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Chemostratigraphy and diagenetic constraints on Neoproterozoic carbonate successions from the Sierras Bayas Group, Tandilia System, Argentina

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Abstract

Carbon and oxygen isotopic data, combined with a detailed diagenetic study, obtained from undeformed and unmetamorphosed dolomite and limestone from the Neoproterozoic Sierras Bayas Group, Argentina, provide a new record of isotopic stratigraphic variations useful for regional and global correlations. The Sierras Bayas Group is subdivided into the Villa Mónica (sandstones and dolomites), Cerro Largo (siliciclastic rocks) and Loma Negra (limestones) formations, unconformably overlain by the Cerro Negro Formation (siliciclastic rocks with basal marls), and grouped into four depositional sequences bounded by unconformities. The dolomite samples from the Villa Mónica Formation show ranges of $\delta^{13}C_{(PDB)}$ values from −1.3 to +2.2‰ and of $\delta^{13}C_{(PDB)}$ values from −2.1 to −6.7‰. Elemental data (Mn/Sr, Fe/Sr and Ca/Sr) and stable isotope compositions point to a moderate to significant degree of diagenetic alteration in samples from this formation. The Loma Negra Formation is composed of homogeneous, non-luminescent micritic limestone with $\delta^{13}C_{(PDB)}$ values of samples between +2.7 and +4.5‰; $\delta^{13}C_{(PDB)}$ values vary from −7.1 to −13.5‰. Selected element ratios using Mn/Sr (<1.4) and Fe/Sr (<30) combined with C/O isotope data suggest near to primary carbon isotope signatures in these samples. The Villa Mónica Formation can be broadly constrained between 800 and 900 Ma, based on Rb/Sr radimetric data and stromatolite morphologies. The Loma Negra Formation fits in global $\delta^{13}C$ and $^{87}Sr/^{86}Sr$ trends that suggest an age range of ~580–590 Ma, which is regionally important as it places constraints on the continuity of Vendian basins in south-western Gondwana. In the same sense, the isotopic signatures of Loma Negra Formation samples along with the preservation of a unique shelly fauna make a direct connection of the Argentinian succession to Vendian intervals in Uruguay (Polanco Formation) and Brazil (Corumbá Group).

Keywords: Argentina; Stable isotopes; Diagenesis; Neoproterozoic; Tandilia System

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1. Introduction

In the present study, a new record of the abundance of C and O isotopes in Neoproterozoic dolostone and limestone from Villa Mónica and Loma Negra formations (Sierras Bayas Group), Argentina, are reported (Figs. 1 and 2). Existing geochronological data from the Sierras Bayas Group are sparse somewhat, inconsistent with the geological framework of the basin. On one hand, an 800–900 Ma age for the basal Villa Mónica Formation was suggested by Poiré (1989, 1993) based on stromatolite biostratigraphy (e.g. Semikhatov, 1975, 1991), which is supported by a 793±32 Ma Rb/Sr age (interpreted as a diagenetic overprint) from interbedded fine-grained sedimentary rocks (Cingolani and Bonhomme 1988). On the other hand, the age of the overlying siliciclastic dominated Cerro Largo Formation is poorly constrained. A whole rock Rb–Sr determinations on shales from this unit indicate an age of 725±36 Ma (Kawashita et al., 1999a). Similarly, Bonhomme and Cingolani (1980) reported a Rb/Sr age of 769±12 Ma on the same unit. The age of Cerro Negro Formation, the youngest unit in the Sierras Bayas Group, is also uncertain.

A Rb–Sr age of 723±21 Ma was determined on fine clay fractions in pelites (Cingolani and Bonhomme, 1982), which is broadly consistent with a subsequent whole rock Rb/Sr age determination of 734±48 Ma on the same formation (Kawashita et al., 1999a). Caution is recommended, however, in the general interpretation of Rb/Sr data. In contrast, a K/Ar whole rock analysis reported by Cingolani et al. (1991) suggests a minimum depositional age of 680 Ma for the Cerro Negro Formation. This age is consistent with the recent discovery of Cloudina — currently regarded as an index fossil for the late Ediacaran Period — in the underlying Loma Negra Formation (Gaucher et al., 2005), and Vendian-to-Cambrian aged acritarchs in the Cerro Negro Formation.

The aim of this study is to show that an understanding of diagenetic processes leads to a better interpretation of elemental and isotope signatures of carbonates. With these complications in mind, the paleontological and stable isotope data make it possible to estimate an age for the largely undeformed carbonates of the Sierras Bayas Group through biostratigraphic and chemostratigraphic correlations.

2. Geology

The Tandilia System is a 350 km long, northwest–southeast oriented orographic belt, located in the Buenos Aires province (Fig. 1). It comprises an igneous-metamorphic basement covered by Neoproterozoic to Lower Palaeozoic sedimentary rocks. The basement rocks are mainly granitoids, orthogneisses and migmatites yielding Sm–Nd model ages averaging 2620±80 Ma (Pankhurst et al., 2003). In the Olavarría area (Fig. 1), the Neoproterozoic succession is composed of the Villa Mónica, Cerro Largo and Loma Negra formations (Sierras Bayas Group), with a thickness of ~170 m (Poiré, 1993), overlain by the Cerro Negro Formation (Figs. 2, 3). Between the crystalline basement and the Neoproterozoic/Lower Paleozoic sedimentary cover, arkosic and quartz–kaolinitic saprolites mark prominent palaeoweathering surfaces (Poiré, 1987; Zalba et al., 1992). The lithostratigraphic units are grouped into four depositional sequences (Fig. 2): Tofoletti (I), Malegni (II), Villa Fortabat (III) and La Providencia (IV) (Spalletti and Poiré, 2000). The succession studied is unmetamorphosed and almost undeformed.

The oldest depositional sequence (Tofoletti, 52 m thick; Fig. 3) is equivalent to the Villa Mónica Formation, and exhibits two sedimentary facies associations: (a) quartz–arenites and arkosic sandstones at the base and (b) dolostone including shallow marine stromatolites dolostone and shales at the top. The dolostone and shale facies association (36 m thick), is composed of laminated stromatolitic dolostone, interdolomitic green shales and supradolomitic red shales with associated mudstone. Eight sedimentary facies have been recognized along these vertical sections: (i) domal biostrome dolostone, made up of columnar, stratiform and bulbous stromatolites, (ii) laminated dolostone, (iii) mottled dolostone, (iv) domal biostrome dolostone composed of stratiform stromatolites, (v) domed bioherm dolostone (vi) laminated friable dolostone, (vii) iterbiostrome green shales and (viii) red shales and marls (Poiré, 1987; Gómez Peral and Poiré, 2003). The dolostone of the Villa Mónica Formation host a rich assemblage of stromatolites, including *Colonella* fm., *Conophyton ?resotti*, *Conophyton* fm., *Cryptozoon* fm., *Gongylina* fm., *Gymnosolem* fm., *Inzeria* fm., *Jacutophyton* fm., *Jurusonia nisvensis*, *Katavia* fm., *Kotuikania* fm., *Kussiella* fm., *Minjaria* fm., *Parmites* fm., *Parmites* cf. *cocrescens* and *Stratifera* fm. (Poiré, 1993).

The Malegni depositional sequence is equivalent to the Cerro Largo Formation, (75 m thick; Figs. 2 and 3) and consists of a basal succession composed of chert breccia, finely laminated glauconitic shale, and fine-grained sandstone. The upper section of this sequence consists of cross-bedded quartz arenite, which are, in turn, overlain by silt- and claystone. This succession represents a shallowing upward sequence, ranging from

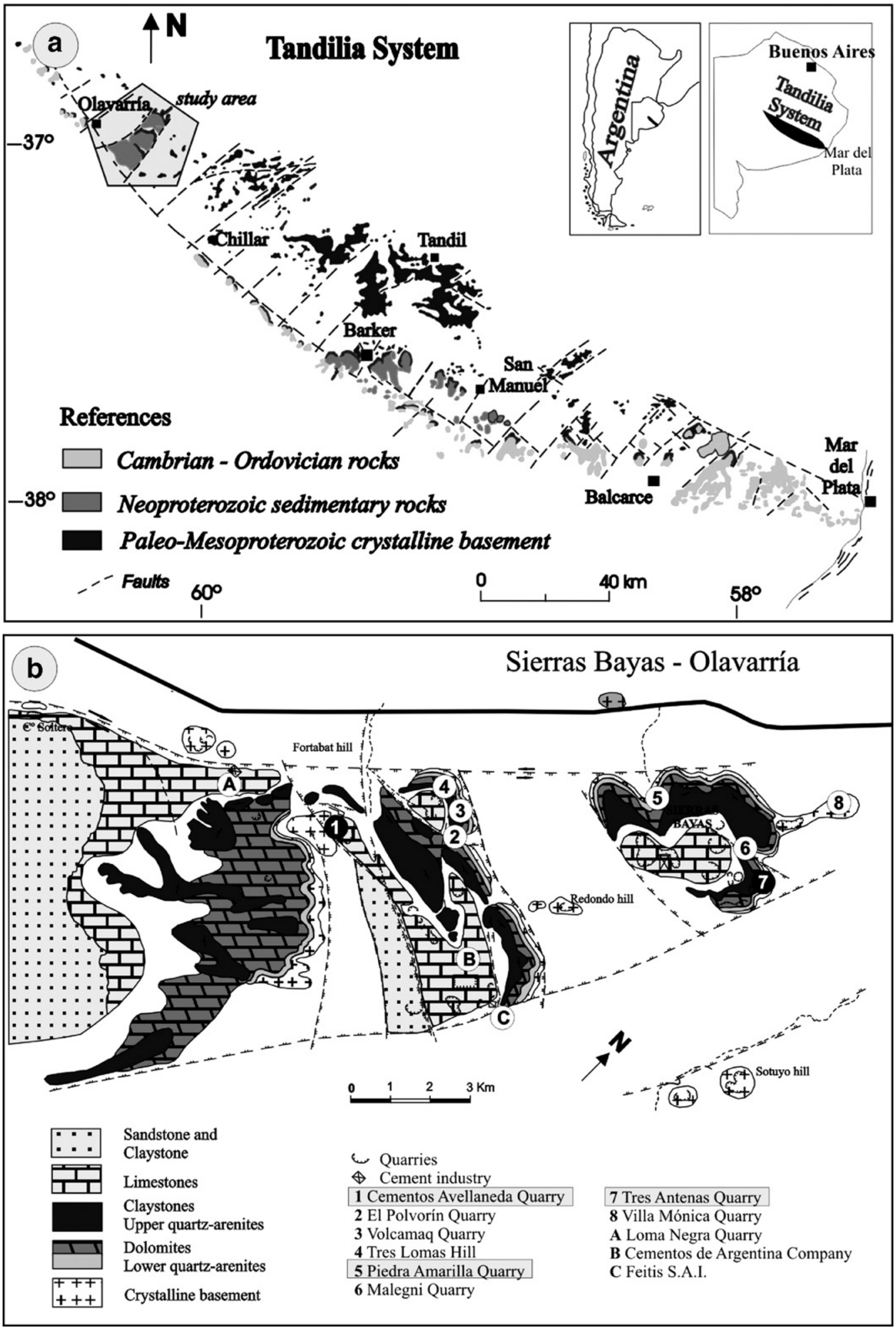

Fig. 1. (a): Study area in the Tandilia System (Buenos Aires Province, Argentina). (b) Geological map of the Sierras Bayas, Olavarría region (northwestern part of the Tandilia System after Iñiguez Rodriguez (1999). Note locations of samples (1, 5 and 7). In the other quarries indicated mainly the Loma Negra Formation is exposed. Numbers 1 to 8 are outcrops, which were sampled for petrographical, geochemical, isotopic, fluid inclusions, XRD and RAI analyses. Quarries A to C were not sampled.

