−5.8	−1.1	0.41	2891	1063	35	266	0.13	tr.	0.70916
	QLF 11	325.0	−5.3	−1.4								
	QLF 12	335.0	−5.3	−0.8								
	QLF 13	345.0	−5.5	−0.6								
	QLF 14	355.0	−5.8	−1.0								
	QLF 15	370.0	−7.1	−1.6	0.39	3846	1172	33	316	0.10	tr.	0.70932
	QLF 16	380.0	−6.2	−1.1								
	QLF 17	390.0	−7.3	−2.2								
	QLF 18	400.0	−4.9	−2.6								
	QLF 19	410.0	−6.1	−1.6								
	QLF 20	420.0	−5.5	−1.9	0.46	4547	1006	14	306	0.05	<10	0.70940
	QLF 21	430.0	−8.8	−2.9								
	QLF 22	440.0	−5.6	−1.7								
	QLF 23	450.0	−5.8	−2.1								
	QLF24A	460.0	−9.0	−2.1	0.08	41949	1061	65	359	0.18	tr.	
	QLF 24B	470.0	−8.1	−2.2								
	QLF 24C	480.0	−7.5	−2.6	0.24	6154	920	24	366	0.06	<10	
	QLF 25	490.0	−6.0	−1.3	0.41	55025	937	85	291	0.29	tr.	0.70942
	QLF 27	500.00	−6.6	−0.9								
	QLF 27a	500.0	−9.2	−1.3								
	QLF 28	510.0	−5.0	−1.3								
	QLF 29	520.0	−6.5	−1.7								
	QLF 30	530.0	−5.5	−1.7	0.42	3955	1308	39	311	0.13	<10	0.70933
	QLF 31	540.0	−5.8	−1.9								
	QLF 32	550.0	−5.8	−1.1								
	QLF 33	560.0	−5.3	−0.8								
	QLF 34	570.0	−6.2	−1.1								
	QLF 35	580.0	−8.0	−1.6	0.06	13407	1272	29	238	0.12	<10	0.70934
	QLF 36	590.0	−6.0	−1.2								
	QLF 37	600.0	−7.4	−0.9								

(continued on next page)

Table 1 (*continued*)

	Sample	Height* (m)	$\delta^{18}O‰_{PDB}$	$\delta^{13}C‰_{PDB}$	Mg/Ca	Si ppm	Fe ppm	Mn ppm	Sr ppm	Mn/Sr	Rb ppm	$^{87}Sr/^{86}Sr$ (1σ)
La Flecha Formation	QLF 38	610.0	−5.1	−1.2								
	QLF 39	620.0	−5.4	−1.8								
	QLF 40	630.0	−7.8	−1.9	0.01	25403	369	21	352	0.06	<10	
	QLF 41	640.0	−8.0	−2.2								
	QLF 42	650.0	−8.3	−2.2								
	QLF 43	660.0	−4.9	−2.6								
	QLF 44	670.0	−6.8	−2.0								
	QLF 45	680.0	−5.9	−3.1	0.33	13670	1337	35	302	0.12	<10	0.70953
	QLF 46	690.0	−9.4	−3.3								
	QLF 47	705.0	−8.5	−5.6								
	QLF 48	721.0	−8.6	−4.6								
	QLF 49	733.0	−8.1	−2.4								
	QLF 50	743.0	−6.4	−2.0	0.18	65364	1479	23	315	0.07	<10	
	QLF 51	759.0	−9.8	−3.2								
	QLF 52	773.0	−10.2	−2.5								
	QLF 53	797.0	−4.9	−1.6								
	QLF 54	807.0	−5.7	−1.3								
	QLF 55	825.0	−8.2	−1.5	0.05	25017	785	15	309	0.05	<10	0.70937
	QLF 56	835.0	−7.9	−2.1								
	QLF 57	845.0	−8.4	−1.7								
	QLF 58	855.0	−8.3	−1.5								
	QLF 59	869.0	−4.9	−1.6								
	QLF 60	879.0	−8.5	−1.2	0.01	3873	344	43	279	0.15	tr.	0.70998
	QLF 61	893.0	−10.2	−1.9								
	QLF 62	905.0	−8.2	−1.7								
	QLF 63	916.0	−5.1	−1.3								
	QLF 64	926.0	−8.1	−2.1								
	QLF 65	936.0	−10.6	−2.0	0.01	26863	630	48	232	0.21	tr.	
	QLF 66	956.0	−11.1	−1.2								
	QLF 67	966.0	−9.1	−1.4								
	QLF 68	971.0	−7.0	−2.5	0.01	8045	830	31	258	0.12	<10	
	QLF 68A	991.0	−8.7	−1.8								
	QLF 68B	996.0	−9.3	−1.8								
	QLF 68C	1001.0	−8.6	−1.2								
	QLF 68D	1006.0	−8.9	−1.8	0.01	4479	499	36	220	0.16	<10	
	QLF 68E	1011.0	−9.2	−1.4								
	QLF 68F	1016.0	−8.8	−1.6								
	QLF 68G	1036.0	−8.7	−0.2								
	QLF 68H	1046.0	−8.1	−0.3	0.01	355	616	24	272	0.08	tr.	0.70911
La Silla Fm.	QLF 68I	1056.0	−9.6	−1.4								
	QLF 69	1136.0	−8.0	−1.1	0.46	4401	699	16	366	0.04	tr.	

* Stratigraphic position in relation to the first sample (QLFZ-21) of the section.

analyzed after cryogenic cleaning in a double inlet, triple collector SIRA II mass spectrometer and results are reported in δ notation in permil (‰) relative to the PDB standard. The uncertainties of the isotope measurements were better than 0.1‰ for carbon and 0.2‰ for oxygen, based on multiple analyses of an internal laboratory standard (BSC).

For determination of the Sr isotopic ratios, powdered samples were leached in 0.5 M acetic acid and centrifuged to separate the soluble from the insoluble fractions. Sr was eluted from solutions by ion exchange chromatography using Sr-Spec resin. $^{87}Sr/^{86}Sr$ values were determined in static mode using a Finnigan MAT 262 seven-collector mass spectrometer at the University of Brasília, Brazil. The isotopic ratios were normalized to $^{86}Sr/^{88}Sr$ value of 0.1194 and the 2σ uncertainty on Sr isotope measurements was less than 0.00009. Repeated analyses of NBS 987 standard indicated the value of 0.71024±0.00007 (2σ) for the $^{87}Sr/^{86}Sr$ ratio.

For the same samples that were analyzed for Sr isotopes, major and some trace element concentrations were analyzed by X-ray fluorescence spectrometry, using fused beads and an automatic RIX-3000 (RIGAKU) unit available at the LABISE. Fused beads were prepared using Li fluoride and uncertainties were better than 5% for Sr and Fe and 10% for Mn. For all geochemical and isotope analyses see Tables 1, 2 and 3.

