

# Sr, C and O isotope geochemistry and stratigraphy of Precambrian and lower Paleozoic carbonate sequences from the Western Sierras Pampeanas of Argentina: tectonic implications

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## Abstract

Sr, C and O isotope data are presented for carbonate rocks from the Sierra de Pie de Palo and other crystalline outcrops of the Western Sierras Pampeanas. These are used to distinguish three groups of rocks of quite different ages within the nappe pile that constitutes the Sierra de Pie de Palo. Carbonates from the Grenville-age ophiolitic unit at the bottom of the pile probably resulted from the interaction between hot seawater and contemporaneous oceanic crust. These carbonates are tentatively classified as ophicalcites. Carbonates from the Difunta Correa Sedimentary Sequence are part of a cover sequence to a Grenvillian basement, together forming the upper nappes. Isotope stratigraphy suggests a middle to Late Neoproterozoic age (580–720 Ma) for these carbonates. This cover might be correlated with cover sequences to the Archean and Early to Middle Proterozoic cratons that are well preserved over large areas of Brazil. This fact, together with the apparently absence of an equivalent Neoproterozoic carbonate-bearing cover in the Appalachian margin of Laurentia, suggests that the Western Sierras Pampeanas, which are considered part of the exotic Argentine Precordillera terrane of allegedly Laurentian derivation, could be autochthonous or para-autochthonous to Gondwana. Other geochemical and geological arguments reinforce this hypothesis. The Caucete Group carbonates underlie the nappe pile and are separated from it by a first order thrust (the Pirquitas thrust). These latter carbonates are Cambrian in age and isotopically similar to the carbonate platform of the Precordillera. We thus conclude that the Pirquitas thrust is the boundary between the exotic Precordillera terrane and the autochthonous or para-autochthonous Western Sierras Pampeanas.

*Keywords:* Isotope stratigraphy; Neoproterozoic; Cambrian; Terrane; Gondwana

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## 1. Introduction

Carbonate rocks of unknown age are common in the Sierras Pampeanas of western Argentina. The

Sierras Pampeanas are mountainous ranges of metamorphic and plutonic igneous basement that were uplifted by reverse west-vergent faulting during the Andean orogeny. The region mostly overlies a segment of the subducting Nazca plate that is almost subhorizontal (e.g. [Jordan and Allmendinger, 1986](#)). The Sierra de Pie de Palo is one of the Western Sierras Pampeanas (WSP) and is formed almost

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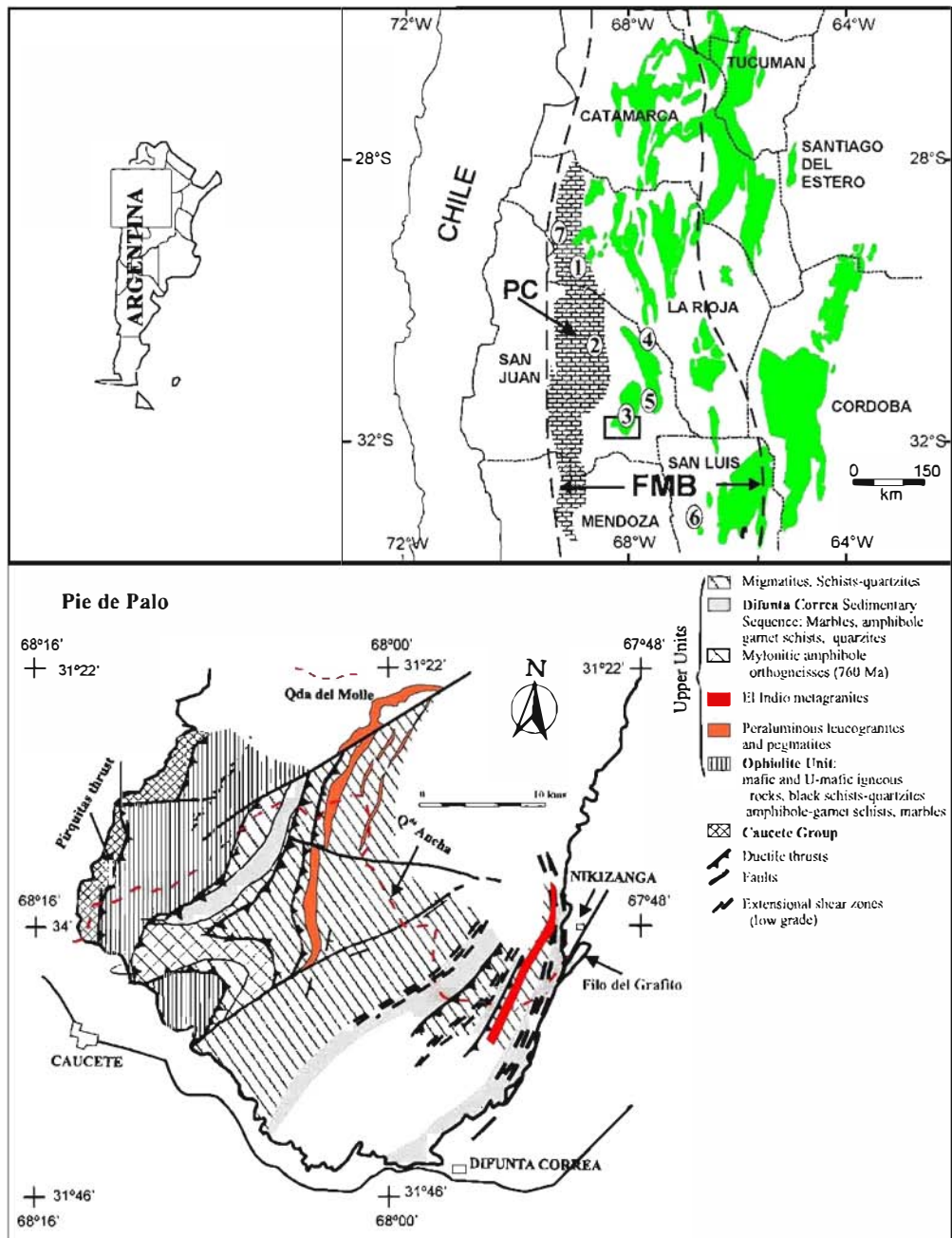


Fig. 1. Location map of sampled areas and enlarged sketch map of southern Sierra de Pie de Palo. Dark grey: Sierras Pampeanas; PC (framed): Argentine Precordillera; 1: Guandacol; 2: Talacasto; 3: Sierra de Pie de Palo; 4: Sierra de Valle Fértil; 5: Cerro de Pan de Azúcar; 6: Sierra del Gigante; 7: Sierra de Umango; FMB: Famatina mobile belt.

exclusively of low- to high-grade metamorphic rocks (Fig. 1).

To the west of the Sierra de Pie de Palo lies the Precordillera (Fig. 1) a mountain range where a long-known but enigmatic sedimentary sequence of Early to Middle Paleozoic age has been the subject of much work in the last decade. This sedimentary sequence consists of Cambrian to Devonian rocks (Astini et al., 1995; Keller et al., 1998) that are thoroughly imbricated as a part of an east-verging fold and thrust belt of Tertiary, i.e. Andean, age (Jordan and Allmendinger, 1986). The lower part of the sequence corresponds to a Cambrian to earliest Mid-Ordovician shallow-marine carbonate platform (Astini et al., 1995; Keller et al., 1998). Benthic faunas of Laurentian affinity are common in most of the carbonate section, merging into mixed Laurentian–Gondwanan faunas towards the top of the sequence (for details see Benedetto, 1998 and references therein; Keller et al., 1998).