subtidal nearshore to tidal-flat deposits. Trace fossils, such as *Palaeophycus* isp. and *Didymaulichnus* isp., are described by Poiré et al. (1984), and an acritarch assemblage from the upper shales of Cerro Largo Formation, consisting of *Paleorivularia ontarica*, *Chuaria olavarriensis* and *Leiosphaeridia* sp., was reported by Pöthe de Baldis and Cuomo (1983).

The Villa Fortabat depositional sequence, the youngest of the Sierras Bayas Group (Figs. 2 and 3), is a 40 m thick unit composed almost exclusively of reddish (lower section) and black (upper) micritic limestones originated by suspension fall-out in open marine ramp and lagoonal environments. This sequence is equivalent to the Loma Negra Formation (Poiré, 1993). The trace fossils *Helminthopsis* isp. and probable medusa resting traces have been recorded (Poiré et al., 2003).

The Sierras Bayas Group is overlain by the Cerro Negro Formation (Barrio et al., 1991) with erosional unconformity. This surface has been related to a eustatic sea-level fall. Erosion and meteoric dissolution of the carbonate sediments formed a karstic surface onto which residual clays and brecciated chert were deposited. Furthermore, phosphate nodules are common at this level, perhaps resulting from apatite recrystallization of amorphous phosphate under oxidizing conditions (Leanza and Hugo, 1987).

The Cerro Negro Formation (La Providencia depositional sequence; Figs. 2 and 3) exceeds 150 m in thickness, and is characterized by claystones and heterolithic, fine-grained sandstone–claystone intercalations, mainly formed in upper to lower tidal-flats. Skolithos-bearing marls and mudstones (Fig. 3) compose the lower part of the unit (Poiré et al., 2003). Acritarchs were reported by Cingolani et al. (1991), consisting of simple forms of Sphaeromorphis such as *Synsphaeridium* sp., *Trachysphaeridium* sp. and *Leiosphaeridia* sp. These authors suggested a Vendian age for the microfossil assemblages.

The Cerro Negro Formation can be correlated with equivalent successions in the central and south-eastern Tandilia System (Las Aguilas or Punta Mogotes formation, Figs. 1 and 2) of similar facies and composition (Spalletti and Poiré, 2000). The presence of diamictites between the crystalline basement and the Cambro–Ordovician Balcarce Formation is a peculiar feature reported in the El Volcán Hill (Sierra del Volcán Diamictites; Fig. 2). Either the whole Sierras Bayas Group is not preserved or those hills represent a paleo-high. The Balcarce Formation (Batán depositional sequence) discordantly overlies the Sierras Bayas Group, and probably reflecting an independent basin.

3. Sampling and methods

3.1. Sampling

Two detailed profiles located in the Tres Antenas and Cementos Avellaneda quarries (Figs. 1, 3 and 4) were surveyed and sampled in detail (see Tables 1 and 2). Dolostone samples from the Villa Mónica Formation were collected from the Tres Antenas quarry located near the town of Sierras Bayas, whereas the micritic limestones of the Loma Negra Formation, and marls from the Cerro Negro Formation were collected at the Cementos Avellaneda quarry near Olavarría (Figs. 1, 3

ERAS-PERIODS	STRATIGRAPHIC UNITS						DEPOSITIONAL SEQUENCES
	NW REGION		CENTRAL REGION		SE REGION		
ORDOVICIAN-CAMBRIAN	Balcarce Fm		Balcarce Fm		Balcarce Fm		Batán Sequence (V)
NEOPROTEROZOIC	Cerro Negro Fm		Las Águilas Fm		Sierra del Volcán Diamictites	Punta Mogotes Fm	La Providencia Sequence (IV)
	Sierras Bayas Group	Loma Negra Fm	Sierras Bayas Group	Loma Negra Fm			Villa Fortabat Sequence (III)
		Cerro Largo Fm		Cerro Largo Fm			Malegni Sequence (II)
		Villa Mónica Fm		La Juanita Fm			Tofoletti Sequence (I)
PALEO-MESO PROTEROZOIC	Buenos Aires Complex						

Fig. 2. Stratigraphic table for the Tandilia System. (Poiré et al., 2003, modified).

and 5). Outcrops were mapped in detail and stratigraphic profiles constructed. High resolution sampling allowed for a comprehensive microfacies and diagenetic study. Detailed petrography, combined with cathodoluminescence (CL), scanning electron microscope (SEM) and microprobe analyses were performed to select the most suitable samples for geochemical and isotopic analysis, avoiding recrystallized veins and fractures. Six new samples were collected from basal dolomite of the Villa Mónica Formation in the lowest part at the Piedra Amarilla Quarry, which was recently exposed during mining operations. These samples were analyzed for carbon and oxygen isotopes by A.J. Kaufman at the University of Maryland, and added to our database.

3.2. Methods

More than 50 polished thin sections were observed and evaluated with a high-resolution Leica DMLP petrographic microscope. Staining with alizarin red S was done to differentiate between and within carbonate (Dickson, 1966).

Polished thin sections were also observed with a Model 8200 Mk II (Waitley) cathodoluminescence stage with acceleration beam of 12–15 kV under vacuum at the Department of Geology at the RAU University.

Scanning electron microscope and energy dispersive system (EDS) analyses were carried out at SPECTRAU (RAU University) on polished thin sections, covered with carbon using the BIO-RAD carbon-coater from Poleron Division, to analyse textures by means of a JEOL JSM-5600.

The same thin sections were used for microprobe analyses with a CAMEBAX from Cameca at SPECTRAU (RAU University).

X-ray diffraction (XRD) analyses were carried out on fine meshed sample material (2–5 µm) (Moore and Reynolds, 1989), measured with a Philips PW 1011/00 diffractometer, with Cu lamp ($k\alpha = 1.5403$ Å) operated at 18 mÅ and 36 kV at the Centro de Investigaciones Geológicas (La Plata, Argentina). The samples were measured from 2 to 40° 2θ, in steps of 0.02°/2 s.

Selected samples were dissolved with weak HCl (0.1 M for limestones, 1 M for dolomites) for X-ray fluorescence analyses. Insoluble clastic material represented less than 5% of both limestones and dolostone samples, with the exception of those near to formation boundaries where higher concentrations (<15%) were observed. However, concentration of certain trace and major elements are not strongly elevated in the lower parts of the adjacent clastic successions (Table 2). The samples were crushed to finest mesh and processed to powder tablets and fused to glass-beads. The sample material was dried above 1200 °C twice in a muffle oven 1.5 h to establish the loss on ignition (LOI). Two press tablets were processed for each sample and Mn, Sr, Ca, Mg and Fe were measured with a Phillips PANANALYTICAL MAGIX PRO. The machine is operated at 50 kV and 50 mA. Detection limits for major elements are related to

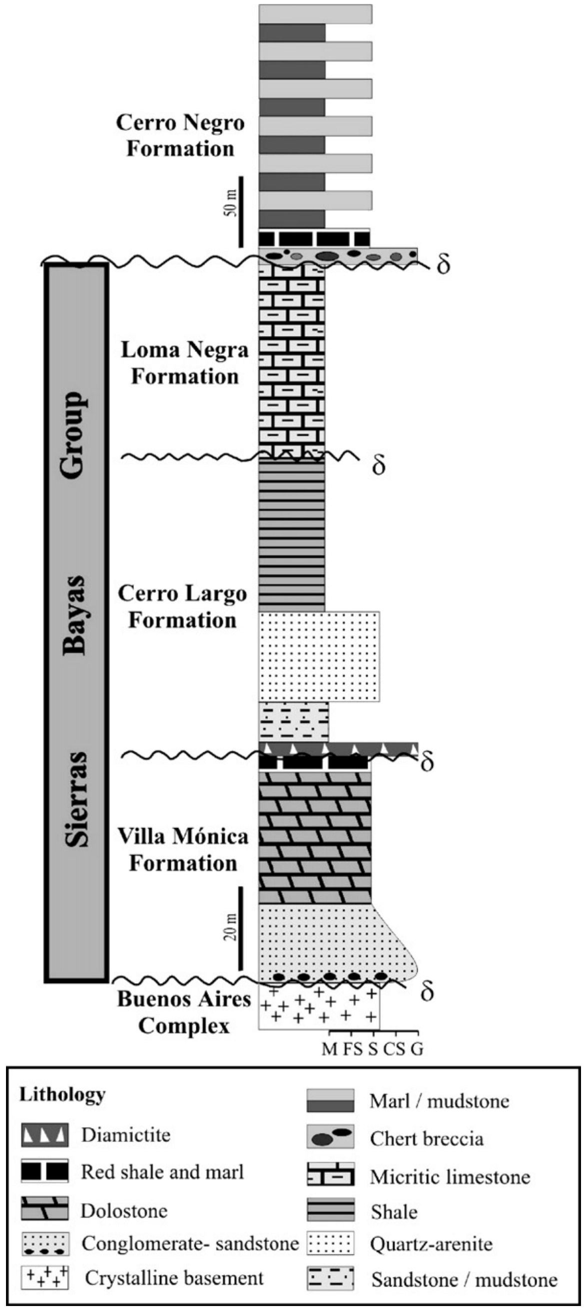

Fig. 3. Idealised stratigraphic column for the Neoproterozoic successions at Olavarría (Tandilia System). (δ = erosional unconformities; M = mud; FS = fine sand; S = sand; CS = coarse sand; G = gravel).