3.2. Evaluating sample quality

There is no general agreement on how to select samples with primary C or O-signals, eliminating those that may have undergone post-depositional change of their isotope values. However, most workers agree on that concentration of Mn, Sr, Rb and Fe helps in selecting samples that have undergone little or no alteration (Kaufman and Knoll, 1995; Kha et al., 1999). Among all the parameters used to make such an evaluation, it seems that the most effective is the Mn/Sr ratio, because Sr is preferentially removed during recrystallization of meta-stable carbonate phases, while Mn becomes enriched during formation of late-stage

Table 2
C, O, Sr isotopes, major and trace elements for carbonate samples from Cerro La Silla, NW Argentina

	Sample	Height* (m)	$\delta^{18}O‰_{pdb}$	$\delta^{13}C‰_{PDB}$	Mg/Ca	Si ppm	Fe ppm	Mn ppm	Sr ppm	Mn/Sr	Rb ppm	$^{87}Sr/^{86}Sr$ (1σ)
La Flecha Formation	FLECHA 01	0.00	−5.0	−0.9	0.44	3090	1278	21	386	0.05	Tr.	
	FLECHA 02	32.00	−4.8	−0.8	0.47	20032	1776	33	327	0.10	3	0.70925
	FLECHA 03	50.50	−4.7	−0.7	0.45	6510	1302	21	334	0.06	Tr.	
	FLECHA 04	59.10	−4.8	−0.3	0.44	17277	1353	24	287	0.08	5	
	FLECHA 05	94.10	−4.8	−0.7	0.01	29245	1828	61	562	0.11	2	
	FLECHA 06	176.10	−4.9	−0.6								
	FLECHA 07	190.10	−4.8	−0.4	0.46	8147	1133	32	231	0.14	0	
	FLECHA 08	201.10	−7.3	−1.4	0.09	7681	756	22	318	0.07	1	0.70914
	FLECHA 09	246.10	−7.5	−0.7	0.07	18168	1083	12	412	0.03	5	
	FLECHA 10	260.10	−7.4	−0.1	0.12	2190	524	27	256	0.11	1	
	FLECHA 11	322.10	−4.6	−0.2	0.47	48938	1997	19	298	0.06	Tr.	
	FLECHA 12	336.10	−4.6	0.1	0.45	12411	1490	23	272	0.08	Tr.	
	FLECHA 13	384.10	−5.4	−0.7	0.37	119166	1859	31	269	0.12	0	
	FLECHA 14	421.10	−5.0	−0.3								
	FLECHA 15	465.10	−5.0	−0.8	0.45	5591	847	31	324	0.10	0	0.70923
	FLECHA 16	514.10	−4.9	−0.7	0.45	4872	1431	25	341	0.07	5	
	FLECHA 17	546.10	−4.9	−0.3	0.45	3599	722	11	286	0.04	0	
	FLECHA 18	581.10	−4.7	0.1	0.44	18968	966	41	245	0.17	1	0.70910
	FLECHA 19	599.10	−4.4	−0.3								
	FLECHA 20	602.90	−8.5	−1.1	0.18	23705	709	35	311	0.11	0	
	FLECHA 21	625.90	−8.0	−0.9								
	FLECHA 22	629.20	−4.7	−0.3								
	FLECHA 23	631.20	−4.7	−0.1	0.48	36565	1205	41	225	0.18	0	
	FLECHA 24	633.20	−4.8	−0.1								
	FLECHA 25	641.90	−4.8	−0.5								
La Silla Formation	FLECHA 26	643.90	−4.7	−0.3	0.46	13366	1105	37	276	0.13	1	0.71011
	FLECHA 27	646.40	−4.8	−1.2								
	SILLA 28	649.40	−8.5	−0.6	0.01	23420	1364	16	171	0.09	5	
	SILLA 29	651.40	−8.5	−0.8								
	SILLA 30	653.40	−8.8	−1.2	0.01	22027	571	24	108	0.22	2	0.70980
	SILLA 31	655.40	−8.7	−1.1	0.01	2482	561	20	208	0.10	1	
	SILLA 32	656.90	−7.6	−0.7								
	SILLA 33	670.90	−8.8	−0.1	0.01	320	728	15	200	0.07	Tr.	
	SILLA 34	678.90	−7.9	0.1								
	SILLA 35	695.90	−8.8	−0.8								
	SILLA 36	699.90	−6.2	−0.5	0.01	2985	522	23	142	0.16	0	
	SILLA 37	701.40	−7.5	−0.1								
	SILLA 38	704.40	−7.2	−0.3								
	SILLA 39	709.00	−7.8	−0.4	0.01	1771	475	21	239	0.09	0	
	SILLA 40	710.40	−7.7	0.1								
	SILLA 41	731.90	−6.7	−0.9								
	SILLA 42	746.40	−7.7	−1.2	0.09	5251	778	25	247	0.10	1	0.70900
	SILLA 43	782.40	−7.4	−1.5								
	SILLA 44	797.40	−7.9	−1.5								
	SILLA 45	803.40	−8.0	−1.5	0.01	2047	533	23	170	0.14	1	
	SILLA 46	809.40	−7.2	−0.9	0.01	2341	427	26	201	0.13	1	0.70898
	SILLA 47	846.40	−7.8	−1.2								
	SILLA 48	871.40	−7.8	0.3	0.01	1474	468	18	200	0.09	0	
	SILLA 49	887.10	−8.2	0.1	0.01	40149	651	19	267	0.07	0	0.70917
	SILLA 50	889.60	−7.8	−0.6								
	SILLA 51	939.60	−7.9	−1.6	0.01	619	952	5	268	0.02	0	
	SILLA 52	984.60	−7.3	−0.9	0.01	684	831	10	235	0.04	0	
	SILLA 53	1051.10	−7.5	−0.9	0.01	2279	1030	10	228	0.04	5	
	SILLA 54	1095.20	−6.1	−0.9	0.01	2338	785	19	307	0.06	5	
San Juan Fm.	SAN JUAN 55	1120.70	−6.9	−2.5	0.02	18041	1616	32	304	0.11	5	

* Stratigraphic position in relation to the first sample (Flecha-01) of the section.

ferroan calcite cement (Ripperdan et al., 1992; Derry et al., 1992; Kaufman et al., 1993; Knoll et al., 1995; Jacobsen and Kaufman, 1999). Although, Kaufman and Knoll (1995) stated that limestones or dolostones with Mn/Sr < 10 commonly retain near primary $\delta^{13}C$ abundances, limestones are considered to be unaltered only when Mn/Sr < 1.5 and $\delta^{18}O > -10‰$ (PDB) according to Fölling and Frimmel (2002).

The Mn/Sr ratios for carbonate rocks from the Zonda, La Flecha and La Silla Formations in the three sections considered here are usually < 0.5 and $\delta^{18}O$ in almost 100% of the cases is $> -10‰$

Table 3
Carbon, O and Sr isotopes, major and trace elements for carbonate samples from Quebrada de La Angostura, NW Argentina

	Sample	Height* (m)	δ^{18}O‰ PDB	δ^{18}C‰ PDB	Mg/Ca	Si ppm	Fe ppm	Mn ppm	Sr ppm	Mn/Sr	Rb ppm	^{87}Sr/^{86}Sr (1σ)
La Flecha Formation	QLH1	0.00	−8.0	−1.0	0.01	4713	956	5	469	0.01	<10	0.70932
	QLH 2	15.00	−8.5	−1.6								
	QLH3	30.00	−8.0	−1.5								
	QLH4	40.00	−8.0	−1.3	0.03	6487	1124	20	389	0.05	<10	0.709.29
	QLH 5	53.30	−8.0	−0.9	0.03	16427	1221	17	420	0.04	<10	0.70940
	QLH 6	68.30	−8.2	−2.3								
	QLH 7	83.30	−8.7	−1.6								
	QLH 8	100.30	−8.3	−1.3	0.02	9427	1394	20	540	0.03	<10	0.70927
	QLH 9	120.30	−8.8	−0.4								
	QLH 10	134.90	−8.8	−0.5	0.05	8867	1212	28	404	0.06	<10	
	QLH 11	149.90	−9.7	−0.5								
	QLH 12	159.90	−8.5	−2.2	0.13	31920	1996	27	407	0.07	<10	0.70939
	QLH 13	182.90	−8.4	−0.1	0.40	11293	1790	33	207	0.16	<10	
	QLH 14	197.90	−10.8	−0.4	0.02	22773	1075	11	374	0.03	<10	
	QLH 15	210.90	−10.5	−2.1	0.41	25247	2641	43	366	0.12	<10	
	QLH 16	224.90	−8.5	−0.5	0.16	12833	1504	29	418	0.07	<10	
	QLH 17	248.90	−9.5	−0.1	0.04	27580	812	16	583	0.03	<10	0.70932
	QLH 18	261.80	−8.5	3.5	0.03	1260	832	19	786	0.02	<10	0.70993
	QLH 19	281.70	−8.6	2.6	0.02	6627	874	12	583	0.02	<10	0.70927
	QLH 20	297.40	−8.9	4.3	0.31	25400	1913	34	464	0.07	<10	
	QLH 21	318.40	−8.6	2.6	0.01	46153	1852	40	376	0.11	<10	
	QLH 22	335.40	−11.4	2.3	0.03	11947	1161	20	446	0.05	<10	
	QLH 23	352.80	−7.45	4.2	0.40	48720	2491	46	403	0.12	<10	
	QLH 24	366.00	−9.5	3.8	0.14	26040	1663	26	1053	0.02	<10	0.70955
	QLH 25	383.50	−8.9	5.7	0.14	12087	1469	44	522	0.08	<10	0.70918
	QLH 26	393.00	−8.2	4.9	0.22	32993	2225	43	579	0.07	<10	
	QLH 27	401.00	−10.7	5.7	0.02	10080	1568	23	497	0.05	<10	0.70953
	QLH 28	406.00	−6.6	4.4	0.50	83627	2689	63	377	0.17	<10	
	QLH 29 A	411.00	−9.4	4.1	0.06	23800	2467	34	437	0.08	<10	0.70934
	QLH 29B	416.00	−12.4	4.4	0.02	5087	902	31	392	0.08	<10	
	QLH 30	421.00	−9.5	5.5	0.02	4760	1527	11	674	0.02	<10	0.70926