The folded and thrust Precordillera sedimentary sequence is underlain by unexposed crystalline basement of Grenville age, the presence of which is inferred from U–Pb ages of xenoliths in Miocene volcanics ( $1102 \pm 6$  Ma, U–Pb zircon, Kay et al., 1996). Rocks of Grenvillian age also crop out in the Sierra de Pie de Palo, as demonstrated by Ar–Ar, Rb–Sr and U–Pb zircon dating (McDonough et al., 1993; Ramos et al., 1996, 1998; Pankhurst and Rapela, 1998). From these ages and other petrographical and geochemical similarities, the concept has emerged that the Grenvillian age rocks and the passive margin carbonate platform of the Precordillera might be parts of a single exotic terrane of Laurentian derivation which was amalgamated to the proto-Andean margin of Gondwana in the early Paleozoic during the Famatinian orogeny (e.g. Astini et al., 1995). This terrane, often referred to in the geological literature as the Argentine Precordillera terrane (Astini et al., 1995) has become a key piece for early Paleozoic Laurentia–Gondwana paleogeographic reconstructions (e.g. Astini et al., 1995; Thomas and Astini, 1996; Dalziel, 1997; Aceñolaza and Toselli, 1999; Condie, 2001; Thomas et al., 2002). However, the precise age and manner of amalgamation of the Precordillera terrane is a long debated matter (e.g. Casquet et al., 2001).

Unfossiliferous limestone and marbles are abundant in the Sierra de Pie de Palo and in other neighbouring

ranges of the Western Sierras Pampeanas (e.g. Sierra de Valle Fértil, Sierra del Gigante) (Fig. 1), albeit in diverse geological settings and with different metamorphic grade. However, the stratigraphic significance of these rocks is still poorly known. In this work we have carried out a Sr, C and O isotope study of these carbonates with two main aims: first to differentiate otherwise indistinguishable carbonate sequences, and second to constrain isotopically the stratigraphy of these rocks. The possibility that carbonate rocks older than the Precordillera carbonate platform might be present in the Western Sierras Pampeanas has stimulated this need to provide new constraints on their alleged derivation.

## **2. Carbonate rocks of the Sierra de Pie de Palo and other WSP**

The Sierra de Pie de Palo, particularly its northern part, is of very difficult access. In consequence geological knowledge of this sierra is still sketchy (Fig. 1). It may be recognised as an imbricate ductile thrust system with a top-to-the-west sense of relative movement (Casquet et al., 2001). Several tectonic units (nappes) of low- to high-grade metamorphic rocks are distinguished, overlying an epimetamorphic basement formed by the Caucete Group sedimentary rocks (Ramos et al., 1996, 1998; Casquet et al., 2001). Protracted thrusting occurred during the Famatinian orogeny, both coincident with and following the peak of regional metamorphism at ca. 460 Ma (Casquet et al., 2001). The lowermost low-angle thrust, i.e. the Pirquitas thrust, at the base of the nappe pile (Fig. 1), was active until ca. 396 Ma (Ar–Ar dating, Ramos et al., 1998).

The lower nappe contains a Grenville-age ophiolite (Vujovich and Kay, 1998). Recent U–Pb SHRIMP zircon dating, combined with other geochronological evidence, has shown for the first time that each of the upper nappes consist of a Grenvillian basement and a younger cover sequence of metasedimentary rocks. The latter, which was named the Difunta Correa Sedimentary Sequence by Baldo et al. (1998), underwent only low- to medium-grade metamorphism of a type between high  $P$ – $T$  type and medium  $P$ – $T$  (Barrovian) type in Famatinian times (ca. 465 Ma; U–Pb SHRIMP, Casquet et al., 2001). The basement, however, exhibits evidence of an older Grenvillian metamorphism

of lower  $P$ – $T$  type that reached high-grade conditions (Casquet et al., 2001).

In this area, carbonate rocks are found in three different geological settings. The first is the Caucete Group, which crops out in the western lower slopes of the sierra (Fig. 1). This is a sedimentary sequence consisting of epimetamorphic sandstones, conglomerates and thick beds of marble, which often display mylonitic foliations and superimposed open folding (Ramos et al., 1996 and references therein; Van Staal et al., 2002). We have distinguished white, grey and minor pinkish calcitic marbles. The second setting is the Difunta Correa Sedimentary Sequence, which consists of conglomerates, quartzites, meta-arkoses, Ca-pelitic schists, para-amphibolites and marbles (Baldo et al., 1998). Syn-schistose folding and mylonitic nappe-related foliations are common in these rocks. Marbles are grey and white and are mostly calcitic with minor silicate impurities. The third setting is the ophiolitic unit. Carbonates of this unit are recognized here for the first time. They form either lenses interlayered with metabasites (amphibolites and green-schists) and light fine-grained siliceous rocks, or anastomosing bands that enclose fine-grained metabasites. Large concentrations of very pure talc (which are still mined), probably resulting from retrogression of former igneous ultrabasic bodies, are found in very near proximity to the carbonates. Mylonitic and phyllonitic foliations are ubiquitous within the ophiolitic unit.

The Filo del Grafito is a small elevation on the eastern slope of the sierra separated from it by a steep fault (Fig. 1). This outcrop consists of white massive marble of unknown age, quartzites and graphite schists.

Carbonate rocks are also found in the Sierra de Valle Fértil, east of the Sierra de Pie de Palo, and in the Sierra del Gigante to the south of it (Fig. 1). The Sierra de Valle Fértil samples analysed here come from the Cerro de Pan de Azúcar outcrop, a very small enigmatic block of crystalline rocks on the western slopes of the sierra (Fig. 1). It consists of a folded sequence of mylonitic, strongly retrogressed, low-grade metamorphic rocks including grey marbles, quartzites, schists/phyllites, phyllonitic orthogneisses and pegmatites. Carbonate rocks from the Sierra del Gigante are grey to white marbles. They form thick beds interlayered with a variety of low-grade metamorphic rocks such as pelitic schist, graphite-rich schists, quartzites, quartz-rich metavolcanic rocks and

magnetite-rich beds. This sequence has been considered part of the Precordillera terrane (Gardini and Dalla Salda, 1997).

### 3. Sampling and analytical methods

Thirty-two samples of carbonate rocks were collected from the aforementioned localities. Four limestones from the lower part of the Precordillera carbonate platform have also been analysed for comparison (Fig. 1). Two of the latter are from the Early to Middle Cambrian Los Hornos Formation near Guandacol (Astini and Vaccari, 1996; Keller et al., 1998) and the other two from the Early to Middle Ordovician (Arenig–Llanvirn) San Juan Formation at Talacasto (Astini, 1994), which contains interbedded K-bentonites (see Huff et al., 1998). Thin sections of all the samples were firstly stained for carbonates and then studied under the microscope. Geographical location, description and mineral composition of the samples are shown in Table 1.

All the samples were analysed for Sr isotope composition. Nineteen samples were chosen for C and O isotope composition determination. Moreover, most samples were analysed for Mn, Mg, Sr and Ca of the carbonate fraction to evaluate the degree of post-sedimentary alteration (geochemical screening). The content of the insoluble residue was also determined. The Sr isotope composition was determined on an automated multicollector SECTOR 54<sup>®</sup> mass spectrometer at the Geochronology and Isotope Geochemistry Centre of the Madrid University.  $^{87}\text{Sr}/^{86}\text{Sr}$  values were normalised to a  $^{86}\text{Sr}/^{88}\text{Sr}$  value of 0.1194. The NBS-987 standard was routinely analysed along with our samples and gave an average  $^{87}\text{Sr}/^{86}\text{Sr}$  value of  $0.710245 \pm 0.00003$  ( $2\sigma$ ,  $n = 20$ ). Analytical uncertainty is estimated to be  $\pm 0.01\%$ . Carbonate samples ( $\sim 30$  mg) were leached in a 10% acetic acid solution and then centrifuged to eliminate the insoluble residue. This method minimises contamination with Sr released from silicates during strong acid attack (Fuenlabrada and Galindo, 2001). The solution was subsequently evaporated and then 3 ml of 2.5N HCl added. Sr was separated using cation-exchange columns filled with BioRad<sup>®</sup> 50W X12 (200/400 mesh) resin. Analytical results are displayed in Table 2.