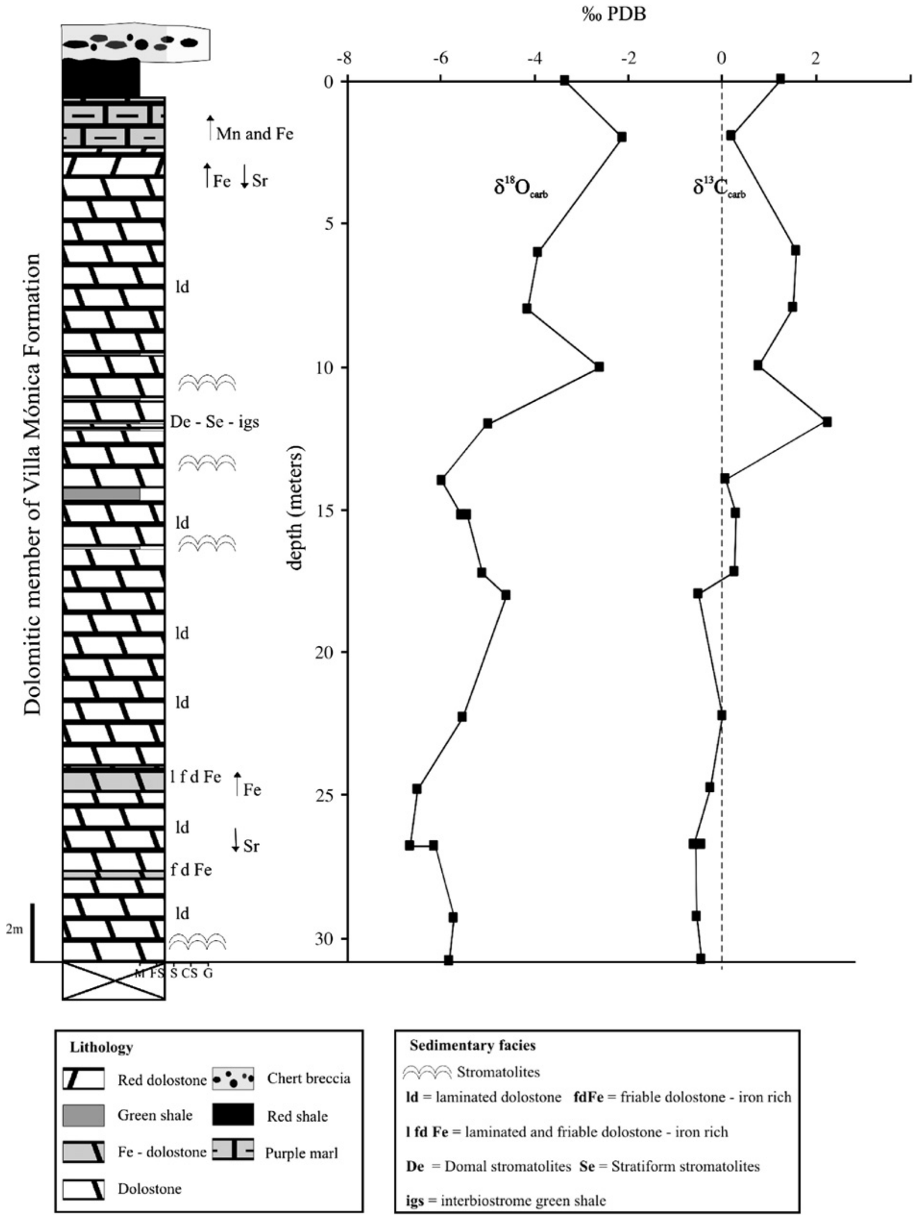

Fig. 4. $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$ (PDB) values for dolostone of the Villa Mónica Formation from the Tres Antenas Quarry, Tandilia System (see Fig. 1b).

the atomic number, with between 1 and 10 μg for medium to heavy elements. Precision is +/−0.5 (1σ), accuracy was controlled by repeated measurements of standards and each sample was measured twice. The errors of major elements vary between 0.5–2%. The data are presented in Tables 1 and 2. Loss on ignition measurements were carried out at the Department of Geology, the XRF analysis and sample preparation at SPECTRAU (RAU University).

Carbon dioxide from carbonates was liberated via phosphorylation at 50 °C (Wachter and Hayes, 1985). The organic carbon isotopic composition was determined via sealed-tube combustion of carbonate-free rock powder with CuO at 850 °C (Strauss et al., 1992). All stable isotope measurements were performed at the Geologisch-Paläontologisches Institut, Westfälische Wilhelms-Universität Münster, Germany, using a ThermoFinnigan Delta plus mass-spectrometer. Results are reported in the usual delta notation relative to the VPDB standard. Reproducibility as determined through replicate analyses was better than ±0.2‰. Analytical results are presented in Tables 1 and 2.

Table 1
Isotopic and geochemical composition of the dolostones and marls from Villa Mónica Formation, Sierras Bayas Group

Outcrop	Sierras Bayas																	
Formation	Quarry	Sample	Height (m)	Lithology–environment	Crystal size (µm)	TC (%)	TIC (%)	TOC (%)	$\delta^{13}C_{carb}$ (‰ PDB)	$\delta^{18}O_{carb}$ (‰ PDB)	Mn (ppm)	Sr (ppm)	Fe (ppm)	Mg/Ca	Sr/Ca × 1000	Mn/Sr	Fe/Sr	Ca/Sr
Villa Mónica	Tres Antenas	D 01`	0.0	ld–Tf	<250	12.23	11.6	0.66	−0.49	−5.83	348	25	6106	0.90	0.12	13.9	244	8491
Villa Mónica	Tres Antenas	D 03	2.0	ld–Tf	<200	12.66	11.9	0.77	−0.58	−5.74	348	29	6595	0.92	0.14	12.0	227	7196
Villa Mónica	Tres Antenas	D5									364	24	7085	0.85	0.11	15.0	293	9019
Villa Mónica	Tres Antenas	D 07	6.0	lfd–Tf	<75	12.57	11.7	0.90	−0.48	−6.14								
Villa Mónica	Tres Antenas	D 09	8.0	lfd–Tf	<50	12.50	11.6	0.93	−0.65	−6.67	348	16	7141	0.90	0.08	21.8	446	13,016
Villa Mónica	Tres Antenas	D 11	10.0	ld–Tf	<200	12.69	11.5	1.22	−0.29	−6.49	364	14	6791	0.90	0.07	25.4	474	13,838
Villa Mónica	Tres Antenas	D 13	12.0	ds–Pr	<150	11.15	10.2	0.92	−0.03	−5.55	418	4	7798	1.00	0.02	104.5	1950	44,973
Villa Mónica	Tres Antenas	D 15	14.0	ds–Pr	<125	11.88	11.2	0.66	−0.54	−4.59	372	9	11,834	0.81	0.04	43.6	1388	24,532
Villa Mónica	Tres Antenas	D 17	15.2	ds–Pr	<150	11.46	10.6	0.87	0.22	−5.12	472	24	10,561	0.93	0.13	20.0	447	7860
Villa Mónica	Tres Antenas	D 20	17.2	ds–Pr	<100	11.87	11.0	0.85	0.26	−5.43	488	30	10,799	0.88	0.15	16.4	363	6556
Villa Mónica	Tres Antenas	D 20	17.2	ds–Pr	<200	10.17	9.3	0.92	0.26	−5.57								
Villa Mónica	Tres Antenas	D 21	18.0	ds–Pr	<200	11.56	10.8	0.77	0.02	−5.97	379	18	8281	0.97	0.12	21.1	460	8327
Villa Mónica	Tres Antenas	D 25									426	25	9792	0.91	0.13	17.3	399	7470
Villa Mónica	Tres Antenas	D 31	22.28	ld–Tf	<250	12.79	11.9	0.91	2.20	−4.98	403	32	9002	0.89	0.15	12.6	282	6577
Villa Mónica	Tres Antenas	D 33	24.78	ld–Tf	<125	11.43	10.6	0.85	0.73	−2.60	945	4	22,690	0.90	0.02	258.2	6201	49,542
Villa Mónica	Tres Antenas	D 35	26.78	ld–Tf	<200	9.19	8.4	0.82	1.46	−4.16	1092	45	26,641	0.78	0.37	24.2	590	2677
Villa Mónica	Tres Antenas	D 35`	26.78	ldcm–Sp					1.52	−3.93								
Villa Mónica	Tres Antenas	D 37	29.29	lm–Sp	<25	4.34	4.0	0.37	0.15	−2.11	813	219	27,201	0.08	0.36	3.7	124	2789
Villa Mónica	Tres Antenas	D 38	30.78	ldcm–Sp	<30	9.33	8.5	0.83	1.21	−3.33	1169	41	23,207	0.90	0.27	28.7	569	3677
Villa Mónica	Piedra Amarilla	PA 0	0.0	Base					−1.14	−5.25								
Villa Mónica	Piedra Amarilla	PA 1	0.5	ds					−1.36	−5.64								
Villa Mónica	Piedra Amarilla	PA 2	1.0	ds					−1.10	−5.47								
Villa Mónica	Piedra Amarilla	PA 3	1.5	ds					−0.27	−5.82								
Villa Mónica	Piedra Amarilla	PA 4	2.0	ds					−0.99	−5.64								
Villa Mónica	Piedra Amarilla	PA 5	2.5	Matrix					−1.08	−5.29								
Villa Mónica	Piedra Amarilla	PA 6	2.5	Stromatolite					−1.07	−5.10								

Lithology: ld = laminated dolomite; lfd = laminated friable dolomite; ds = domed stromatolites; ldcm = laminated dolomitic calcitic marl; lm = laminated marl.
Environment: Tf = tidal flat; Pr = platform reef; Sp = supratidal pounds.