* Stratigraphic position in relation to the first sample (QLH1) of the section.

(PDB). In the δ^{13}C and δ^{18}O crossplots for both formations (Fig. 6), apparently scatter rather than co-variance seems to predominate. These observations imply that the δ^{13}C values in most of the analyses reported here are primary or near primary values.

3.3. Results

3.3.1. C and O-isotope stratigraphy

3.3.1.1. Quebrada de La Flecha section. One hundred and six samples were collected from the carbonates at this locality, comprising 21 from the Zonda Formation (only about 200 m were sampled) and the rest from the La Flecha Formation (over 800 m were sampled). At this section, the Zonda Formation is entirely composed of massive dolomite that, in places, exhibits well-developed SH and LLH-type stromatolites. The lower boundary of the La Flecha Formation is characterized by the presence of stromatolites (LLH and SH-types) and thrombolites, and its upper boundary is drawn where the content of stromatolite decreases and dolomite predominates. The δ^{13}C stratigraphic profile revealed a discrete positive anomaly (+0.6‰) in the Zonda Formation dolomite about 200 m below the upper boundary (Fig. 7, labelled I), whereas all remaining δ^{13}C values lie between −1 and −2‰. As the Zonda Formation carbonates were deposited during the Steptoean (Keller, 1999), we speculate that this positive anomaly corresponds to the extremity of the upper limb of the SPICE excursion but this requires further confirmation.

In the La Flecha Formation, cyclicity in sedimentation is well reflected in the C-isotope profile and five discrete positive excursions were observed and one pronounced negative anomaly (−5.6‰) about 350 m below the upper boundary of this formation (Fig. 7, labeled II). As the La Flecha Formation in this section was deposited during the Sunwaptan (Keller, 1999) we correlate this minimum in the δ^{13}C profile to that observed in the Sunwaptan carbonates of Black Mountain, Australia (Ripperdan et al., 1992), or Lawson Cove, North America (Ripperdan and Miller, 1995). The distribution of δ^{18}O is less uniform in this section than at Cerro La Silla. An important drop in the δ^{18}O values (from around −7 to around −9‰ PDB) was recorded towards the top of this formation (Fig. 7).

3.3.1.2. Cerro La Silla. Fifty samples from the Cerro La Silla were analyzed for C and O isotopes, including carbonates from the Zonda, La Flecha, La Silla and San Juan Formations. The C- and O-isotope profiles display clear differences in the isotopic behavior of these three formations (Fig. 8). As already observed

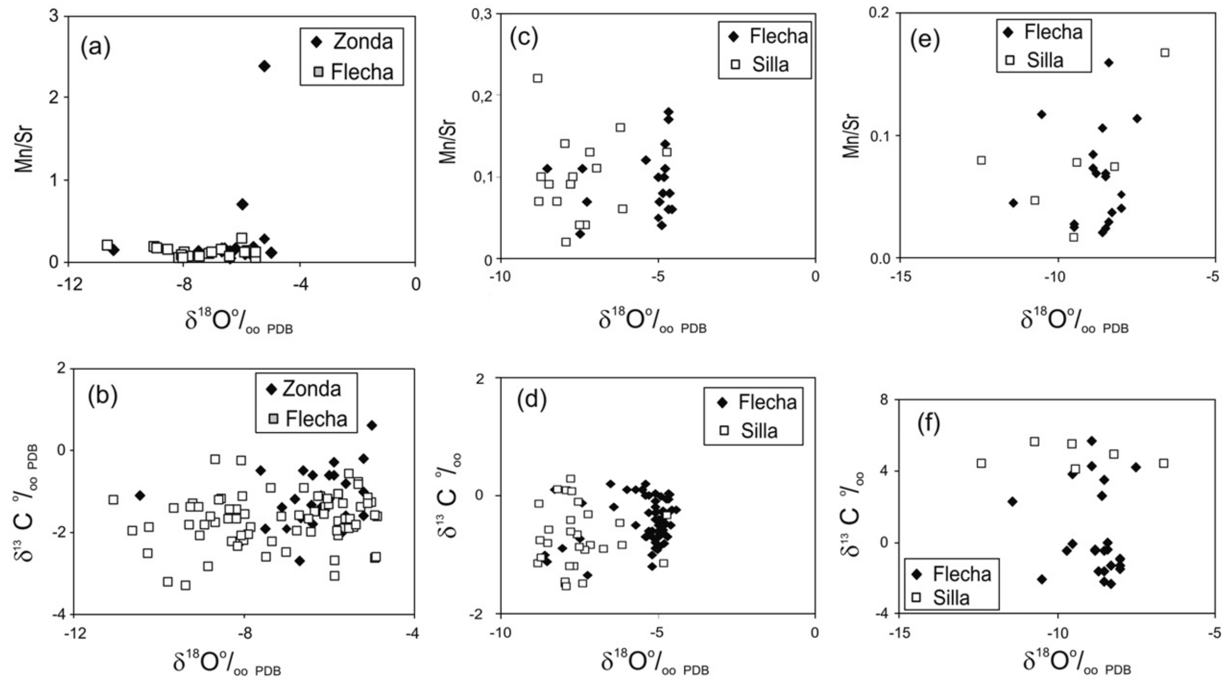

Fig. 6. (a) Mn/Sr vs. $\delta^{18}O‰_{PDB}$ ratios for carbonates of the La Flecha and Silla Formations (data from Quebrada de la Flecha, Cerro La Silla and Quebrada de La Angostura). Almost all Mn/Sr ratios are below 0.2, an indication of near-primary isotope values; (b) $\delta^{13}C$ vs. $\delta^{18}O‰_{PDB}$ for carbonates of the La Flecha and Silla Formations (data from the three sections discussed in the text). Scatter rather, than co-variance, predominates.

by Baldis et al. (1981, 1982) and Baldis and Bordonaro (1982), the La Flecha Formation was deposited in a shallow environment of low-energy conditions, with water of restricted circulation and periodic sub-aerial exposure, with only little or no terrigenous sediment input. Such environmental conditions would imply, in principle, that these carbonates should display some ^{13}C- and ^{18}O-enrichment, when compared with isotopic signatures of coeval marine carbonates.