Table 1

Location, field description and mineral composition of carbonate rocks

	Latitude	Longitude	Rock description	Mineralogy
<b>Precordillera</b>				
TAL-6072	31°00'34.3''	68°46'16.1''	Grey fossiliferous limestone	Cal (Chl)
TAL-6074	31°01'35.0''	68°45'03.8''	Grey fossiliferous limestone	Cal (Qtz, Chl)
TOT-6068	29°28'10.5''	68°40'34.1''	Grey limestone (finely recrystallized)	Cal (Chl)
TOT-6069	29°28'10.5''	68°40'34.1''	Pale grey limestone (finely recrystallized)	Cal (Chl)
<b>Sierra Pie de Palo</b>				
<b>Caucete Group</b>				
SPP-400	31°26'50''	68°11'54''	Grey marble	
SPP-401	31°26'50''	68°11'54''	Grey banded marble	Cal (Gr, Op)
SPP-6077	31°33'17.0''	68°17'38.3''	Grey marble (mylonitic)	Cal, Dol (Gr, Ab)
SPP-6079	31°29'41.6''	68°14'22.4''	White marble	Cal (Qtz, Ms, Ab)
SPP-898	31°29'52''	68°15'17''	Pink marble	Cal, Dol (Qtz, Ms, Op)
SPP-899	31°29'52''	68°15'17''	Grey marble (mylonitic)	Cal (Qtz, Ms, Op)
SPP-897	31°29'52''	68°15'17''	Dark grey marble (mylonitic)	Cal (Dol, Gr, Op)
SPP-6080	31°33'20.4''	68°17'38.2''	Grey marble	Cal (Dol, Qtz, Gr, Op)
SPP-6081	31°33'25.9''	68°17'34.9''	White marble	Cal (Op)
SPP-900	31°29'42''	68°14'21''	Grey marble	Cal (Qtz, Ms, Ab)
<b>Filo del Grafito</b>				
PPL-46	31°36'04''	67°52'23''	White marble	Cal (Qtz, Ab, Ms, Gr, Op)
<b>Difunta Correa Sequence</b>				
SPP-6090	31°42'12.4''	68°05'45.3''	Grey marble	Cal (Qtz, Ms, Op, Gr, Zrn)
PPL-18b	31°42'22''	67°05'43''	Grey marble	Cal (Ms, Ab, Ap, Gr, Op)
PPL-24	31°43'13''	67°59'11''	Grey marble	Cal (Qtz, Ms, Ab, Ap, Gr, Ttn)
PPL-26	31°43'22''	67°58'47''	Grey marble	Cal (Qtz, Ms, Ab, Ap, Gr, Ttn)
PPL-54	31°33'32''	67°52'19''	Grey marble	Cal (Gr, Ms, Ab, Ap, Zrn, Ttn)
PPL-59	31°43'59''	67°58'36''	Grey marble	Cal (Qtz, Ms)
SPP-2019	31°37'33''	67°55'30''	Grey marble	Cal, Di, Ep (Ttn, Bt, Ms, Pl, Scp)
SPP-2020	31°37'33''	67°55'30''	Grey marble	Cal, Di, Ep (Ttn, Bt, Aln)
SPP-2024	31°37'16''	67°57'34''	Grey marble	Cal (Qtz, Ms, Chl)
SPP-2049	31°29'33''	68°04'04''	Grey marble	Cal (Gr, Op, Ms, Bt, Ttn)
SPP-6092	31°43'57.9''	67°58'34.4''	Grey marble	Cal (Qtz, Ms, Op, Gr, Ap)
SPP-435	31°44'04''	67°58'38''	Grey marble	Cal (Op, Gr, Ms, Ttn)
<b>Ophiolitic unit</b>				
SPP-912	31°29'12''	68°10'51''	White banded marble	Cal, Act, Ep (Ttn, Tlc)
SPP-408	31°28'01''	68°09'32''	White banded marble	Cal, Act (Op, Gr)
<b>Sierra del Gigante</b>				
GIG-6099	32°53'43.8''	66°50'12.4''	Grey marble	Cal, Dol, Qtz (Ms, Gr)
GIG-6100	32°53'43.8''	66°50'12.4''	White marble	Cal (Qtz, Op)
GIG-6105	32°54'57.2''	66°49'11.0''	White banded marble	Cal (Qtz, Ms, Ab, Gr)
<b>Pan de Azucar</b>				
LCH-6200	31°24'44''	67°27'44''	Grey marble	Cal, Qtz (Ms, Py, Gr)
LCH-6202	31°24'44''	67°27'44''	Grey marble	Cal (Qtz)
LCH-6207	31°24'47''	67°27'40''	Dark grey marble	Cal, Qtz (Py)
LCH-6211	31°24'53''	67°27'28''	Dark grey marble	Cal, Qtz (Py)

Mineral abbreviations after Kretz (1983). Minerals within parentheses are accessory (10% in volume).

Table 2

Elemental composition, insoluble residual weight percent value and Sr, C and O isotope composition of carbonates