Table 2
Isotope and geochemical composition of the limestones from Loma Negra Fm (and its transition to Cerro Negro Fm), Sierras Bayas Group

Outcrop	OLAVARRIA																	
Formation	Sample	Litholology–environment	Crystal size (μm)	TC (%)	TIC (%)	TOC (%)	$\delta^{13}C_{carb}$ (‰PDB)	$\delta^{13}C_{org}$ (‰PDB)	$\Delta\delta^{13}C$ (‰PDB)	$\delta^{18}O_{carb}$ (‰PDB)	Mn (ppm)	Sr (ppm)	Fe (ppm)	Mg/Ca	Sr/Ca × 1000	Mn/Sr	Fe/Sr	Ca/Sr
Loma Negra	MR 2,6	orl–R	<35	11.0	10.8	0.24	3.8	−28.0	31.8	−13.5	519	362	4336	0.016	1.22	1.43	11.98	823
Loma Negra	MR 4,0	lrl–R	<20	9.9	9.9	−0.01	3.8			−13.4	418	378	5805	0.016	1.35	1.10	15.34	740
Loma Negra	MR 5,8	lrl–R	<20	9.6	9.5	0.08	4.0			−12.9	403	305	6980	0.015	1.07	1.32	22.85	934
Loma Negra	MR 6,7	lrl–R		9.2	9.2	0.03	4.2			−13.1								
Loma Negra	MR 8,0	lrm–R	<25	8.4	8.4	0.01	4.5	−27.8	32.3	−13.3	372	330	30761	0.048	1.96	1.13	93.35	511
Loma Negra	MR 9,0	lrl–R	<20	9.2	9.0	0.21	4.5			−13.1	287	315	3959	0.013	0.97	0.91	12.57	1035
Loma Negra	MR 10,0	lrl–R	<15	9.9	10.0	−0.04	3.6			−12.9	379	408	5938	0.012	1.46	0.93	14.54	684
Loma Negra	MR 11,0	lrl–R		10.0	10.0	0.05	3.7	−28.0	31.7	−12.4	356	401	10,512	0.015	1.50	0.89	26.21	667
Loma Negra	MR 12,2	lrl–R		10.0	9.9	0.15	3.5	−27.2	30.7	−12.6	387	374	6442	0.013	1.31	1.04	17.24	762
Loma Negra	MR 13,0	lrl–R	<30	10.5	10.6	−0.05	3.5			−12.5	379	374	6190	0.014	1.30	1.01	16.54	772
Loma Negra	MR 14,1	lbl–L	<30	10.7	10.8	−0.07	3.2			−11.5	318	333	3889	0.011	1.07	0.95	11.67	932
Loma Negra	MN 15,4	lbl–L		11.1	10.8	0.28	3.1			−11.2								
Loma Negra	MN 16,3	lbl–L		11.2	10.9	0.33		−26.7	26.7		364	342	2874	0.011	1.06	1.06	8.40	942
Loma Negra	MN 17,3	lbl–L	<15	10.8	10.7	0.14	3.8	−27.2	31.0	−7.9	333	401	4322	0.010	1.27	0.83	10.79	788
Loma Negra	MN 18,3	lbl–L		11.1	10.8	0.28	3.6	−27.4	31.0	−7.8	418	352	3993	0.009	1.09	1.19	11.34	915
Loma Negra	MN 19,4	lbl–L		10.8	10.7	0.14	3.4	−27.2	30.6	−7.8	318	328	2840	0.011	1.01	0.97	8.67	994
Loma Negra	MN 20,4	lbl–L		10.7	10.5	0.21	3.1	−27.4	30.5	−7.0	356	297	6302	0.012	0.91	1.20	21.20	1093
Loma Negra	MN 21,2	lbl–L		10.8	10.8	−0.03	3.0			−7.1	449	366	5805	0.011	1.16	1.23	15.88	859
Loma Negra	MN 22,3	lbl–L	<30	10.6	10.6	0.00	2.8	−27.9	30.7	−7.1	356	340	3560	0.009	1.04	1.05	10.47	966
Loma Negra	MN 23,0	lbl–L		11.1	11.0	0.04	2.8	−28.1	30.9	−7.1								
Loma Negra	MN 24,2	lbl–L	<30	11.0	11.0	0.06	3.1			−7.4								
Loma Negra	MN 25,6	lbl–L	<30	11.1	11.0	0.04	3.3			−7.7	341	337	3029	0.010	1.02	1.01	8.98	985
Loma Negra	MN 26,3	lbl–L	<30								426	401	5896	0.010	1.29	1.06	14.70	772
Loma Negra	MN 27,0	lbl–L	<30	11.6	11.2	0.35					457	398	4127	0.009	1.23	1.15	10.36	813
Loma Negra	MN 28,0	lbl–L		11.2	11.1	0.12	3.6	−28.0	31.6	−8.1	418	371	3497	0.010	1.10	1.13	9.41	911
Loma Negra	MN 29,0	lbl–L		11.0	10.9	0.08	3.7	−27.1	30.8	−8.8	434	391	4211	0.009	1.18	1.11	10.77	850
Loma Negra	MN 30,0	lbl–L	<30	11.1	11.1	0.04	3.4			−9.2								
Loma Negra	MN 31,0	lbl–L	<30	10.8	10.9	−0.02	3.4			−10.1	426	348	4567	0.011	1.08	1.23	13.14	926
Loma Negra	MN 32,0	lbl–L	<30	10.9	10.9	0.07	2.7			−10.7	410	353	4148	0.01	1.09	1.16	11.74	918
Loma Negra	MN 33,0	lbl–L	<30	11.5	11.3	0.21	3.2	−27.4	30.6	−12.1	356	346	4651	0.01	1.03	1.03	13.45	970
Loma Negra	MN 34,0	lbl–L		11.3	11.3	0.04	3.2			−12.0	341	347	3427	0.010	1.06	0.98	9.88	939
Loma Negra	MN 35	lbl–L	<30	10.9	11.1	−0.15	3.6			−12.7	287	343	3595	0.012	1.05	0.84	10.49	955
Loma Negra	MN 36	lbl–L		9.9	9.8	0.03	3.5	−27.2	30.7	−12.9	596	321	11,562	0.017	1.02	1.86	36.06	983
Loma Negra	MN 37	lbl–L	<10	10.6	10.7	−0.02	3.1			−14.1	287	439	3609	0.015	1.31	0.65	8.23	765
Cerro Negro	Mar-41	tbm–Tsw	<15	10.2	10.0	0.16	3.5			−13.9								
Cerro Negro	Mar-42	tbm–Tsw	<15	9.1	9.1	−0.02	3.9			−13.9								
Cerro Negro	Mar-43	tbm–Tsw	<15	9.7	9.7	0.00	4.3	−28.0	32.3	−14.1								

Lithology: orl = ondulitic redish lime–mudstone; lrl = laminated redish lime–mudstone; lbl = laminated black lime–mudstone; and tbm = thin bedded marl.
Environments: R = ramp; L = lagoon; Tsw = transgressive shallow water.

We used various techniques to identify the least altered samples in our collection, as only little altered materials are useful for evaluating primary depositional isotope trends (e.g. Veizer, 1983; Derry et al., 1992; Bartley et al., 2001 and herein). Macroscopic selection and microscopic studies helped to avoid samples containing veins and other neo-formed carbonate minerals during fluid flow through the rocks, clays and micas. Strongly oxidised samples were considered unsuitable for isotopic correlation. Samples showing bright luminescence were considered suspect, and highly luminescent phases were avoided. In carbonates, luminescence is activated by high concentrations of Mn and quenched by high concentrations of Fe (Marshall, 1988). Samples preferred for isotope analyses were only non- to moderately-luminescent (Knoll et al., 1995).

4. Results

The difference in composition between a carbonate rock (and the water from which it precipitated) and a diagenetic fluid is the primary factor in determining the rate and extent of elemental and isotopic exchange. Several theoretical, experimental and analytical studies of carbonate diagenesis have been undertaken over the past two decades (Brand and Veizer, 1981; Veizer, 1983; Jacobsen and Kaufman, 1999; Anadón et al., 2002), and some generalisations about carbonate alteration have emerged. However, each carbonate succession shows a unique history of diagenetic alteration that can be elucidated only by detailed petrographic and geochemical studies, which incorporate a comprehensive diagenetic analysis. Such an analytical approach provides a reasonable basis for the interpretation of stable isotope data.

4.1. Petrography

Thin sections of stromatolitic and micritic carbonates were evaluated for grain size, degree of recrystallization, as well as the abundance of authigenic and detrital components, stylolites, veins, and alteration processes associated with surface weathering. The objective was to assess the complete diagenetic history of the rocks.

4.1.1. Dolostones of the Villa Mónica Formation

Four main types of dolostones were identified:

Type 1 dolostone occurs as an idiotopic mosaic of rhombohedral crystals of dolomite ranging in size from 10 μm to more than 150 μm. The phases were generally uniformly recrystallized to microsparite–sparite (<60 mm), but in some cases recrystallization resulted in even larger grain sizes and destruction of primary sedimentary fabrics.

Type 2 dolostone is the principal constituent of columnar stromatolites and is much finer grained. This type consists of subhedral to euhedral and occasionally anhedral crystals, up to 50 μm in size and a hypidiotopic to idiotopic texture.

Type 3 dolostone is characterized by centimetric red brownish mottles, where rhombohedral dolomite crystals are zoned. Those crystals contain concentric, alternating zones of iron-rich (red) and iron-poor (clear) dolomite that marks stages of growth of the rhombohedral grains. The clear inter-mottled dolomite is formed by rhombohedral limpid crystals. The crystal size ranges from 30 to 150 μm.

Type 4 dolostone constitutes a cement of dolosparite with planar euhedral rhombohedras. The grain size is variable ranging between 100 and 750 μm. This cement is typically concentrated in voids along inter-crystalline boundaries. The crystals may coalesce to form dense mosaics, and their formation being thus controlled by inter-crystalline porosity.

Dolostone samples frequently include calcite cements in voids and veins, which are composed of euhedral to anhedral, limpid crystals of pure or ferroan calcium carbonate. Crystal-sizes vary from 500 μm to 2 cm.

Quartz often occurs as silt-sized clasts dispersed in the dolomite matrix, as well as multi-generational cement inside voids. Occasionally silica is present as fine chert, which fills voids or replaces carbonate. This is evident in thin section due to the presence of carbonate cleavage shadows. Furthermore, chert filled veins also appear penetrative and continuous.

Illite clay and other accessory minerals were also identified in the petrographic analysis. The former is composed of fibrous aggregates in form of mainly non-oriented fans, which occupy voids and pores. Accessory minerals, not specifically identified include iron oxides and different clay minerals filling irregular fracture planes.

Stylolites are an important fabric component in the dolomite samples. Whereas some of them show only a single dissolution plane, others show multiple planes accentuated by concentrations of quartz, illite and undifferentiated material. It is common to identify hummocky, columnar and high-amplitude peaked stylolites based on the classification by Logan and Semeniuk (1976).