The $\delta^{18}O$ values are slightly higher (mostly ~−5‰ PDB), with few exceptions, than those observed in the La Silla Formation (~−7 to −8‰ PDB; Fig. 8). Such a situation indicates that most $\delta^{18}O$ values are primary and implies that environments in which these two formations were deposited differed from each other, the La Flecha Formation environment being more restricted, of hypersaline tendency, approaching a sabkha.

There is always a potential for isotopic alteration during dolomitization (Sheppard and Shwarcz, 1970) but apparently, in the uppermost portion of this section, dolomitic limestones do not show a substantial change in Mn/Sr ratios in relation to the underlying marly limestones as shown in Fig. 8. All $\delta^{13}C$ values obtained in the entire section in the present study are negative, except for 8 points (very close to 0‰ PDB). In this $\delta^{13}C$ stratigraphic profile, two excursions seem to be of stratigraphic importance (labelled I and II in Fig. 8). The upper boundary of the La Flecha Formation is dolomite-dominated and the transition to the La Silla Formation is marked by the presence of black shales and *Thallasinoids*. A discrete positive, asymmetric excursion (labelled I), recorded in dolomites, is interpreted as corresponding to SPICE. It is, however, less developed, because of dolomite deposition from water of restricted circulation. The negative excursion labelled II, in the La Silla Formation, is probably equivalent to SNICE, recorded in limestones deposited in open sea.

3.3.1.3. Quebrada de La Angostura. A total of 31 samples were analyzed from the Quebrada de La Angostura and $\delta^{18}O$ is mostly between −8 and −9‰ (Fig. 9) with stronger fluctuation towards the top of the La Flecha Formation. Some of the $\delta^{18}O$ values reach values as low as −13‰ and are regarded here as altered. As expected, $\delta^{13}C$ ratios exhibit a more consistent behavior and display negative values up to half way of the chemostratigraphic profile and up-section these ratios become positive, reaching values as high as +5.6‰ at the level that is composed of transgressive black shale and intercalated marly limestone. Unfortunately, thrust faults have precluded us from sampling stratigraphically up-section.

We interpret this positive excursion as a record of SPICE which implies a deposition of the uppermost La Flecha Formation, in this section, during the Steptoean stage. This situation implies that the La Flecha Formation in the northern Central Precordillera was deposited synchronously with the deposition of the Zonda Formation in the eastern Precordillera (San Juan sub-basin) at the Quebrada de La Flecha during the Steptoean and confirms the assumption made by Keller (1999) concerning the diachronous character of these units.

3.3.2. Sr-isotope stratigraphy

At Quebrada de La Flecha, $^{87}Sr/^{86}Sr$ ratios for the Zonda Formation carbonates vary from 0.70924 to 0.70955, and for the La Flecha Formation from 0.70908 to 0.70942. At Cerro La Silla, this ratio varies, for the La Flecha Formation, from 0.70914 to 0.70923, with only one exception (0.71011), at the transition to

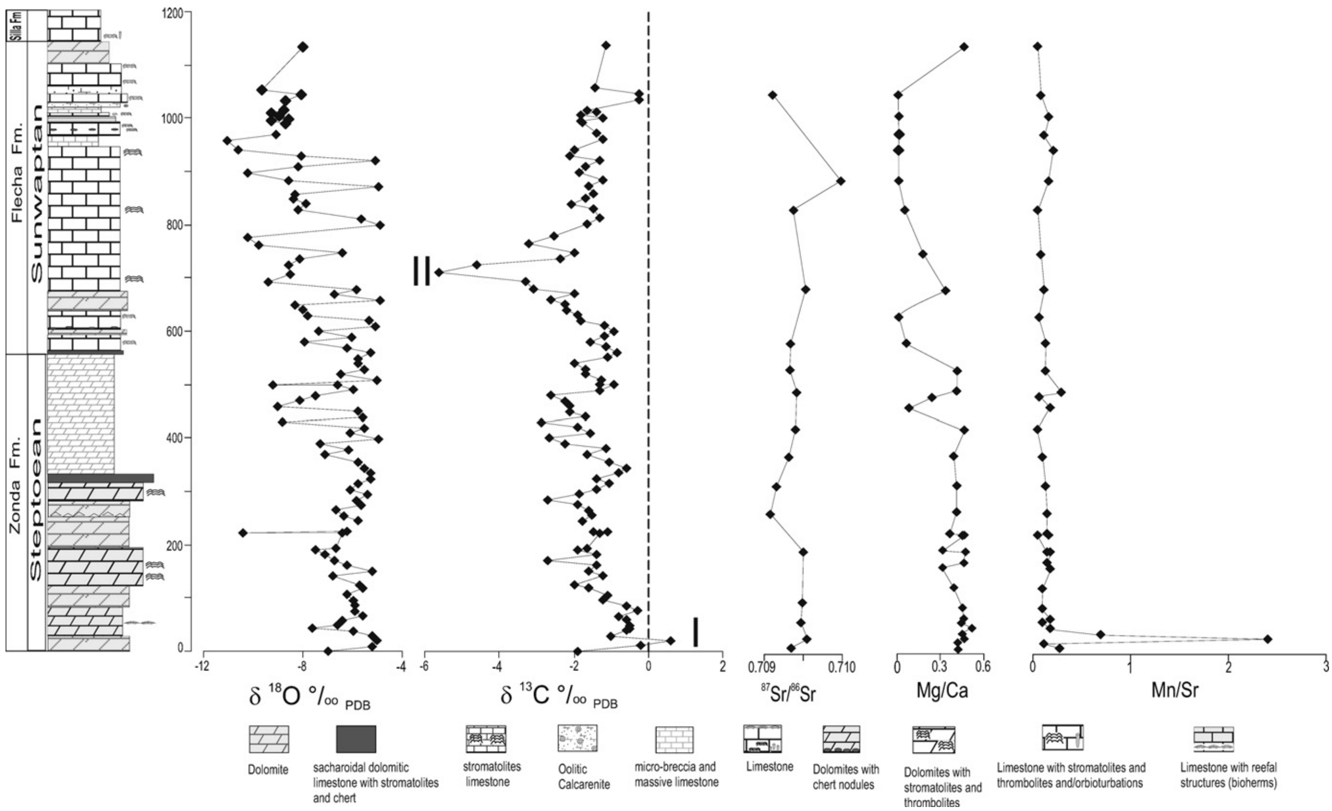

Fig. 7. C-, O- and Sr-isotope chemostratigraphy and chemical stratigraphy of the La Flecha Formation at the Quebrada de La Flecha (type locality), Sierra Chica de Zonda, Eastern Precordillera.

the La Silla Formation where intercalated black shales indicate an important continental siliciclastic contribution whereas the La Silla Formation carbonates display ratios from 0.70898 to 0.70980. The important change in the general trend of $^{87}Sr/^{86}Sr$ in this section is observed in the dolomite from the uppermost part of the La Flecha Formation, and in the transition to the La Silla Formation where a more substantial contribution from the continent is observed.

At the Quebrada de La Angostura, $^{87}Sr/^{86}Sr$ values for the La Flecha Formation carbonates are in the range from 0.70918 to 0.70993. The overall variation of Sr isotope ratios in these carbonates is consistent with globally reported Upper Cambrian seawater values around 500 Ma (Burke et al., 1982; Montañez et al., 2000), and are therefore, little affected by depositional environmental changes or secondary alteration.