	$\delta^{87}\text{Sr}/^{86}\text{Sr}$	$\delta^{13}\text{C}_{\text{PDB}}$	$\delta^{18}\text{O}_{\text{SMOW}}$	Mg (%)	Ca (%)	Mn (ppm)	Sr (ppm)	Mn/Sr	Mg/Ca	Insoluble residue (wt.%)
<b>Precordillera</b>										
TAL-6072	0.708813			0.11	39.53	93	1274	0.073	0.003	4.6
TAL-6074	0.708856									
TOT-6068	0.709038			0.20	36.44	8	2667	0.003	0.005	1.0
TOT-6069	0.709030									
<b>Sierra Pie de Palo</b>										
<b>Caucete Group</b>										
SPP-400	0.709565									
SPP-401	0.709017									
SPP-6079	0.709284	+0.02	+20.16	0.25	37.28	122	1452	0.084	0.007	2.7
SPP-6077	0.711032			7.14	37.56	86	257	0.335	0.190	9.4
SPP-898	0.710923			10.40	24.59	135	211	0.641	0.423	10.2
SPP-899	0.709378			0.16	36.05	115	605	0.190	0.004	15.1
SPP-897	0.710745			6.10	36.72	93	271	0.343	0.166	9.1
SPP-6081	0.709241			0.15	35.84	62	504	0.123	0.004	3.3
SPP-6080	0.710299			8.21	35.53	86	109	0.792	0.231	5.6
SPP-900	0.709165			0.59	37.14	71	689	0.103	0.016	0.3
<b>Filo del Grafito</b>										
PPL-46	0.709016	-0.46	+20.33	0.18	38.36	32	941	0.034	0.005	4.0
<b>Difunta Correa Sedimentary Sequence</b>										
SPP-6090	0.707316	+10.48	+20.27	0.23	36.32	25	758	0.033	0.006	3.0
PPL-18b	0.707361	+9.91	+19.60	0.24	37.39	18	1500	0.012	0.006	6.1
PPL-24	0.707390	+4.33	+19.00	0.28	37.64	58	1055	0.055	0.007	1.2
PPL-26	0.707408	+2.61	+20.29	0.15	39.46	46	1353	0.034	0.004	0.3
PPL-54	0.707354	+8.25	+18.17	0.15	39.92	54	1200	0.045	0.004	0.0
PPL-59	0.707321	+10.60	+20.26	0.10	38.20	38	655	0.058	0.003	1.5
SPP-2019	0.707963	+0.23	+14.70	18.37	32.34	145	209	0.693	0.568	25.2
SPP-2020	0.707819	-2.264	+14.35	15.96	28.87	139	262	0.530	0.553	27.4
SPP-2024	0.707392	+11.35	+20.36	0.10	35.78	22	688	0.032	0.003	0.6
SPP-2049	0.707422	+8.52	+20.36	0.16	35.18	100	1515	0.066	0.005	1.8
SPP-6092	0.707321	+10.91	+19.55	0.19	35.91	97	1644	0.059	0.005	0.2
SPP-435	0.707416	+2.81	+20.30	0.12	36.94	26	1857	0.014	0.003	3.5
<b>Ophiolitic unit</b>										
SPP-912	0.703979	-5.17	+10.70	1.01	35.17	123	1309	0.094	0.029	22.6
SPP-408	0.704652									
<b>Sierra del Gigante</b>										
GIG-6099	0.709634			3.86	38.60	823	417	1.974	0.100	12.6
GIG-6100	0.709955	+0.34	+21.58	0.35	43.10	204	344	0.593	0.008	7.0
GIG-6105	0.711752	-0.29	+18.98	2.47	39.40	478	537	0.858	0.063	9.2
<b>Pan de Azucar</b>										
LCH-6200	0.713150			1.11	39.90	925	747	1.238	0.028	48.4
LCH-6202	0.710458	+1.18	+11.78	1.49	41.30	112	511	0.219	0.036	8.4
LCH-6207	0.711862			3.36	38.60	209	119	1.757	0.087	29.1
LCH-6211	0.712280	-0.26	+12.56	0.3	43.80	1249	420	2.974	0.007	20.2



Oxygen and C isotope determinations were carried out on a double inlet Micromass SIRA-II® mass spectrometer at the Salamanca University Isotope Laboratory following the method of McCrea (1950). Rocks were first reacted with 100% orthophosphoric acid at 25 °C to liberate CO<sub>2</sub>. Oxygen-isotope compositions were corrected after Craig (1957). Oxygen and C isotope compositions are reported in  $\delta$  (‰) notation on the PDB and SMOW scales. Analytical errors are  $\pm 0.057\text{‰}$  for C and  $\pm 0.198\text{‰}$  for O ( $1\sigma$ ;  $n = 21$ ). Results are shown in Table 2.

Mn, Mg, Sr and Ca in the carbonate fraction were determined by conventional atomic absorption spectrometry after digestion in acetic acid solution. Analytical error is  $\pm 2\%$  ( $1\sigma$ ). Mn/Sr and Mg/Ca ratios for the carbonate fractions are quoted in Table 2. The weight percent of insoluble residue was also determined (Table 2).

## 4. Results

Most samples contain calcite as the only carbonate mineral, with less than 10% by volume of impurities (mineral impurities are reported in Table 1). An alternative estimate of the total impurity content is provided by the insoluble residue weight percent (Table 2). In most samples this value is lower than 10% (mostly <5%), in agreement with optical determinations. Quartz is by far the main impurity in all samples. Dolomite was optically recognised in only four samples from the Caucete Group and one from the Sierra del Gigante. Absence of dolomite correlates well with the Mg/Ca value of the carbonate fraction, which is low ( $\leq 0.087$ ) in most samples. The most anomalous samples are marbles SPP-2019 and SPP-2020 from the Difunta Correa Sedimentary Sequence, which contain abundant metamorphic minerals such as diopside (Table 1). In these samples Mg-rich calcite (no dolomite has been recognised) probably formed because of prograde metamorphic reactions.

### 4.1. Elemental ratios

Mn/Sr and Mg/Ca ratios are particularly useful for evaluating the importance of secondary processes undergone by sedimentary carbonates during diagenesis

and metamorphism (e.g. Brand and Veizer, 1980). High values of these two parameters could suggest secondary modification; according to Melezhik et al. (2001), values of Mn/Sr > 0.2 and Mg/Ca > 0.01 are indicative of alteration. Thus, geochemical screening of the rock samples is of paramount importance to the drawing of stratigraphical conclusions from isotope data. Most samples collected here show Mn/Sr and Mg/Ca values lower than 0.2 and 0.01, respectively (Table 2) thus indicating minimum post-sedimentary alteration. However, a few samples from the Caucete Group and the Difunta Correa Sedimentary Sequence show higher values of Mn/Sr (between 0.34 and 0.79), which correlate well with higher values of the Mg/Ca ratio (0.19–0.57).

### 4.2. Isotope composition

The four  $^{87}\text{Sr}/^{86}\text{Sr}$  values determined for limestone carbonates from the Precordillera are remarkably consistent for each formation: 0.70903 and 0.70904 in the Los Hornos Formation and 0.70881 and 0.70885 in the San Juan Formation. The low Mn/Sr, Mg/Ca and insoluble residue weight percent values testify to the relative purity of these limestones.

Sr isotope compositions of marble carbonates from the Caucete Group and Filo del Grafito (PPL-46) define two groups of rocks (Fig. 2a and b). Five samples have low Mn/Sr (<0.2) and Mg/Ca ratios (<0.03) and may be presumed to be unaltered. The lowest  $^{87}\text{Sr}/^{86}\text{Sr}$  value (0.70902) comes from the Filo del Grafito sample, whereas the four values from the Caucete Group are slightly higher, ranging from 0.70917 to 0.70938. The highest value corresponds to a marble with a Mn/Sr value of 0.19, i.e. close to the limiting value of 0.2. However, the rock contains some dolomite (Table 1), suggesting that it may have undergone slight alteration. Those samples with Mn/Sr ratios higher than 0.2, i.e. altered rocks, have significantly more radiogenic Sr,  $^{87}\text{Sr}/^{86}\text{Sr}$  ranging from 0.71029 to 0.71103. Mn and elemental Sr concentration data are not available for SPP-400 and 401, but the latter can probably be included within the first group using the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio (0.70902) as an indication of weak alteration. SPP-400, with a  $^{87}\text{Sr}/^{86}\text{Sr}$  value of 0.70956, probably underwent some alteration. O and C isotope composition are available for two unaltered samples and are very similar

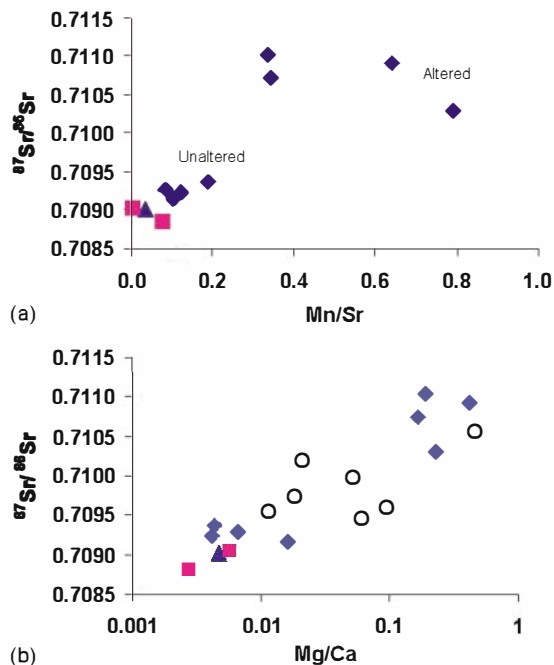


Fig. 2. Plots of  $^{87}\text{Sr}/^{86}\text{Sr}$  vs. Mn/Sr (a) and Mg/Ca (b) for carbonates from the Caucete Group, Filo del Grafito and Early to Middle Cambrian Los Hornos Formation near Guandacol (Argentine Precordillera). Diamonds: Caucete Group; triangles: Filo del Grafito; squares: Los Hornos Formation. Circles are data for the Caucete Group from Sial et al. (2001) (see text).

in both ( $\delta^{18}\text{O}_{\text{SMOW}} = +20.17$  and  $+20.34\%$ , and  $\delta^{13}\text{C}_{\text{PDB}} = +0.02$  and  $-0.46\%$ , respectively).