Organic-rich layers occur in the interior of stromatolites where dolomite crystals range from 20 to 50 mm with a xenotopic to idiotopic texture. These are differentiated from detrital layers by their larger crystal size (ranging from 100 to 200 mm) and predominant idiotopic texture. In the detrital layers the replacement of dolomite by chert is occasionally observed, but crystal morphologies are maintained.

Microprobe analyses indicate that some rhombohedral dolomite was completely replaced by Fe-oxides or chert.

Mineralogical compositions of samples were also determined by X-ray diffraction and approximate abundances calculated. Dolomite represented some 75-95% of the samples with less amounts of calcite (1–5%), quartz and chert (1–15%), clay minerals (<2%) and feldspar (<1%). Insoluble acid residue (IAR) was also quantified and it was found that siliciclastic material present in these rocks ranged between 4.7% and 16.8%. It is significant that in type 3 dolostone a distinction can be made between the clear sparitic base and the reddish mottles, with IAR values of 6.6% and 14% respectively, which suggest diagenetic selectivity, since the rhombohedral crystals of the mottles contain abundant goethite. Goethite also appears as smooth nodules < 8 cm in diameter in some samples.

4.1.2. Micritic limestones — Loma Negra Formation

The Loma Negra Formation is made up entirely of micritic limestones (grain size up to 35 μm), which are divided in two main types. *Type A:* reddish micritic limestones (rml) rich in chlorite and illite, and *Type B:* black micritic limestones (bml) rich in organic matter.

The micritic limestones samples preserve a homogeneous micritic to microsparitic calcite with xenotopic texture. Silica-rich fluids penetrated into the uppermost few centimeters of the limestone dominated formation, which is recognized as a karstic surface (or Unit 3, Fig. 5).

Microprobe analysis shows that crosscutting veins are filled by sparitic to sub-sparitic calcite and very fine-grained chert (up to 5 μm), whereas illite, chlorite and different Fe-oxides fill irregular stylolites.

Under cathodoluminescence, the volumetrically dominant, fine-grained base of the limestones is

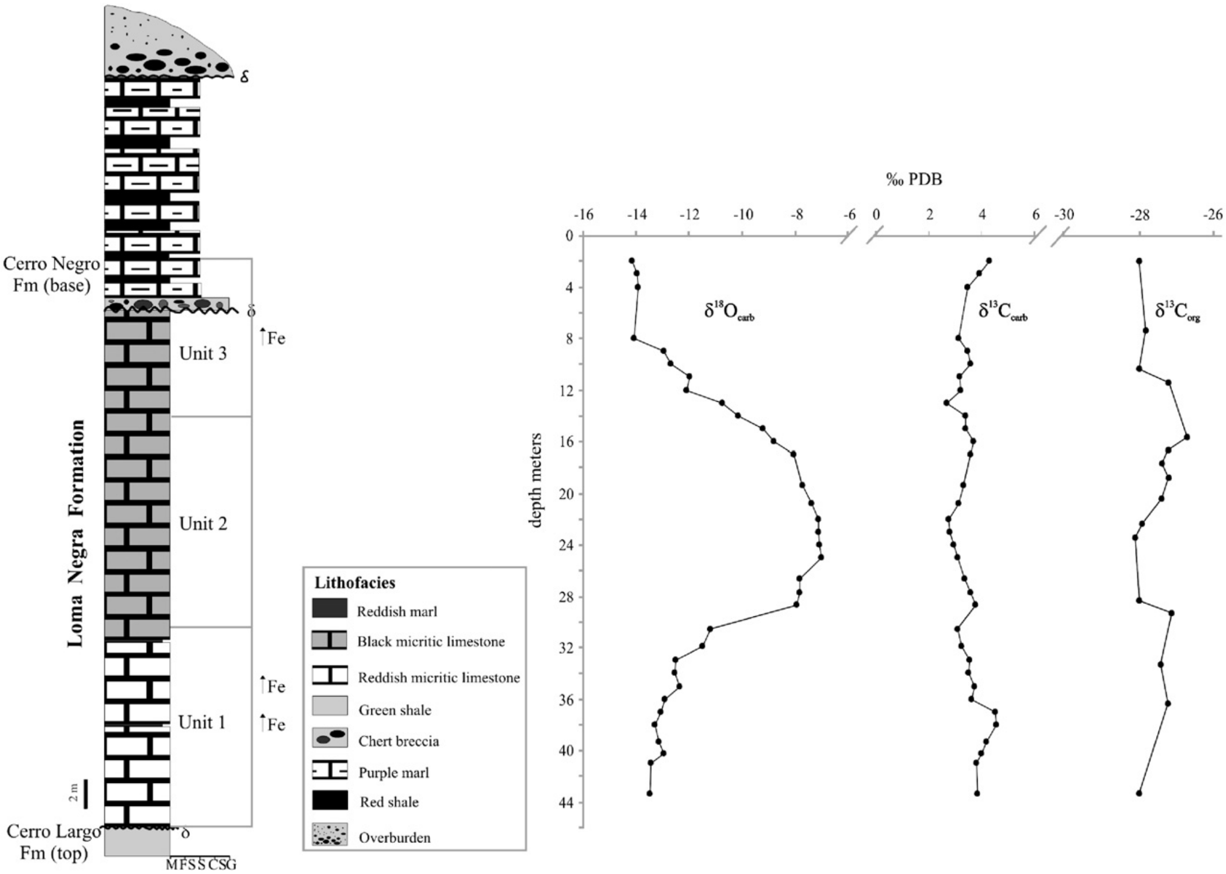

Fig. 5. $\delta^{13}C_{carb}$ $\delta^{13}C_{org}$ and $\delta^{18}O_{carb}$ (PDB) values for the Loma Negra Formation and its transition to the Cerro Negro Formation (Cementos Avellaneda Quarry, Tandilia System, Fig. 1b). Note the strong excursion $\delta^{18}O_{carb}$ in the central part of the profile. $\delta^{13}C_{carb}$ do not correlate with fluctuations in $\delta^{18}O_{carb}$. (for further discussion see text; abbreviations as in Fig. 3).

composed of non-luminescent calcite. Clear luminescent calcite generation could be observed inside small veins and voids. Two different classes of veins occur. The former (up to 250 μm wide) shows a low orange luminescent calcite, whereas the later (up to 30 μm wide), which crosscuts the earlier, contains bright yellow luminescent calcite.

The following mineralogical abundances for the Loma Negra Fromation samples arise from X-ray diffraction analyses: calcite 70–95%, quartz and chert 1–15%, and clay minerals <5%. Insoluble acid residues (IAR) of carbonate range between 3.6% and 30.6% with black micritic limestone samples exhibiting somewhat lower average values. Residues were mainly composed of quartz, chert, chlorite, illite, Fe-oxides, and small rounded zircon crystals.

4.1.3. Clastic sequences

Fine-grained conglomerates, quartz–arenite, arkosic sandstone and shale dominate the lower Villa Mónica Formation (Fig. 3). Shale also occurs as thin intercalations between biostrome dolostone beds and as a red stained horizon in the uppermost Villa Mónica Formation. Sandstone intervals are texturally mature. Quartz grains are sub-angular and moderately sorted. Large plagioclase grains, all altered to albite, are more abundant than alkali-feldspar. Accessory minerals include illite and smectites, hematite, muscovite and a Ti-phase as well as calcite and dolomite. In one section (Villa Mónica quarry) basal sandstone, representing a paleosol, is overlain by a thin conglomerate and sandstone; these lithologies are capped by stromatolitic dolostone. The overlying Cerro Largo Formation is dominated by very well rounded quartz–arenites and shales, as well as hetherolitic facies. Accessory minerals present in the quartz–arenite are muscovite, several Fe-oxide phases, illite, smectite, illite–smectite mixed-layers and kaolinite, as well as magnetite, rutile and apatite. The Cerro Negro Formation comprises mainly shales and silt- to sandstones. These rocks are texturally less mature than those from the Cerro Largo Formation and show a similar mineralogical composition, but also include chlorite and chlorite–smectite mixed-layers. Quartz is less rounded and most of the clastic components are finer grained than those from the Cerro Largo Formation.

4.2. Diagenesis

The magnitude and direction of chemical changes in carbonate rocks depend on the stability of original carbonate phases, the water/rock ratio, the difference in chemical composition of seawater and meteoric water, and the deviation of any particular partitioning coefficient (fractionation factor) from unity (Brand and Veizer, 1981). Strontium and Manganese are good indicators for diagenetic alteration, since one is abundant in seawater and the other in fresh water (Brand and Veizer, 1981; Veizer, 1983). To interpret secular trends of C and Sr isotopes in seawater a low Mn/Sr is deemed necessary (Derry et al., 1992; Kaufman et al., 1993; Knoll et al., 1995; Jacobsen and Kaufman, 1999). Rocks of Neoproterozoic age, which fulfill this precondition, are rare. However, comparisons within and between basins can be made if the analyzed rocks and their diagenetic histories are well established. With few exceptions, Sr-isotope data in dolomites appears to be strongly altered and consequently they must be excluded from further considerations (Derry et al., 1992; Kaufman et al., 1993).

Diagenetic effects can be deciphered by careful investigation of variations in major and trace element concentration (Ca, Fe, Mn and Sr) as well as oxygen isotopic compositions of carbonate rocks. These studies reveal diagnostic alteration trends resulting from interaction of unaltered marine sediments with diagenetic fluids (Veizer, 1983; Jacobsen and Kaufman, 1999).

According to Fölling and Frimmel (2002), limestone is considered to be “unaltered” when Mn/Sr < 1.5 and $\delta^{18}O > -10‰$. Therefore, $\delta^{18}O$ values between −10 and −14‰ are interpreted as slightly altered, and samples with $\delta^{18}O < -14‰$ are clearly altered.

Additionally, insofar as most dolostones have lower Sr and higher Mn than limestones, they are often considered unaltered when Mn/Sr < 3, Fe/Sr < 50, and $\delta^{18}O > -10‰$ (of Bartley et al., 2001). Those authors demonstrated that Mn/Sr < 10 appear to be little altered and higher ratios (> 10) should correlate with anomalous $\delta^{13}C$ values, suggesting diagenetic alteration.

4.2.1. Villa Mónica Formation

The paragenesis of Villa Mónica Formation samples began with the development of a dolomitic mosaic, where crystals recrystallized from a micritic precursor either uniformly or in steps. The mosaics probably grew from a primitive low-Mg-calcite precursor early during compaction and lithification. Later these samples were further dolomitized during deep burial conditions.