4. Palynology of the SPICE interval (uppermost La Flecha Formation)

4.1. Methods

Two samples of black shale occurring at peak $\delta^{13}C$ values of the SPICE anomaly in the Flecha Formation were prepared at the Micropalaeontology Laboratory of the Facultad de Ciencias (Montevideo, Uruguay). All samples come from the Quebrada de La Angostura section. Following crushing and digestion of samples (ca. 150 g) with concentrated HCl, 72% HF was applied for 24 h to the silicate/organic residues. After neutralisation, boiling, concentrated HCl was used to dissolve fluorides. Remaining organic residues were recovered by means of a 5 µm sieve, stored in glass flasks and mounted with glycerin–gelatine on standard glass slides. Throughout the preparation, gravity settling was used instead of centrifugation, to avoid destruction of fragile, large acritarchs. Microfossils were determined and counted under a Leica DM LP polarizing microscope, using transmitted, reflected, and combined reflected–transmitted light (in the latter cases with oil immersion objectives). This allowed observation of opaque (carbonized) microfossils, and also to assess the fossil nature of the isolated microstructures. This method, developed by Pflug and Reitz (1992, and references therein), makes possible the comparison of the reflectivity and transparency of microfossils. Modern contaminants are non-reflective, regardless of their transparency and colour, because they have not undergone carbonisation. Moreover, the epi-illumination method allows to discard opaque mineral structures that resemble microfossils (e.g. pyrite framboids). All the structures described here are clearly reflective and organic in nature.

4.2. Results

Thermal alteration index (TAI, Staplin, in Hunt, 1996) according to the schemes of Hunt (1996) and Teichmüller et al. (1998) is TAI 4 for palynomorphs of the La Flecha Formation, indicating palaeotemperatures between 170–220 °C. The black shale samples of the uppermost La Flecha Formation yielded a

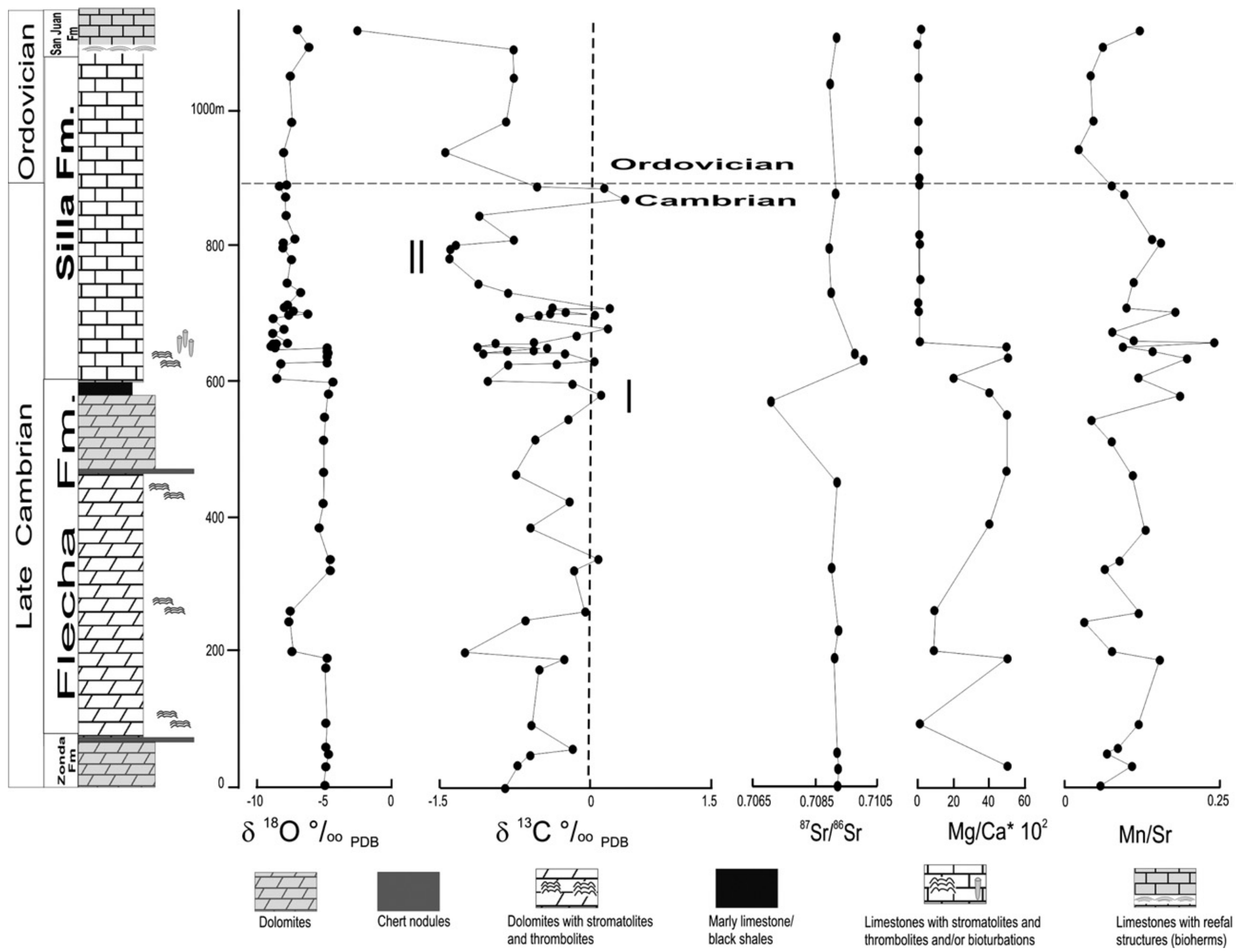

Fig. 8. C-, O- and Sr-isotope chemostratigraphy and chemical stratigraphy of the La Flecha and La Silla Formations, Cerro La Silla near Jachal, Central Precordillera.

depauperate acritarch assemblage strongly dominated by abundant spheroidal microfossils, with a microgranular, "foamy" structure and 20 to 64 μm in diameter (mean = 37 μm, 8 specimens measured; Fig. 10 a–b). Their opacity is dependent on vesicle diameter, the largest specimens being almost opaque. They possibly consist of irregularly packed microspheres that are less than 1 μm in diameter, although this needs to be confirmed. They resemble *Bavlinella* (Schepeleva) Vidal (1976), but lack its characteristic, regular arrangement of microspheres, which are much better developed in the mentioned genus, even in highly carbonized specimens (Gaucher et al., 2003, 2005). Apart from these possibly microbial colonies, only two other acritarch forms occur, namely sphaeromorph acritarchs with microgranular (possibly corroded) vesicles showing concentric folds and ranging in diameter from 30 to 236 μm (Fig. 10 e), which may be assigned to *Leiosphaeridia* or *Saharidia*; and a single, well-preserved vesicle 28 μm in diameter (Fig. 10 c–d), showing short processes (up to 2 μm) and walls forming a polygonal network, here classified as *Cymatiogalea* Deunff (1961).

4.3. Significance of the Acritarch assemblage

Cymatiogalea is a characteristic representative of Late Cambrian to Early Ordovician plankton worldwide (Deunff, 1961; Reitz and Höll, 1990; Montenari and Servais, 2000; Vergel et al., 2002; Rubinstein et al., 2003; Servais et al., 2004), thus supporting the age assignment of the positive carbon isotope anomaly described here. On the other hand, the acritarch assemblage recovered from the uppermost La Flecha Formation differs from the relatively diverse assemblages typical of the period. In particular, acanthomorphs and polygonomorphs are completely absent, and sphaeromorphs and possible spheroidal bacterial colonies dominate the assemblage. We envisage that this is due to the nearshore environment where the analyzed shales were deposited, as also shown by underlying stromatolites and thrombolites. Reitz et al. (1995) showed that sphaeromorph-dominated, low-diversity but high-abundance acritarch assemblages are typical of Lower Ordovician nearshore successions. Correlative, open-marine facies in the same basins are characterized by acanthomorphs and polygonomorphs (Reitz et al., 1995).

In northwestern Argentina, a somewhat similar (but more diverse) assemblage has been described from the lower Santa Rosita Formation (Vergel et al., 2002 and references therein; Rubinstein et al., 2003), and also interpreted as a shallow-water assemblage.