Marble carbonates from the Difunta Correa Sedimentary Sequence (Fig. 3) show consistently lower  $^{87}\text{Sr}/^{86}\text{Sr}$  values (0.70732–0.70742), together with very low Mn/Sr ( $<0.07$ ) and Mg/Ca ( $<0.01$ ) ratios signifying a lack of alteration. The homogeneity of

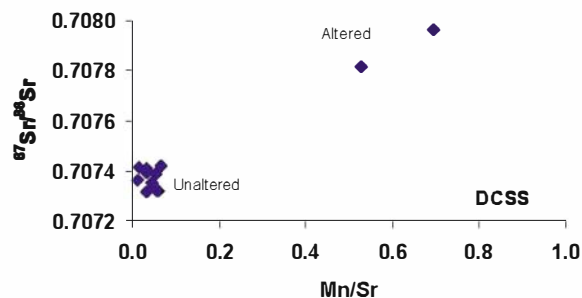


Fig. 3. Plot of Sr isotope composition vs. Mn/Sr ratio for carbonates from the Difunta Correa Sedimentary Sequence.

this group of carbonates is also borne out by the insoluble residue weight percent values of 0.0–6.1. There are only two exceptions: SPP-2019 and SPP-2020 carbonates underwent significant chemical changes during diagenesis and metamorphism as suggested by the high Mn/Sr and Mg/Ca ratios and the abundance of metamorphic minerals (Table 2). In consequence Sr isotope values are much more radiogenic for these samples ( $^{87}\text{Sr}/^{86}\text{Sr} = 0.70796$  and  $0.70782$ , respectively) (Fig. 3). O and C isotope compositions of the first group of carbonates are more variable than in the Caucete Group ( $\delta^{18}\text{O}_{\text{SMOW}} = +18.17$  to  $+20.36\%$  and  $\delta^{13}\text{C}_{\text{PDB}} = +2.61$  to  $+11.35\%$ ). On the other hand isotope compositions of the two altered marble carbonates show significant heavy-isotope depletions ( $\delta^{18}\text{O}_{\text{SMOW}} = +14.70$  and  $+14.35\%$  and  $\delta^{13}\text{C}_{\text{PDB}} = +0.23$  and  $-2.36\%$ , respectively), probably in part because of metamorphic devolatilisation reactions. In fact, diopside is an abundant phase in these rocks (Table 1) suggesting that dolomite consuming reactions played a role during prograde rock evolution. Low oxygen isotopic values could also be related to oxygen isotope exchange between the carbonates and other O-bearing minerals as suggested by the high insoluble residue values.

The two carbonates from the Sierra de Pie de Palo ophiolitic unit show very low  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios (0.70398 and 0.70465) and heavy-isotope enriched O and depleted C isotope compositions ( $\delta^{18}\text{O}_{\text{SMOW}} = +10.70$  and  $\delta^{13}\text{C}_{\text{PDB}} = -5.17\%$ , respectively). Mn/Sr and Mg/Ca ratios are moderately low in the one geochemically analysed sample (0.09 and 0.03, respectively).

$^{87}\text{Sr}/^{86}\text{Sr}$  ratios of marble carbonates from the Sierra del Gigante and Cerro Pan de Azucar are remarkably radiogenic, particularly in the case of the latter area (0.70963–0.71175 and 0.71046–0.71228, respectively). As expected, none of these samples has Mn/Sr  $<0.2$  typical of unaltered carbonates; the one with the lowest Mn/Sr (0.22) has a relatively low  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio (0.71048), but even this must be considered to have been affected to some degree by alteration.  $\delta^{13}\text{C}$  values are near zero in both localities ( $-0.29$  and  $+0.34\%$  in the former,  $-0.26$  and  $+1.18\%$  in the latter), but  $\delta^{18}\text{O}_{\text{SMOW}}$  values are much lower in the Cerro de Pan de Azucar ( $+11.78$  and  $+12.56\%$ ) than in the Sierra del Gigante ( $+18.98$  and  $+21.58\%$ ).



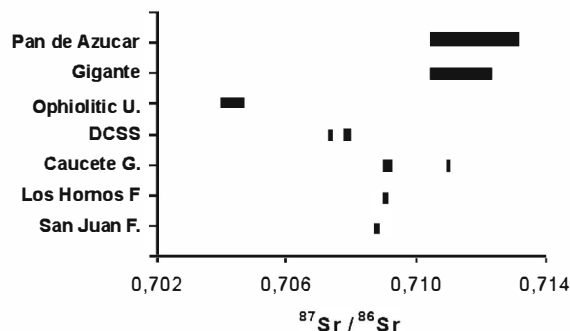


Fig. 4. Box diagram of  $^{87}\text{Sr}/^{86}\text{Sr}$  values of carbonates from the different sampled areas and settings. DCSS: Difunta Correa Sedimentary Sequence.

## 5. Significance of the isotope compositions of carbonates

Sr isotope compositions of carbonates are summarised in Fig. 4 according to their geological setting, making visible the significant differences among them. We can conclude that carbonate rocks from the Western Sierras Pampeanas have several different origins and/or ages.

Carbonates from the ophiolite unit are the least radiogenic. The geological significance of these carbonates is still uncertain. One possibility is that these rocks could be ophicalcites, i.e. carbonates—sedimentary and hydrothermal—that fill veins or replace ultrabasic rocks that were exhumed and exposed on the sea floor (e.g. Früh-Green et al., 1990; Lavoie and Cousineau, 1995, and references therein). In favour of this interpretation is the fact that carbonates from the ophiolite unit form anastomosing bands and are found near large talc concentrations, which probably derive from ultrabasic bodies retrogressed under low-grade metamorphic conditions, but original relationships have been masked by strong mylonitic deformation. Fluid-rock interaction probably led to fluids with Sr isotope compositions between those of seawater and the oceanic crust values at the time of ophiolite formation (e.g. Chapman and Spooner, 1977). Unfortunately, published Sr isotope data are not available for the ophiolite rocks of the Sierra de Pie de Palo. However, one unpublished value is available from a biotite-schist of the ophiolite unit:  $^{87}\text{Sr}/^{86}\text{Sr} = 0.7033$  at the rate of 1000 Ma, which suggests that the source of the sediments, i.e. probably igneous rocks, was isotopi-

cally primitive. In fact, uniform reservoir (Bulk Earth)  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios at 1.0 and 1.1 Ga would have been 0.7033 and 0.7032, respectively (constants as in Borg et al., 1990). On the other hand seawater  $^{87}\text{Sr}/^{86}\text{Sr}$  values at 1.0–1.1 Ga were probably somewhere between 0.7050 and 0.7060 (Gorokhov et al., 1995; Fig. 9). The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of the ophiolite carbonates ( $^{87}\text{Sr}/^{86}\text{Sr} = 0.70398$  and 0.70465) lie between the Bulk Earth and seawater values. Thus, if truly ophicalcites, the Sr isotope composition of fluids from which carbonates were precipitated was probably a mixture of marine and igneous Sr. C isotope composition in one ophiolite carbonate is low ( $\delta^{13}\text{C}_{\text{PDB}} = -5.17\%$ ) for a Grenvillian marine source alone (Kah et al., 1999) and is compatible with either a juvenile carbon (e.g. Hoefs, 1997) or an organic carbon contribution. O isotope composition values are less diagnostic since oxygen can easily exchange with fluids during metamorphism.