Additionally, three stages of cementation can be distinguished: *Stage 1*: dolosparitic cement (100 to 750 μm); *Stage 2*: quartz cement, (500 μm to 7 cm); and *Stage 3*: high-Mg-calcite (HMC) cement (~650 μm); (see Section 4.1.1).

All these cements fill voids and fractures up to 15 cm in width and diameter respectively and their origin is likely related to the interaction of rock and meteoric fluids at low temperatures.

4.2.2. Loma Negra Formation

In the micritic limestones facies, the following diagenetic processes are interpreted:

Stage 1: Neomorphism of the micrite precursor to microsparite (1–10 μm), microsparite (10–25 μm) or sparite preserving the existing microstructure (1–25 μm).
Stage 2: Chemical dissolution generating porosity in form of veins and vugs.
Stage 3: Precipitation of calcite cements filling porosity generated in Stage 2.
Stage 4: Pressure-solution producing irregular stylolites and their mineralogical components.
Stage 5: Silicification caused by precipitation of silica gels along veins and as partial replacement of carbonate crystals.

The later processes (stage 5) more pervasively affected the uppermost part of the unit. Limestone of the Loma Negra Formation is mainly composed of diagenetic low-Mg-calcite (LMC) exhibiting <4 mol% of $MgCO_3$ (Veizer, 1983).

4.3. Geochemistry and stable isotopes

Mineralogical stabilization during carbonate diagenesis involves dissolution–reprecipitation processes during which reaction occurs between the sediment/ sedimentary rock and a fluid phase. Solutions may be either seawater during very early stages of marine diagenesis, formation waters during burial diagenesis or meteoric water during later (sometimes much) stages of near surface diagenesis. Such reactions alter the original trace element and isotopic composition (e.g. Brand and Veizer, 1981). The magnitude of changes depends on a multitude of causes, most importantly the compositional difference between water and rock, the water to rock ratio, and the reaction time.

Throughout the years, several proxy signals, sensitive to diagenesis, have been developed as quality criteria in assessing the degree of post-depositional alteration (e.g., Kaufman et al., 1993; Kaufman and Knoll, 1995; Jacobsen and Kaufman, 1999). Most prominently, Mn/Sr ratios <2 and $\delta^{18}O$ lower than −10‰ are viewed as reflecting a moderate degree of diagenetic alteration, leaving the carbonates still suitable for a chemostratigraphic interpretation of their carbonate carbon and strontium isotopic compositions. Furthermore, a homogenous isotopic difference of 28–32‰ between the carbonate and organic carbon isotopic composition ($\Delta\delta=\delta^{13}C_{carb}-\delta^{13}C_{org}$) has been regarded as reflecting little alteration of the carbon isotopic composition as a consequence of microbial reworking and/or substantial thermal alteration of sedimentary organic matter.

The effects of diagenesis on $\delta^{13}C$ values can often be recognized in $\delta^{13}C$ vs. $\delta^{18}O$ plots (c.f. Jacobsen and Kaufman, 1999). Such plots have similarly been used to infer depositional environments (Williams, 1979; Anderson and Arthur, 1983).

In a $\delta^{13}C$ vs. $\delta^{18}O$ diagram (Fig. 6) from Villa Mónica and Loma Negra Formations is possible to distinguish five distinct fields, according to the kind of rock analyzed. The different clusters represent different facies and/or depositional environments, including: (i) dolostone deposited on a stromatolitic platform; (ii) dolostone, shale and marls in a tidal-flat facies; (iii) reddish micritic limestone (rml) deposited on a carbonate-ramp; (iv) black micritic limestone (bml) from a lagoonal environment; and (v) red marl (rm) representing transgressive shallow water facies (Poiré, 1993).

As mentioned above, based on the complexity of carbonate precipitation and the strong facies dependence, geochemical variations in the same succession could be produced by similar diagenetic processes. Furthermore, composition of meteoric water during the Neoproterozoic is not well established and mixing scenarios remain hypothetical. In addition to the facies change recorded by Poiré (1993), the compositional difference we here present here allow us to better understand the various isotope signatures of lithologies.

4.3.1. Dolostone — Villa Mónica Formation

Abundances of total, carbonate and organic carbon (Table 1) identify most samples from the Villa Mónica Formation as dolostone containing on average 0.8% organic carbon. Lower values for total inorganic carbonate in the uppermost samples likely reflect a higher content of siliciclastic material. $\delta^{13}C$ values vary between −0.65 and +2.20‰. $\delta^{18}O$ values range from −6.67 to −2.11‰. This results are from the Tres Antenas Quarry (middle and upper section) in which the basal section were not exposed. The most recent analyses of samples from the basal section of the dolomitic member reveal negative $\delta^{13}C$ values ranging from −1.36 to −1.00‰ and $\delta^{18}O$ values from −5.82 to −5.10‰.

On the other hand, many samples from the Villa Mónica are regarded as diagenetically altered, as

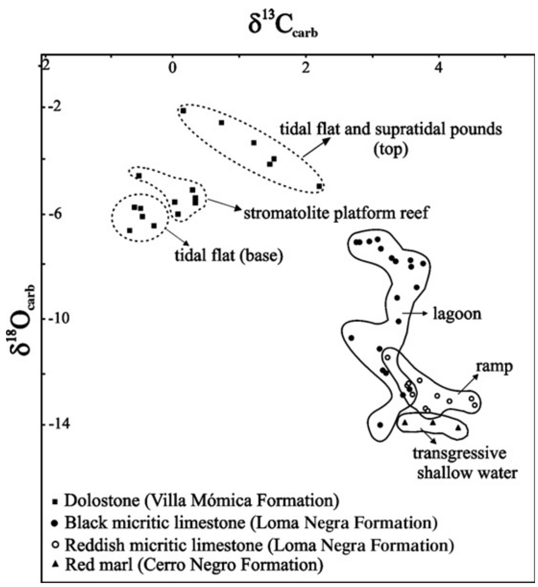

Fig. 6. $\delta^{13}C_{carb}$ vs. $\delta^{18}O_{carb}$ for the Villa Mónica and Loma Negra Formations and the basal Cerro Negro Formation. It is possible to distinguish six fields according to the depositional environment of the analyzed rocks, (see text for further discussion).

discernible from very low Sr concentrations and strongly elevated Mn and Fe concentrations. In particular, the top part of this unit, containing a higher proportion of siliciclastic material, preserves the highest Mn and Fe concentrations. Microprobe analyses show replacement of rhombohedral dolomite nuclei by Fe-oxides (mainly goethite). All features point to a rather pervasive alteration of the Villa Mónica dolostone with an iron-rich fluid. This is reflected in high ratios of Mn/Sr and Fe/Sr (Figs. 7 and 8). Fig. 7 shows $\delta^{13}C$ vs. Mn/Sr and $\delta^{13}C$ vs. $\delta^{18}O$ cross plots.

Applying the above mentioned criteria for assessing the diagenetic alteration of carbonates, the elevated Mn/Sr ratios (> 10) particularly reflect strong alteration. Following Kaufman et al. (1993) and others, carbonate carbon and strontium isotope data have to be regarded as too strongly altered, most likely shifted in a substantial way from their primary isotopic composition.

On the other hand, the oxygen isotopic compositions for all Villa Mónica samples are significantly enriched, which is contrary to the expectation for diagenetically altered carbonates. In fact, towards the top of the interval $\delta^{18}O$ values rise to as high as –2‰. We consider that the higher $\delta^{18}O$ values may reflect partial equilibration with ^{18}O enriched siliciclastics or seawater that has been strongly evaporated.

4.3.2. Loma Negra Formation

This sequence can be divided in three units (Fig. 5) based on petrographic observations. Unit 1 (MR 2.6 to MN 16.3) is comprised of reddish micritic limestones (rml). It is followed by black micritic limestones from

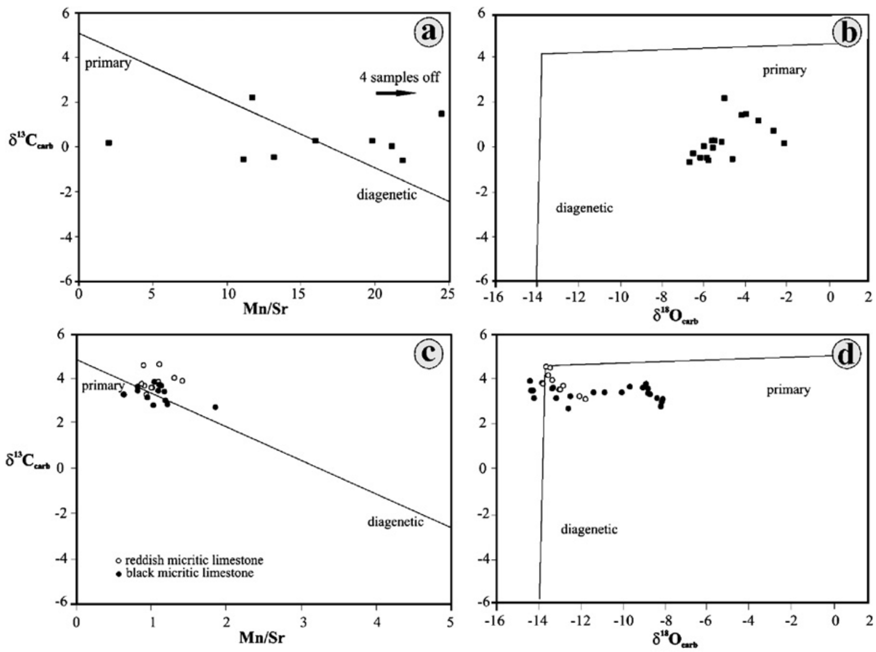

Fig. 7. Diagrams of elemental ratios against isotopic data for Villa Mónica and Loma Negra Formations (after Jacobsen and Kaufman, 1999).