The high organic-matter content of shales hosting the acritarchs described here suggests high bioproductivity and/

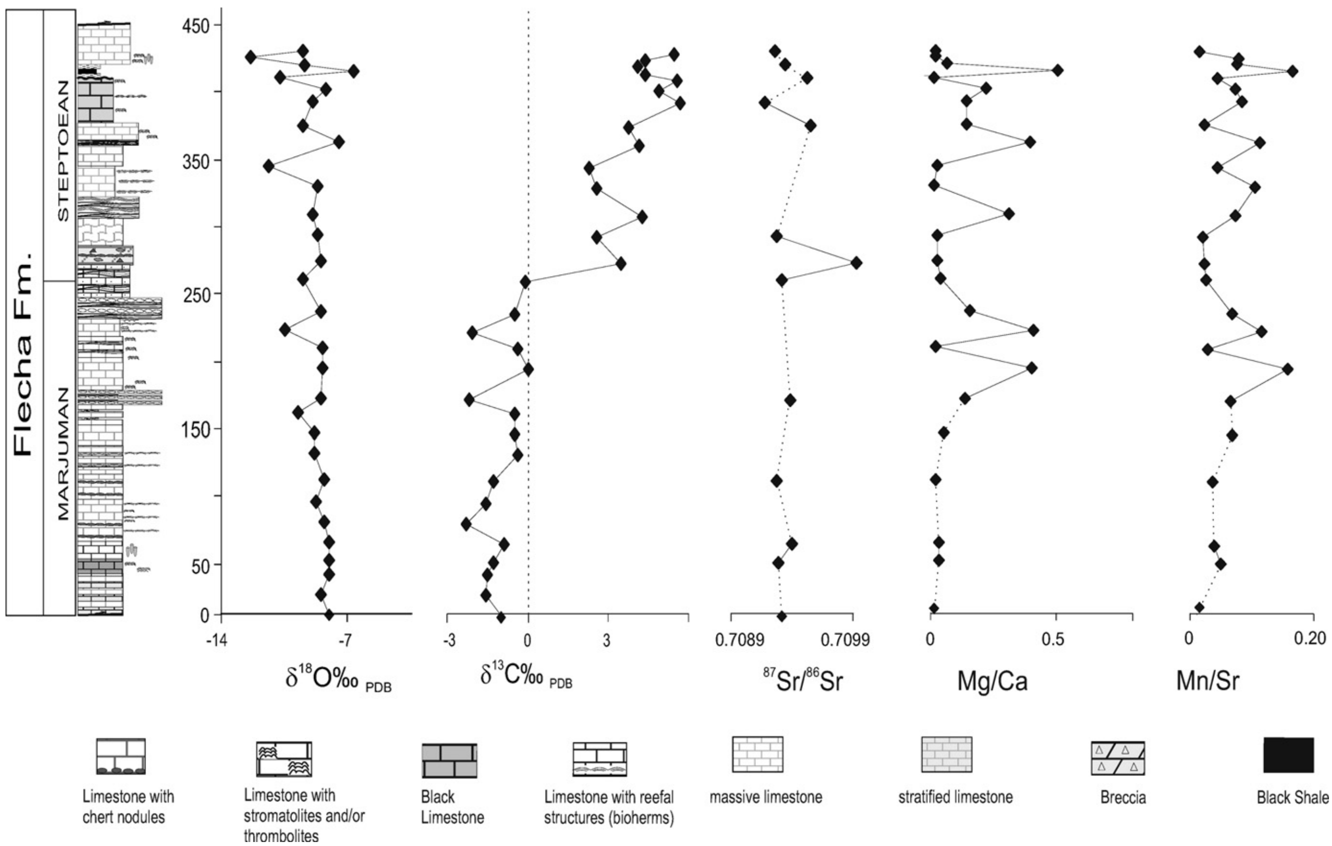

Fig. 9. C-, O- and Sr-isotope chemostratigraphy and chemical stratigraphy of La Flecha Formation, Quebrada de Angostura, near Guandacol, Central Precordillera, about 200 km north of San Juan.

or enhanced rates of organic matter burial. This might have contributed to the anomalously positive δ^{13}C values of coeval carbonates. If this represents a global pattern or just a local effect remains to be determined.

5. Conclusions

The combined C-, O- and Sr-isotope data for the Quebrada de La Flecha, Cerro La Silla and Quebrada de La Angostura sections improve considerably our understanding of the Upper Cambrian paleoenvironmental evolution of the Precordillera of Western Argentina.

The δ^{18}O variation curve at Cerro La Silla shows an average difference of about 2‰ between La Silla and La Flecha Formation carbonates. This divergence simply reflects the variation in the Mg/Ca composition of the corresponding carbonates, which in turn reflects changes in the depositional environment. La Flecha carbonates are more dolomitic, δ^{18}O averaging −5‰ (PDB) and representing hypersaline, restricted, sabkha environments, whereas the La Silla Formation, with δ^{18}O averaging −7‰, represents open marine conditions.

The carbonate sequences at Cerro La Silla and Quebrada de La Angostura are coeval but the absence of dolomite in the uppermost portion of the La Flecha Formation at the Quebrada de La Angostura indicates that this unit was deposited in open marine conditions thus making it possible for SPICE to be recorded. This was not the case at Cerro La Silla. It is not possible to have the complete C-isotope stratigraphy of the Steptoean Zonda Formation at Quebrada de La Flecha where SPICE has been likely recorded.

This study suggests that SNICE is likely a global excursion and combined with SPICE can be a valuable tool in Upper Cambrian stratigraphic correlation. It also suggests that likely SPICE and SNICE are, respectively, related to important transgressive and regressive marine events.

Acknowledgements

Field and laboratory work have been supported by projects from VITAE (B-11487/10B003) and PROSUL/CNPq (AC-38/2002, AC-38/2003, 490349/2004-8), granted respectively to V. P. Ferreira and A.N. Sial. The Universidad Nacional de San Juan provided field vehicles. Thanks are due to G. M. Santana and V. S. Bezerra for the assistance with C and O isotope analyses at the Stable Isotope Laboratory (LABISE, Recife, Brazil), M. H. Silva for XRF analyses, and to S. Gioia (University of Brasilia) for assistance with Sr isotope analyses. S. D. S. Barros, N. C. Guerra (Federal University of Pernambuco), and V. Mullet (Universidad Nacional de San Juan) helped with Figure drafting. Hartwig Frimmel and Graham Shields read an early version of this manuscript and their critical evaluation improved the quality of this paper. This is the contribution n. 234 of the NEG-LABISE