The Sr isotope compositions of carbonates from the Difunta Correa Sedimentary Sequence marbles are significantly different from those of the Caucete Group and the Precordillera (Fig. 4), suggesting that they cannot be stratigraphically correlated with either of these. In previous hypotheses, the low-to-medium grade Difunta Correa Sedimentary Sequence was either correlated with the lower part of the Precordillera carbonate platform sequence or considered older, i.e. Neoproterozoic (Casquet et al., 2001). Moreover, the unaltered  $^{87}\text{Sr}/^{86}\text{Sr}$  values (0.70732–0.70742) found here are remarkably similar to those found recently by Varela et al. (2001) in the Sierra de Umango (Fig. 1), the westernmost of the Sierra Pampeanas, where marbles of unknown age are also abundant. After chemical screening of 35 samples, Varela et al. (2001) concluded that unaltered  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios (only three samples do not show significant alteration) range between 0.7072 and 0.7075. C isotope compositions of the carbonates also compare well in the two cases:  $\delta^{13}\text{C}_{\text{PDB}} = -2.00$  to  $+10.20\%$  (Umango; Varela et al., 2001) and 2.60–11.35% (Difunta Correa Sedimentary Sequence; this work). As the C isotope composition is less affected by post-sedimentary alteration, these similarities greatly support the correlation between the Umango carbonates and the Difunta Correa Sedimentary Sequence. Thus, we infer that the sedimentary cover to the Grenvillian basement involved in the Sierra de Pie de Palo nappes is also

present in the Sierra de Umango. In consequence the Difunta Correa Sedimentary Sequence is a sedimentary unit of regional extent in the Western Sierras Pampeanas.

The Sr isotope compositions of unaltered carbonate rocks from the Caucete Group (including the Filo del Grafito) are remarkably similar to those from the Precordillera carbonate platform (Figs. 2 and 4). Particularly noteworthy is the coincidence with the Precordillera Early to Middle Cambrian Los Hornos Formation ( $^{87}\text{Sr}/^{86}\text{Sr} = 0.70903$ ). However, Sr from carbonates from the Precordillera Early to Middle Ordovician San Juan Formation is slightly but significantly less radiogenic ( $^{87}\text{Sr}/^{86}\text{Sr} = 0.70881\text{--}0.70885$ ) than that of the Caucete Group. C and O isotope compositions of the Caucete Group rocks are compatible with those of slightly modified

Paleozoic marine carbonates (Faure, 1986; Hoefs, 1997). Sial et al. (2001) have also analysed O, C and Sr isotopes in carbonates from the Caucete Group and from the Early to Middle Cambrian La Laja Formation (equivalent to Los Hornos Formation) of the Precordillera carbonate platform (e.g. Keller et al., 1998). Unfortunately most of the rocks collected by these authors were affected by significant post-sedimentary alteration. In fact, only one out of seven samples analysed by Sial et al. (2001) for Sr isotopes from the Caucete Group, and two samples out of eight analysed from the Precordillera, satisfy the chemical requirements for little post-sedimentary alteration. With the exception of one sample, the remaining 14 carbonates of Sial et al. (2001) show  $^{87}\text{Sr}/^{86}\text{Sr}$  values (0.7094–0.7102) well above those expected for seawater in the Cambrian and the Late Precambrian

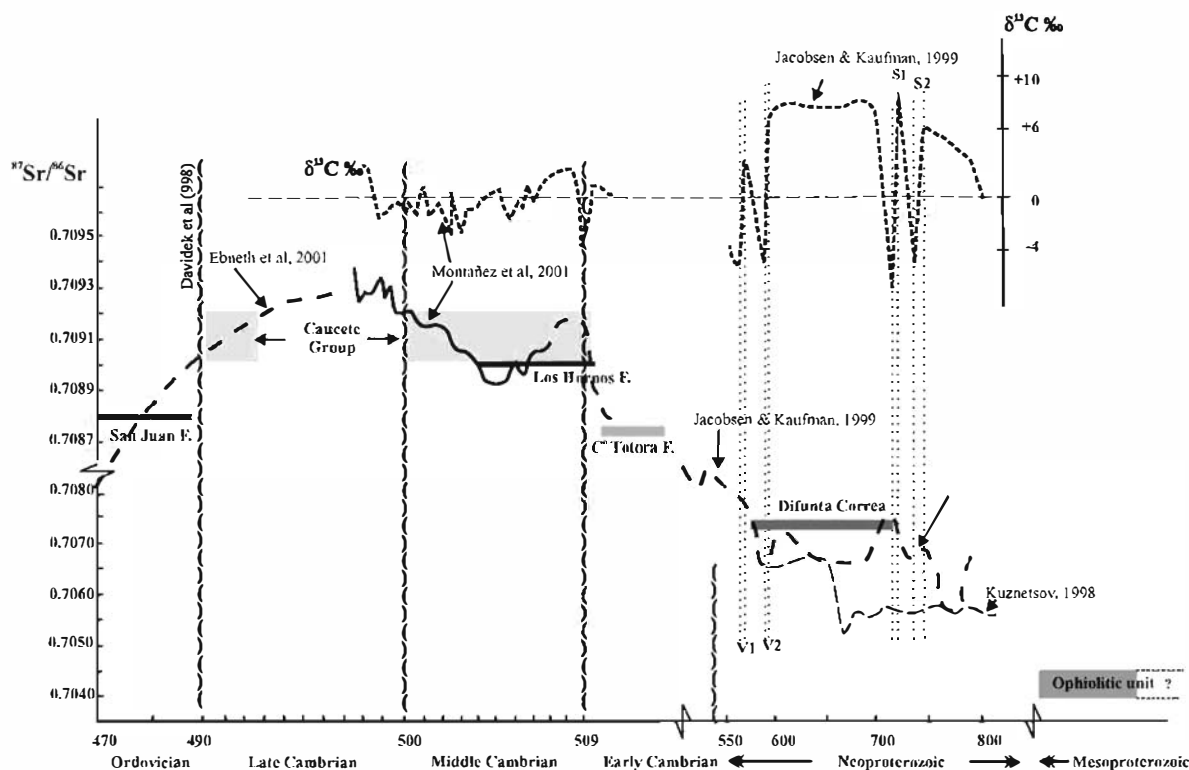


Fig. 5. Temporal trends of  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $\delta^{13}\text{C}_{\text{PDB}}$  in seawater in Neoproterozoic and Cambrian times. Cambrian time scale after Davidek et al. (1998). Boxes in grey:  $^{87}\text{Sr}/^{86}\text{Sr}$  values of least altered carbonates from the Difunta Correa Sedimentary Sequence, Caucete Group, Precordillera carbonate platform and Ophiolite unit. Intersections with the secular Sr isotope curve provide age constraints for the deposition of these carbonate rocks. Also indicated is the range of the less radiogenic Sr isotope compositions of gypsum from the Cerro Totora Formation (Thomas et al., 2001).