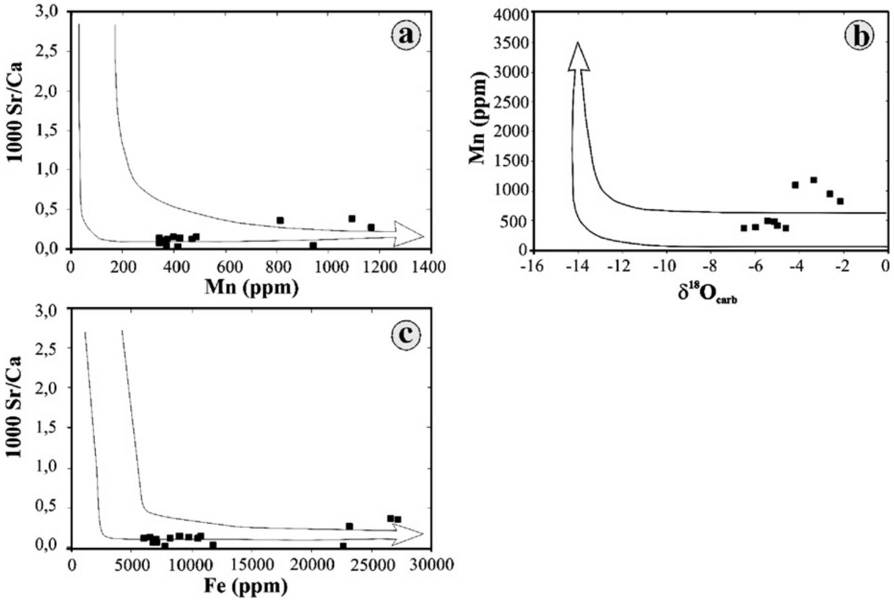

Fig. 8. Diagrams relating element concentrations and isotope data for the Villa Mónica Formation. (a) Sr/Ca (× 1000) vs. Mn (ppm), (b) Mn (ppm) vs. δ^{18}O and (c) Sr/Ca (×1000) vs. Fe (ppm). Arrows indicate generalised alteration trends during diagenesis. (after Veizer, 1983).

Unit 2 (MN 17.3 to MN 28). Finally, Unit 3, which includes the uppermost black micritic limestones as well as marls of the basal Cerro Negro Formation, (MN 29 to Mar 43) reflects a stronger influence of siliciclastic material to the top. Field observations indicate that diagenetic alteration and fluid flow were more pronounced in the upper portion of this unit, particularly in the contact whit the disconformably overlying Cerro Negro Formation.

Trace element data are distributed rather uniformly across the entire Loma Negra Formation with an average Sr concentration of 360 ppm, an average Mn concentration of 390 ppm and an average Fe concentration of 5900 ppm. Most Mn/Sr values are <1.5, suggesting a somewhat low degree of diagenetic alteration (Fig. 7c and d).

Interestingly, the oxygen isotopic composition for samples from the Loma Negra Formation displays a clear stratigraphic variation reflecting petrographic differences observed in thin section. δ^{18}O values between −13.5 to −11.2‰ characterize the reddish micritic limestones from Unit 1. The black micritic limestones in Unit 2 display substantially less negative values, ranging from −7.9 to −7.1‰. Towards the top of the succession (Unit 3), the δ^{18}O values become as negative as −14.1‰. No other geochemical parameter studied here shows a comparable stratigraphic variation. It is unclear whether this unusual distribution in δ^{18}O is related to the late diagenetic silicification (diagenetic Stage 5) or whether this could even reflect some preserved near-primary feature. Fig. 9 shows Sr/Ca vs. Mn (ppm); Mn (ppm) vs. δ^{18}O; Sr/Ca vs. Fe (ppm); and Sr (ppm) vs. ^{87}Sr/^{86}Sr for the Loma Negra Formation all geochemical parameters point to a generally unaltered suite of limestones.

Based largely on the even stratigraphic distribution of trace element compositions throughout the Loma Negra Formation, but also acknowledging the fact that no correlation exists between the δ^{18}O data and any trace element composition or ratio, we regard the carbon isotope data for the Loma Negra Formation as near-primary seawater signal. δ^{13}C values are all positive, ranging from +2.8 to +4.5‰. Such data are consistent with carbon isotope values for other Neoproterozoic carbonate successions. Based on a simple mass balance consideration, they reflect the enhanced proportional burial of sedimentary organic matter in the depositional basin (e.g., Hayes et al., 1999). Alternatively, Rothman (2002) proposed a sluggish carbon turnover in the Neoproterozoic global ocean as a plausible cause for ^{13}C-enriched carbonate carbon.

Finally, the difference between the carbonate and organic carbon isotopic compositions ($\Delta\delta$) recorded for the Loma Negra Formation varies from 30.5 to 32.3‰, with no discernible stratigraphic variation, (Fig. 5). The latter suggests that the organic matter has not been post-depositionally altered to any great extent. This range in $\Delta\delta$ indicates photosynthetic carbon fixation. Neither

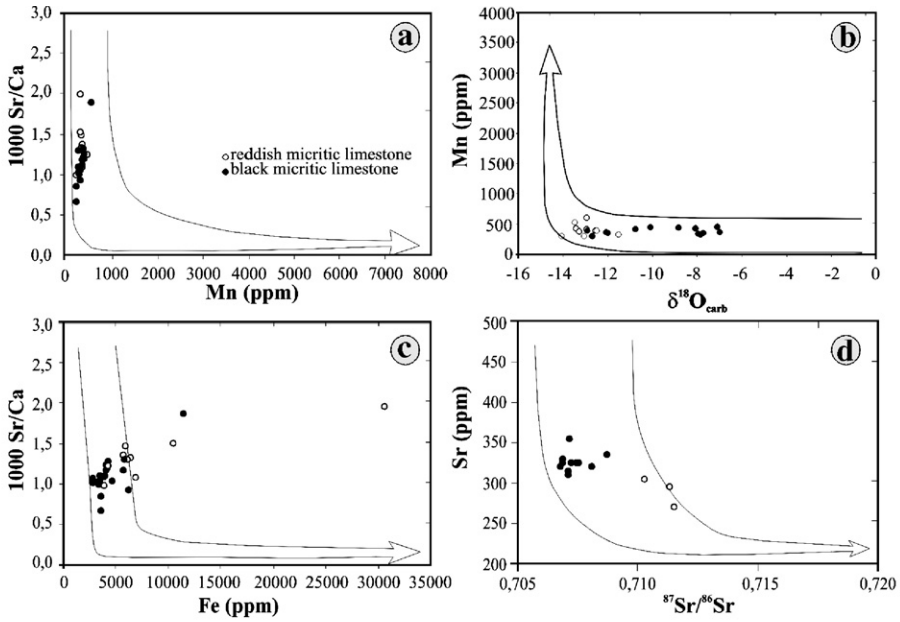

Fig. 9. Diagrams relating element concentrations and isotope data for the Loma Negra Formation. (a) Sr/Ca (×1000) vs. Mn (ppm), (b) Mn (ppm) vs. $\delta^{18}O$ (c) Sr/Ca (×1000) vs. Fe (ppm) and (d) Sr concentration (ppm)/$^{87}Sr/^{86}Sr$ diagrams. Arrows indicate generalised alteration trends during diagenesis (cf. Veizer, 1983; Bartley et al., 2001). Sr concentration (ppm) and $^{87}Sr/^{86}Sr$ data from Kawashita et al. (1999a,b).

enhanced thermal maturation nor a substantial contribution of ^{13}C depleted bacterial biomass is indicated.

5. Implications of the geochemical and isotopic data

5.1. Sediment diagenesis

Elemental composition and oxygen isotope data are regarded as sensitive indicators of carbonate diagenesis, usually combined with petrographic and/or cathodoluminescence studies (e.g., Brand and Veizer, 1981; Kaufman et al., 1993). Both units studied here, the Villa Mónica Formation and the Loma Negra Formation, display their own unique and equally complex compositional features.

For the Villa Mónica Formation four different types of dolostone can be distinguished. They differ in grain size and content of insoluble siliciclastic components. The entire unit displays high Mn and Fe and low Sr abundance as well as high Mn/Sr and high Fe/Sr ratios (Table 1, Figs. 7a, 8a and c). Such values point to severe diagenetic alteration rendering these carbonates unsuitable for an assessment of their primary carbon and strontium isotopic compositions. Stratigraphic distributions documents the highest Mn and Fe values for the uppermost marly portion of the formation. It is interesting to note, however, that the significant diagenetic alteration of elemental compositions did not result in a concomitant change to more ^{18}O depleted oxygen isotope values. In fact, based solely on the $\delta^{18}O$ data, the Villa Mónica dolostones would pass the commonly applied threshold of $\delta^{18}O > -10‰$ (Table 1, Figs. 7b and 8b).

Nonetheless, the observations concerning carbonate diagenesis for the Villa Mónica Formation clearly indicate a severe loss of Sr and the addition of Mn and Fe.

The commonly observed shift towards more negative $\delta^{18}O$ values as a consequence of meteoric diagenesis is not indicated. In addition, strongly negative $\delta^{13}C$ reflecting the incorporation of carbon dioxide from recycled sedimentary organic matter, is equally absent from this unit. Furthermore, no positive correlation exists between the carbonate carbon and oxygen isotopic compositions (Figs. 4, 7b and 8b).

Rocks from the Loma Negra Formation are entirely micritic limestone; these are, reddish in the lower 8.3 m followed by black micrites for the remaining part of this unit. Despite the petrographic evidence for fluid flow and recrystallization, a uniform stratigraphic distribution of elemental abundance and ratios suggest only a moderate degree of diagenetic alteration. No severe loss of Sr and no significant increases in Mn and Fe, as observed in the Villa Mónica Formation, characterize the carbonates in the Loma Negra Formation (Figs. 7, 8 and 9). Either the compositional difference between the original carbonate and the diagenetic fluid was small and/or the diagenetic system was buffered by the rock composition (low water–rock ratio). Furthermore, low organic carbon abundance and positive $\delta^{13}C$ values throughout the entire succession suggest that microbial reworking of sedimentary organic matter did not alter carbon isotopic compositions. In sum, we consider the micritic limestones of the Loma Negra Formation and their carbon isotope data as near-primary in composition. They would, thus, be suitable for evaluating the original seawater carbon isotopic composition.

What remains somewhat enigmatic is the stratigraphic distribution of the oxygen isotope data, where the middle portion between 8.3 and 16.5 m display $\delta^{18}O$ values that are 3‰ heavier than the underlying and overlying parts of this section (Fig. 5). The upper part of the Loma Negra Formation (Unit 3) exhibits an evolution towards more negative $\delta^{18}O$ values. Field evidence and petrography indicates the development of a karstic surface on the Loma Negra Formation (Barrio et al., 1991). Downward penetration of ^{18}O depleted meteoric fluids is likely and could explain this stratigraphic distribution in $\delta^{18}O$ values for the upper part of the formation (Figs. 7d and 9b).