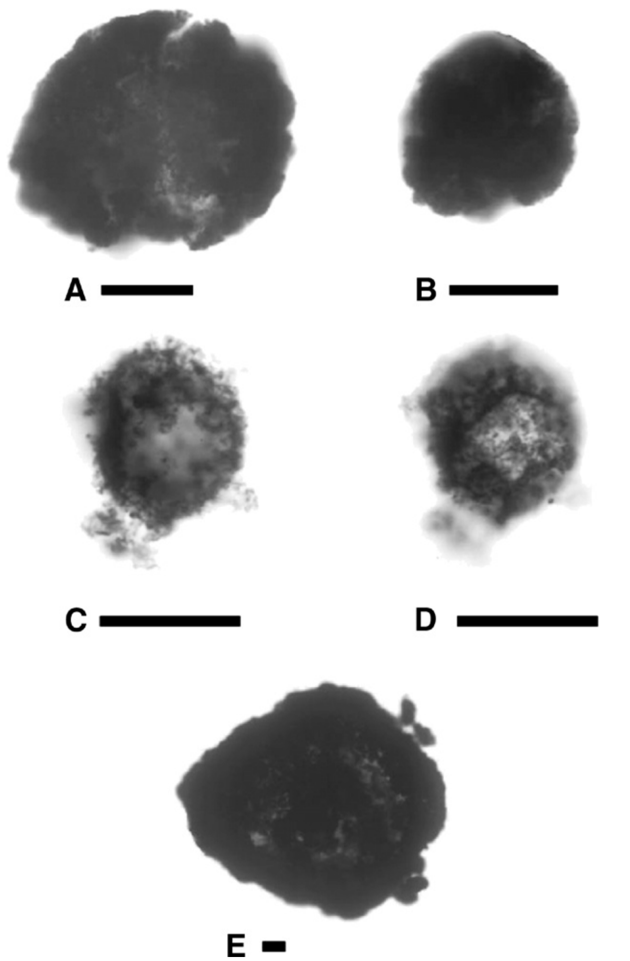

Fig. 10. Organic-walled microfossils in palynological macerations of black shales, lower La Silla Formation, Quebrada de La Angostura. (a–b) Sphaeroidal, microgranular vesicles or colonies of probable bacterial affinity; (b–c) *Cymatiogalea* Deunff (1961). (c) lower focus level, showing short processes at the vesicle margin; (d) higher focus level showing characteristic polygonal fields; (e) Large sphaeromorph, possibly *Leiosphaeridia* or *Saharidia*. All scale bars represent 20 μm. Specimens illustrated are kept in the collection of the Departamento de Geología, Facultad de Ciencias (Montevideo, Uruguay).

and a contribution to the IGCP project n. 478 (“Neoproterozoic-Early Paleozoic Events in SW-Gondwana”).

References

Aceñolaza, F.G., Toselli, A., 1988. El Sistema de Famatina: Su interpretación como orógeno de margen continental activo. V Congreso Geológico Chileno. Santiago de Chile, vol. 1, pp. 55–67.

Aceñolaza, F.G., Toselli, A.J., 1999. Argentine Precordillera: allochthonous or autocthonous Gondwanic? Zentralblatt für Geologie und Paläontologie Teil II 7/8, 1–14.

Aceñolaza, F.G., Miller, H., Toselli, A., 2002. Proterozoic–Early Paleozoic evolution in western South America — a discussion. Tectonophysics 354, 121–137.

Astini, R.A., Vaccari, N.E., 1996. Sucesión evaporítica del Cámbrico Inferior de la Precordillera: significado geológico. Revista de la Associación Geológica Argentina 51, 97–106.

Astini, R.A., Benedetto, J.L., Vaccari, N.E., 1995. The Early Paleozoic evolution of the Argentine Precordillera as a Laurentian rifted, drifted, and collided terrane: a geodynamic model. Geological Society of America Bulletin 107, 253–273.

Astini, R.A., Ramos, V.A., Benedetto, J.L., Vaccari, N.E., Cañas, F.L., 1996. La Precordillera: Un terreno exótico a Gondwana. Actas XIII Congreso Geológico Argentino y III Congreso de Exploración de Hidrocarburos. Buenos Aires, vol. 5, pp. 293–324.

Baldis, B.A.J., Bordonaro, O., 1982. Comparación entre El Cámbrico de la “Great basin” norteamericana y la Precordillera de San Juan, Argentina, su implicación intercontinental. Actas V Cong. Latinoamericano de Geol. Buenos Aires, Argentina, vol. 1, pp. 97–108.

Baldis, B.A., Bordonaro, O.L., Beresi, M.S., Uliarte, E.R., 1981. Zona de dispersión estromatolítica en la secuencia calcáreo-dolomítica del Paleozoico inferior de San Juan. VIII Congreso Geológico Argentino. San Luis, vol. 2, pp. 419–434.

Baldis, B.A., Beresi, M.S., Bordonaro, O.L., Vaca, A., 1982. Síntesis evolutiva de la Precordillera Argentina. V Congreso Latinoamericano de Geología. Actas, Buenos Aires, vol. 4, pp. 399–445.

Baldis, B., Beresi, M., Bordonaro, O., Vaca, A., 1984. The Argentine Precordillera as a key to the Andean structure. Episodes 17, 14–19.

Baldis, B., Peralta, S.H., Villegas, C.R., 1989. Esquematizaciones de una posible transcurrencia del Terrane de Precordillera como fragmento continental procedente de áreas Pampeano-Bonaerenses. Serie Correlación Geológica. INSUGEO-UNT, San Miguel de Tucumán, vol. 5, pp. 81–100.

Benedetto, J.L., 1993. La hipótesis de la aloctonía de la Precordillera argentina: Un test estratigráfico y bioestratigráfico. XII Congreso Geológico Argentino & II Congreso de Exploración de Hidrocarburos. Mendoza, vol. 3, pp. 375–384.

Bordonaro, O.L., 1980. El Cámbrico en la Quebrada de Zonda. Revista de la Asociación Geológica Argentina 35, 26–40.

Bordonaro, O.L., 2003a. Review of the Cambrian Stratigraphy of the Argentine Precordillera. Geológica Acta, Barcelona, 1, 11–21.

Bordonaro, O.L., 2003b. Evolución paleoambiental y paleogeográfica de la cuenca cámbrica de la Precordillera argentina. Revista de la Asociación Geológica Argentina, Buenos Aires 58, 329–346.

Brasier, M.D., Sukhov, S.S., 1998. The falling amplitude of carbon isotopic oscillations through the Lower to Middle Cambrian: northern Siberia data. Canadian Journal of Earth Sciences 35, 353–373.

Buggisch, W., Keller, M., Lehnert, O., 2003. Carbon isotope record of Late Cambrian to Early Ordovician carbonates of the Argentine Precordillera. Paleogeography, Palaeoclimatology, Palaeoecology 195, 357–373.

Burke, W.H., Denison, R.E., Hetherington, E.A., Koepnick, R.B., Nelson, H.F., Otto, J.B., 1982. Variation of seawater $^{87}Sr/^{86}Sr$ throughout Phanerozoic time. Geology 10, 516–519.

Derry, L.A., Kaufman, A.J., Jacobsen, S.B., 1992. Sedimentary cycling and environmental change in the late Proterozoic: evidence from stable and radiogenic isotopes. Geochimica et Cosmochimica Acta 56, 1317–1329.

Deunff, J., 1961. Un microplancton à Hystrichosphères dans le Tremadoc du Sahara. Revue Micropaléontologie 4, 37–52.

Ekdale, A.A., Bromley, R.G., Pemberton, S.G., 1984. The Use of Trace Fossils in Sedimentology and Stratigraphy. Society of Economic Paleontologist and Mineralogist (SEMP), Tulsa, Oklahoma. 316 pp.

Finney, S.C., Gleason, J.D., Gehrels, G.G., Peralta, S.H., 2002. Early Gondwanian affinity of the Argentine Precordillera: evidences from U–Pb geochronology of detrital zircon population from Cambrian and Ordovician sandstones. Geological Society of America, Annual Meeting with Program, Denver, Colorado.

Finney, S.C., Gleason, J.D., Gehrels, G.G., Peralta, S.H., Aceñolaza, G.F., 2003. Early Gondwanan connection for the Argentine Precordillera Terrane. Earth and Planetary Science Letters 205, 349–359.

Fölling, P.G., Frimmel, H.E., 2002. Chemostratigraphic correlation of carbonate succesions in the Gariep and Saldania Belts, Namibia and South Africa. Basin Research 13, 1–37.

Gaucher, C., Boggiani, P.C., Sprechmann, P., Sial, A.N., Fairchild, T.R., 2003. Integrated correlation of the Vendian to Cambrian Arroyo del Soldado and Corumbá Groups (Uruguay and Brazil): palaeogeographic, palaeoclimatic and palaeobiologic implications. Precambrian Research 120, 241–278.