(Figs. 2 and 5).  $\delta^{13}\text{C}$  values quoted by Sial et al. (2001) range from  $-1.30$  to  $1.33\%$  encompassing our results for the Caucete Group and the Filo del Grafito.

Isotope data thus suggest that Early to Middle Cambrian or isotopically equivalent Precordillera platform carbonates might be involved in the Caucete Group sedimentary sequence of the Sierra de Pie de Palo. This suggestion implies that the Precordillera platform extends eastward farther than previously considered. The position of the Caucete Group at the base of the Sierra de Pie de Palo pile of metamorphic nappes is probably the consequence of protracted thrusting of the inner part of the Famatinian mobile belt westward along the low-angle Pirquitas thrust (Fig. 1) (Ramos et al., 1998; Casquet et al., 2001). The fact that rocks with an Sr isotope signature similar to those of the Caucete Group also crop out in the Filo del Grafito can be explained as resulting from a younger (probably Andean) westward directed steep thrust located between the Filo del Grafito and the Sierra de Pie de Palo (Fig. 1).

Sr isotope ratios of carbonates from the Sierras del Gigante and Cerro Pan de Azucar are high, encompassing the values of carbonates from the Caucete Group (Fig. 4). These rocks probably underwent significant post-sedimentary alteration, though rather less in the Sierra del Gigante, where Sr isotope values approach those of the unaltered Caucete Group samples. Moreover, C and O isotope values from the Sierra del Gigante are also remarkably similar to those of the Caucete and the Filo del Grafito samples (including C isotope data from Sial et al., 2001). All this suggests that carbonate rocks from the Caucete Group (and the Filo del Grafito) and the Sierra del Gigante might be correlated. In the case of the Cerro Pan de Azucar the correlation is less evident on the basis of isotope composition alone.

## 6. Isotope stratigraphy of the carbonate rocks

The C- and Sr- (and to a lesser extent O-) isotope composition of unfossiliferous marine carbonates is a powerful tool with which to estimate their depositional age. C and Sr isotope secular variation curves of marine carbonates are well known for the early Paleozoic and Neoproterozoic, extending as far

back as 1.5 Ga (e.g. Burke et al., 1982; Kaufman and Knoll, 1995; Gorokhov et al., 1995; Kuznetsov, 1998; Jacobsen and Kaufman, 1999; Kah et al., 1999; Veizer et al., 1999; Melezhik et al., 2001, 2002; Kennedy et al., 2002). Combined systematic variation of the C- and Sr-isotope composition of marine carbonates in this time interval may allow quite accurate constraint on the age of these rocks.

Fig. 5 shows the secular Sr isotope curve (and parts of the  $\delta^{13}\text{C}$  curve) for Cambrian and Middle to Late Neoproterozoic marine carbonates, based on Derry et al. (1989, 1992), Kuznetsov (1998), Melezhik et al., 2002), Jacobsen and Kaufman (1999), Montañez et al. (2000) and Ebner et al. (2001). The most likely ages of the Caucete Group, Difunta Correa Sedimentary Sequence and Precordillera carbonates are also indicated in Fig. 5. The Sr isotope composition of the Caucete Group carbonates and the Precordillera los Hornos Formation corresponds to that of Late Early Cambrian and Middle Cambrian seawater, in good agreement with the stratigraphic evidence for the earliest part of the Precordillera sequence. The unaltered Caucete Group rocks with relatively high  $^{87}\text{Sr}/^{86}\text{Sr}$  values of  $\sim 0.7092$  probably record Cambrian ages younger than those of Los Hornos Formation. On the other hand, a very Late Cambrian age would also be feasible for the Caucete Group simply on the basis of Sr isotope composition (see Fig. 5). This inferred age for the Caucete Group contradicts previous suggestions of a Proterozoic age (e.g. Ramos et al., 1996). Sr isotope data are also available for gypsum from the Early Cambrian Cerro Totorá Formation near Guandacol (Thomas et al., 2001). This formation underlies the Los Hornos Formation and is the lowermost formation of the Precordillera passive margin sedimentary record. The data scatter widely, suggesting mixing between a less radiogenic (marine) and a more radiogenic meteoric components (Thomas et al., 2001). The less radiogenic values, i.e. those between 0.70871 and 0.70877, which are probably representative of the marine component (see Fig. 7; Thomas et al., 2001) have been incorporated in Fig. 5 for comparison. The age is in good agreement with the stratigraphic position of this formation.

Sr isotope compositions of the Difunta Correa Sedimentary Sequence carbonates are coincident with those quoted for Late Proterozoic carbonates (Fig. 5). An age of 580–720 Ma is inferred taking into account

of both the  $^{87}\text{Sr}/^{86}\text{Sr}$  values and the world-wide large variation of the  $\delta^{13}\text{C}$  values for this period, from about  $-4$  to  $+8\%$ , i.e. a range very similar to that found here. Anomalously high  $\delta^{13}\text{C}$  values ( $\geq +10\%$  and as high as  $+14\%$ ) have also been reported for this period of time (Knoll et al., 1986; Magaritz et al., 1986; Misi and Veizer, 1998; Jacobsen and Kaufman, 1999). The Difunta Correa Sedimentary Sequence is thus identified as a cover to the Grenvillian basement older than the Precordillera carbonate platform. The inferred age of its carbonates is Middle to Late Neoproterozoic. Similar conclusions were attained by Varela et al. (2001) from carbonate rocks of the sierra de Umango.

## 7. Implications for the origin of the Western Sierras Pampeanas

Similarities between the lower Paleozoic carbonate platforms of the Precordillera and the Appalachian passive margin of Laurentia were first recognized by Ramos et al. (1986). Subsequent lithological, paleogeographical and paleontological evidence was accumulated that reinforced the idea of a Laurentian connection for the Argentine Precordillera (see Astini et al., 1995; Thomas and Astini, 1996; Benedetto, 1998 and references therein; Keller, 1999), leading to models of Precordillera derivation and Laurentia–Gondwana interaction in the early Paleozoic. In most of these models the Precordillera carbonate platform is seen as a remnant of the Laurentian passive margin resulting from the break-up of Rodinia, amalgamated to the proto-Andean margin of Gondwana in early Paleozoic times (Dalla Salda et al., 1992; Astini et al., 1995; Thomas and Astini, 1996; Dalziel, 1997; Rapela et al., 1998). Since recognition of a crystalline basement of Grenville age in the Sierra de Pie de Palo (McDonough et al., 1993), the Western Sierras Pampeanas have generally been integrated with the Precordillera as a single block of Laurentian derivation, the exotic Precordillera terrane (or Cuyania) (Astini et al., 1995; Ramos et al., 1998; Dalla Salda et al., 1998; Rapela et al., 1998; Casquet et al., 2001). The Laurentian origin of the Precordillera terrane has, however, been questioned by, among others, Aceñolaza and Toselli (1999) and Aceñolaza et al. (2002), who claimed that it originated from the

South America–Antarctica–South Africa region by strike–slip translation along the proto-Andean margin of Gondwana. A new argument in support of this idea has been provided by Finney et al. (2003), who determined U–Pb ages of detrital zircons in Lower Cambrian and Upper Ordovician sandstones in the Argentine Precordillera. They interpret the patterns of such ages as indicative of Gondwanan rather than Laurentian provenance, and, incidentally, question the Ordovician collision inherent in many models.