5.2. Tentative chemostratigraphy

Over the past twenty years, secular variations in the carbon and strontium isotopic compositions of Neoproterozoic seawater have been documented in numerous detailed studies (for a summary see Jacobsen and Kaufman, 1999, but also Walter et al., 2000; Melezhik et al., 2001; Halverson et al., 2004). Characteristic features include up to four distinct negative $\delta^{13}C$ excursions to values as low as −5‰ associated with Sturtian (ca. 740 Ma) and Vendian/Marinoan (ca. 600 Ma) glaciations. Each negative anomaly is followed by a rise to highly positive $\delta^{13}C$ values of as much as +11‰.

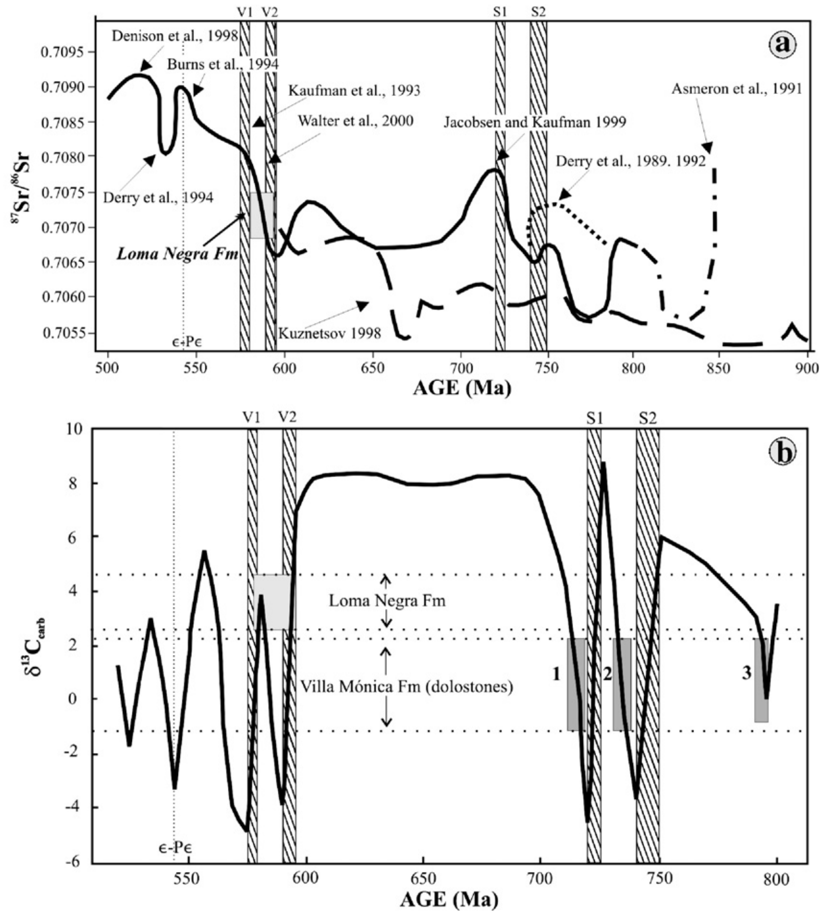

Fig. 10. Temporal $^{87}Sr/^{86}Sr$ and $\delta^{13}C_{carb}$ evolution curves for the Neoproterozoic seawater according to Melezhik et al. (2001) and Jacobsen and Kaufman (1999). Grey area in (a) corresponds to the range of $^{87}Sr/^{86}Sr$ values obtained by Kawashita et al. (1999a,b) from Loma Negra Formation, (b) $\delta^{13}C$ data for the Loma Negra Formation, plotted on global curve presented by Jacobsen and Kaufman (1999). The area in light grey marks the most probable ages for this unit. The three areas in dark grey show the possible ages for the dolostone of Villa Mónica Formation (See text for further discussion).

Similarly, low $^{87}Sr/^{86}Sr$ values between 0.7056 and 0.7068 characterize the time span between 800 and 750 Ma prior to the Sturtian glaciations, whereas a steep increase in $^{87}Sr/^{86}Sr$ from 0.7067 to 0.7088 occurs between 580 and 550 Ma following the Vendian glaciations (Fig. 10a).

Considering the carbon isotope data at face value, the recent analyses of basal Villa Mónica dolostone samples may reflect one of the glacially related excursions recorded in Neoproterozoic times. Following the scheme of Jacobsen and Kaufman (1999), three different ages can be postulated for the Villa Mónica Formation: (1) close to 720 Ma, (2) around 740 Ma, or (3) near 800 Ma (Fig. 10b). The latter age (Fig. 10b: I) is more consistent with reported Rb/Sr age of 793±32 Ma (Cingolani and Bonhomme, 1988) and ca. 850 Ma by stromatolite biostratography (Poiré, 1993). To date, no glacial diamictite has been observed beneath the basal Villa Mónica dolostones, but these beds overly had a condensed interval containing both iron-rich sediments and abundant phosphate nodules suggestive of an unconformable surface that may laterally be equivalent to glacial deposits. Further investigation of this surface and the basal dolostone is warranted.

Positive carbonate carbon isotope values around +3.5‰ and strontium isotope data between 0.7068 and 0.7075 published by Kawashita et al. (1999a) support an Ediacaran age for the Loma Negra Formation. More specifically, an age of ca. 580–590 Ma (Fig. 10) appears plausible given existing chemostratigraphic schemes for the Neoproterozoic. In the same sense, the presence of Cloudina reported by Gaucher et al. (2005) in the micritic limestones supports the Ediacaran designation for this formation.

Similar isotope data reported here were described for limestones of the Polanco Formation (Arroyo del Soldado Group) in Uruguay (Gaucher, 2000; Gaucher et al., 2003a,b) and Corumbá Group in Brazil (Boggiani, 1998; Boggiani et al., 2003). The age of the Polanco Formation has been determined as Ediacaran (ca. 555–580 Ma) on the basis of acritarch biostratigraphy, Cloudina and C and Sr chemostratigraphy (Gaucher, 2000; Gaucher et al., 2004, 2005). The age of the Corumbá Group was determined to be between 600 and 535 Ma based on Sr chemostratigraphy and biostratigraphy (Boggiani et al., 2003). Furthermore, the regional geological context shows similarities as well with glacial deposits and cap carbonates being absent from the Sierra Bayas Group. The age of the Loma Negra Formation is interpreted here as uppermost Neoproterozoic (Ediacaran). This is in contradiction to previously advocated views based on Rb–Sr and K–Ar data (summarized by Kawashita et al., 1999a).

Overlying diamictites of the Volcán Formation (Spalletti and Del Valle, 1984) in other localities of the Tandilia System might be a relict of a post-Marinoan glacial event (Gaskiers or even lowermost Cambrian, Bertrand-Sarfati et al., 1995; Halverson et al., 2004), since both the Loma Negra and Cerro Negro Formations are of Ediacaran age.

6. Conclusions

Petrographic, geochemical and isotopic data are combined to constrain the age and climatic evolution of the Neoproterozoic rocks from the Tandilia System (Argentina). Two carbonate successions were analyzed in detail, dolostone of the Villa Mónica Formation and limestone of the Loma Negra Formation, divided by a siliciclastic sequence (Cerro Largo Formation). Dolostone of the Villa Mónica Formation are definitely older than the Loma Negra Formation and reflect strongly altered isotope values, as well as a very high distinctive diagenetic evolution.

For the Villa Mónica and Loma Negra formations, the following conclusions can be drawn:

Villa Mónica Formation:

1. Diagenesis of the dolostone of Villa Mónica Formation included two dolomitizing events affecting depositional LMC micrites. Subsequently, three principal stages of cementation are recognized (Stage 1, dolosparitic cement occasionally showing crystals with iron-rich nuclei; Stage 2, quartz cement in the form of euhedral crystals; and Stage 3, high-Mg-calcite cement made up of anhedral to euhedral macrosparitic crystals).
2. Sedimentary facies include very conspicuous stromatolites representing a stromatolitic platform and clastic, non-stromatolitic carbonates, probably deposited in an intertidal environment.
3. Carbonate geochemistry points to a strong enrichment of Mn and Fe and a strong depletion in Sr. Such a high degree of diagenetic alteration has likely affected the isotope signature of our samples, excluding them from further chemostratigraphic interpretations.
4. Dolostone of the Villa Mónica Formation yielded $\delta^{18}O$ (PDB) values (>−10‰) ranging from −6.7 to −2.1‰ and $\delta^{13}C$ values vary between −0.7 to +2.2‰. There is a notable correlation between $\delta^{13}C$ data and facies. Whereas stromatolitic dolostone show $\delta^{13}C$ from −0.7 to +0.3‰, clastic intertidal carbonates yielded positive values from +0.2 to +2.2‰. As a final conclusion, however, we do not consider the carbon and oxygen isotope values as primary. Hence, no further

conclusions are drawn with respect to the original seawater composition.

Loma Negra Formation:

1. Diagenetic processes can be divided in five stages: Stage 1, recrystallization of the precursor micrite mosaic; Stage 2, porosity-generating dissolution; Stage 3, precipitation of calcite cements; Stage 4, stylolitization; and Stage 5, silica cementation.
2. Two main sedimentary facies have been recognized in this carbonate succession: a lower facies dominated reddish micritic limestone from a marine ramp environment, and an upper facies comprised of black micritic limestone interpreted as a lagoon deposit.
3. Mn/Sr < 1.5, Fe/Sr < 50, Ca/Sr < 1100, Rb/Sr > 0.001 and $\delta^{18}O > -11‰$ are considered to indicate a low degree of diagenetic alteration in samples from the Loma Negra Formation. Most of these limestone samples fulfill these geochemical constraints, suggesting that these carbonates record essentially primary isotopic signatures. This appears to be particularly true for the black micritic limestones, rendering them suitable for chemostratigraphic (C, Sr) considerations.
4. Non-luminescent micritic limestones facies from Loma Negra Formation yielded $\delta^{13}C_{carb}$ values between +2.7 and +4.5‰ and strontium isotope ratios between 0.7068 and 0.7075 support an Ediacaran age for this succession. The clear difference in $\delta^{18}O$ between the black micritic limestones (−8.1 to −7.1‰. Unit 2) and (−14 to −12‰. Unit 3) could be due to the penetration of ^{18}O depleted meteoric fluids into the upper part of formation.
5. It is possible to correlate $\delta^{13}C$ excursions and Sr isotope data recorded for the Loma Negra Formation with those reported for the Polanco Formation (Uruguay) and Corumbá Group (Brazil). The correlation implies an age of ca. ~580–590 Ma for the Loma Negra Formation, as the comparable successions are controlled by biostratigraphic markers.

This contribution shows that a detailed reconstruction of diagenetic pathways can help to interpret C, O and Sr-isotope data and give more insights into Precambrian chemostratigraphy and basin evolution.

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