Gaucher, C., Frimmel, H.E., Germs, G.J.B., 2005. Organic-walled microfossils and biostratigraphy of the upper Port Nolloth Group (Namibia): implications for the latest Neoproterozoic glaciations. Geological Magazine 142, 539–559.

Hunt, J.M., 1996. Petroleum Geochemistry and Geology, 2nd ed. W.H. Freeman & Co., New York.

Jacobsen, S.B., Kaufman, A.J., 1999. The Sr, C and O isotopic evolution of Neoproterozoic seawater. Chemical Geology 161, 37–57.

Kaufman, A.J., Knoll, A.H., 1995. Neoproterozoic variations in the C-isotopic composition of seawater: stratigraphic and biogeochemical implications. Precambrian Research 73, 27–49.

Kaufman, A.J., Jacobsen, S.B., Knoll, A.H., 1993. The Vendian record of Sr and isotopic variations in seawater: implications for tectonics and paleoclimatic. Earth Planetary Sciences Letters 120, 409–430.

Keller, M., 1999. Argentine Precordillera. Geological Society of America Special Publication, vol. 341. 140 pp.

Keller, M., Cañas, F., Lehnert, O., Vaccari, N.E., 1994. The Upper Cambrian and Lower Ordovician of the Precordillera (Western Argentina): some stratigraphic reconsiderations. Newsletter Stratigraphy 31, 115–132.

Kha, L.C., Sherman, A.G., Narbonne, G.M., Knoll, A.H., Kaufman, A.J., 1999. $\delta^{13}C$ stratigraphy of the Proterozoic Bylot Supergroup, Baffin Island, Canada: implications for regional lithostratigraphic correlations. Canadian Journal of Earth Sciences 36, 313–332.

Knoll, A.H., Kaufman, A.J., Semikhatov, M.A., 1995. The carbon isotopic composition of Proterozoic carbonates: Riphean successions from northwestern Siberia (Anabar Massif, Turukhansk Uplift). American Journal of Science 295, 823–850.

Longacre, S., 1970. Trilobites of the Upper Cambrian Ptychaspid Biomere, Wilberns Formation, Central Texas. Journal of Paleontology, Tulsa 44 (pl. II), 1–70.

Ludvigsen, R., Westrop, S., 1983. Franconian trilobites of New York State. Memoire New York State Museum 23, 1–44.

Ludvigsen, R., Westrop, S., Kindle, C.H., 1989. Sunwaptan (Upper Cambrian) trilobites from the Cow Head Group, Western Newfoundland, Canada. Paleontographica Canadiana 6, 1–175.

Montañez, I.P., Osleger, D.A., Banner, J., Mack, L.E., Musgrove, M., 2000. Evolution of the Sr and C isotope composition of Cambrian Oceans. GSA Today 10, 1–7.

Montenari, M., Servais, T., 2000. Early Paleozoic (Late Cambrian–Early Ordovician) acritarchs from the metasedimentary Baden–Baden–Gaggenau zone (Schwarzwald, SW Germany). Review of Palaeobotany and Palynology 113, 73–85.

Ortiz, A., Zambrano, J.J., 1981. La Provincia Geológica Precordillera Oriental. VIII Congreso Geológico Argentino. San Luis, vol. 3, pp. 59–74.

Pflug, H.D., Reitz, E., 1992. Palynostratigraphy in Phanerozoic and Precambrian Metamorphic Rocks. In: Schidlowski, M., Golubic, S., Kimberley, M.M., McKirdy, D.M., Trudinger, P.A. (Eds.), Early Organic Evolution: Implications for Mineral and Energy Resources. Springer, Berlin, pp. 509–518.

Ramos, V.A., Jordan, T.E., Allmendiger, R.W., Kay, S., Cortés, J.M., Palma, M.A., 1984. Chilenia: un terreno alóctono en la evolución paleozoica de los Andes Centrales. Actas, IX Congreso Geológico Argentino. San Carlos de Bariloche, vol. 2, pp. 84–106.

Ramos, V.A., Jordan, T.E., Allmendiger, R.W., Mpodozis, C., Kay, S., Cortés, J.M., Palma, M.A., 1986. Paleozoic terranes of the Central Argentine–Chilean Andes. Tectonics 5, 855–880.

Reitz, E., Höll, R., 1990. Biostratigraphischer Nachweis von Unterordovizium in der Innsbrucker Quarzphyllitserie (Ostalpen). Jahrbuch Geologische Bundesanstalt 133, 603–610.

Reitz, E., Anderle, H.-J., Winkelmann, M., 1995. Ein erster Nachweis von Unterordovizium (Arenig) am Südrand des Rheinischen Schiefergebirges im Vordertaunus: Der Bierstadt-Phyllit (Bl. 5915 Wiesbaden). Geologisches Jahrbuch Hessen 123, 25–38.

Ripperdan, R.L., Miller, J., 1995. Carbon isotope ratios from the Cambrian–Ordovician boundary section at Lawson Cove, Ibex area, Utah. In: Cooper, J.D., Droser, M.L., Finney, S.C. (Eds.), Ordovician Odyssey. Pacific section SEPM, vol. 77, pp. 129–132.

Ripperdan, R.L., Magaritz, M., Nicoll, R.S., Shergold, J.H., 1992. Simultaneous changes in carbon, sea level, and conodont biozones within Cambrian–Ordovician boundary interval at Black Mountain, Australia. Geology 20, 1039–1042.

Rubinstein, C.V., Mángano, M.G., Buatois, L.A., 2003. Late Cambrian acritarchs from the Santa Rosita Formation: implications for the Cambrian–Ordovician boundary in the Eastern Cordillera, northwest Argentina. Revista Brasileira Paleontologia 6, 43–48.

Saltzman, M.R., Runnegar, B., Lohmann, K.C., 1998. Carbon isotope stratigraphy of the Upper Cambrian (Steptoean Stage) sequence of the eastern Great basin: record of a global oceanographic event. Geological Society of America Bulletin 110, 285–297.

Saltzman, M.R., Ripperdan, R.L., Brasier, M.D., Lohmann, K.G., Robison, R.A., Chang, W.T., Pemf, S., Ergaliev, E.K., Runnegar, B., 2000. A global carbon isotope excursion (SPICE) during the Late Cambrian: relation to trilobite extinctions, organic-matter burial and sea level. Palaeogeogeography, Palaeoclimatology, Palaeoecoloy 162, 211–223.

Servais, T., Stricanne, L., Montenari, M., Pross, J., 2004. Population dynamics of galeate acritarchs at the Cambrian–Ordovician transition in the Algerian Sahara. Palaeontology 47, 395–414.

Sheppard, S.M.F., Shwarcz, H.P., 1970. Fractionation of carbon and oxygen isotopes and magnesium between coexisting metamorphic calcite and dolomite. Contributions to Mineralogy and Petrology 26, 161–198.

Teichmüller, M., Littke, R., Robert, P., 1998. Coalification and maturation. In: Taylor, G.H., Teichmüller, M., Davis, A., Diessel, C.F.K., Littke, R., Robert, P. (Eds.), Organic Petrology. Gebrüder Borntraeger, Berlin, pp. 86–174.

Thomas, W.A., Astini, R.A., 1996. The Argentine Precordillera: a traveler from the Ouachita embayment of North American Laurentia. Science 273, 752–752.

Vergel, M.M., Araoz, L., Rubinstein, C.V., 2002. Ordovician palynomorphs of Argentina: An integrated approach. In: Aceñolaza, F.G. (Ed.), Aspects of the Ordovician system in Argentina. Serie Correlación Geológica, vol. 16, pp. 209–224.

Vidal, G., 1976. Late Precambrian microfossils from the Visingsö Beds in southern Sweden. Fossils and Strata 9, 1–57.