The recognition from our work of a Neoproterozoic carbonate-bearing sedimentary cover in the Western Sierras Pampeanas is an appropriate point at which to reopen debate over the inclusion of the latter in the Precordillera terrane and the relationship of both to Laurentia. Recent paleogeographic reconstructions of Rodinia agree in locating Laurentia contiguous to the proto-Andean margin of Gondwana in Neoproterozoic times (e.g. Dalziel, 1997; Keppie and Ramos, 1999), although no sedimentary cover of this age containing significant carbonate rocks is apparently known along the southern Appalachian margin of Laurentia.

A Neoproterozoic rift-related cover to the Grenvillian basement has long been recognised along the southern Appalachian margin of Laurentia in the Blue Ridge province. Two formations have long been distinguished: Mount Rogers and Catoclin (Thomas, 1991, and references therein; Thomas, personal communication). They consist of volcanic rocks (basalt to rhyolite) and subordinated continental clastic sediments. The age of these rift-related formations has been inferred from geochronology of related igneous rocks. An early rift event, represented by the Crossmore Complex and bimodal volcanic rocks of the Mount Rogers Formation, is dated at  $758 \pm 12$  Ma; and a later rift event, recorded by volcanic rocks of the Catoclin Formation, is dated at  $572 \pm 5$  Ma to  $564 \pm 9$  Ma (Aleinikoff et al., 1995). This range of ages is broadly equivalent to that inferred here for the Difunta Correa Sedimentary Sequence. However, the Blue-Ridge Neoproterozoic successions do not contain carbonates. They are unconformably overlain by the Early Cambrian Chilhowee Group, a transgressive clastic succession representative of the transition from rift to passive margin following Rodinia (Pannotia) break-up (Thomas, 1991).

The Ocoee Supergroup of the Blue Ridge province was long considered equivalent to the Neoproterozoic

succession described above. It was also deposited in a rift basin (e.g. Thomas, 1991 and references therein). For the most part this is a clastic continental-to-marine succession, but the upper part, the Walden Creek Group, contains marine carbonates (e.g. Unrug et al., 2000). However, paleontological findings demonstrate that the Walden Creek Group is Late Silurian in age or younger (Unrug and Unrug, 1990; Unrug et al., 2000), and the apparent absence of unconformities within the Ocoee Supergroup led Unrug et al. (2000) to suggest that the entire supergroup was deposited in a Paleozoic transtensional basin. Although this final suggestion is questioned by others (e.g. Brewer and Thomas, 2000) the conclusion of interest to us is that, irrespectively, the carbonates of the Walden Creek Group cannot be correlated with the Difunta Correa Sedimentary Sequence.

In contrast to these Laurentian environments in the Neoproterozoic, marbles are very important in the Sierra de Pie de Palo and in the Sierra de Umango (Fig. 1) (Varela et al., 2001) where they can reach thicknesses of hundreds of metres. Thus, the Neoproterozoic cover sequence to the Grenville basement in the Western Sierras Pampeanas is apparently lithologically different from that exposed along the Appalachian margin of Laurentia. The tectonic implications of this can be interpreted in two ways. The first is that the Western Sierras Pampeanas are part of the basement of a Laurentia-derived exotic terrane along with the overlying Precordillera sedimentary sequence, i.e. the Precordillera terrane, as formerly argued. The reason why this carbonate-bearing cover has not been recorded along the Laurentian Appalachian margin would remain conjectural: either it might have been eroded away or else it is preserved but hidden somewhere in the roots of the Blue Ridge nappes. The alternative is that the Difunta Correa Sedimentary Sequence and its Grenvillian basement are autochthonous or para-autochthonous to Gondwana and independent of the Precordillera terrane. In both hypotheses, the Difunta Correa Sedimentary Sequence was probably deposited during an earlier rifting stage of Rodinia in the Middle to Late Neoproterozoic, when Laurentia and South America were still contiguous (Dalziel, 1997; Keppie and Ramos, 1999). Final break-up of this part of Rodinia (or Pannotia) probably took place in the Early to Middle Cambrian according recent studies in the Ellsworth Mountains

(Curtis, 2001) and in the Sierra de la Ventana fold belt (Rapela et al., 2003). In this hypothesis the Western Sierras Pampeanas might represent the conjugate rift margin of Laurentia.

Neoproterozoic limestones are known from many places in South America, particularly in central Brazil where they form part of an extensive cover sequence to the Archean and Paleoproterozoic basement. The sediments fill extensional basins that resulted from the initial break-up of Rodinia between 1000 and 700 Ma (e.g. Brito Neves, 1999; Trompette, 2000). Limestones of the Una Group of the Irecê basin (Bahia State) and the correlative of the Bambuí Group of the São Francisco basin in central Brazil have yielded (after chemical screening)  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of 0.70745–0.70765. These values, along with  $\delta^{13}\text{C}_{\text{PDB}}$  values of  $-4.4$  to  $+9.4\text{‰}$ , suggest an age of 600–670 Ma (Misi and Veizer, 1998; a Pb–Pb isochron age of  $688 \pm 69$  Ma for carbonate rocks at the base of the Bambuí Group was obtained by Santos et al., 2000). These isotope values are similar to those of the Difunta Correa Sedimentary Sequence, and although not conclusive evidence, reinforce the possibility of a Gondwana connection for the Western Sierras Pampeanas Neoproterozoic cover sequence and its Grenvillian basement.

Support for the essentially autochthonous origin of the Western Sierras Pampeanas comes from the conclusion of Abruzzi et al. (1993) that correlation between the Sierra de Pie de Palo basement and the unexposed basement of the Precordillera (as inferred from xenoliths in Miocene volcanic rocks) is not straightforward. In spite of some similarities, they differ in significant geochemical details, such as Pb-isotope composition, in mafic rock chemistry, and in the absence in the Sierra de Pie de Palo of a Th-depletion event which is well recognized in the xenoliths in Miocene volcanic rocks of the Precordillera (Abruzzi et al., 1993). This suggests that the Western Sierras Pampeanas might not be part of the Precordillera terrane. Finally, the ages of biotite granites that intrude the Difunta Correa Sequence in the Sierra de Pie de Palo (El Indio granite  $481 \pm 6$  Ma, Pankhurst and Rapela, 1998; Difunta Correa granite  $470 \pm 10$  Ma, authors' unpublished data in collaboration with C.M. Fanning) fall within the range of the Early Ordovician Famatinian granite event of the Sierras Pampeanas (e.g. Pankhurst et al., 2001). These are difficult to explain if the WSP were part of the basement to



the Precordillera, which at this time had not reached its present position, but can be readily explained if the WSP were part of the autochthonous Gondwana margin. This still allows the possibility that the Precordillera and its unexposed basement were indeed derived from Laurentia (or another part of Gondwana). In this case, the boundary between terranes would be the Pirquitas thrust, between the Caucete Group (Precordillera terrane) and the Grenvillian basement with the Difunta Correa Sedimentary Sequence of the Sierra de Pie de Palo (Fig. 1).

## 8. Conclusions

Sr and C isotope (and to a lesser extent O) composition of carbonate rocks from the Sierra de Pie de Palo and other neighbouring sierras allow, after accounting for post-sedimentary chemical alteration, distinction of three groups of rocks of quite different age. From older to younger these are:

- (1) Carbonates from the Sierra de Pie de Palo ophiolitic unit. These probably resulted from the interaction between hot seawater and oceanic (basic and ultrabasic) Grenvillian crust. These carbonates are thus tentatively classified as ophicalcites.
- (2) Difunta Correa Sedimentary Sequence carbonates. These form part of a cover sequence to a Grenvillian basement in the Sierra de Pie de Palo and other Western Sierras Pampeanas. Isotope stratigraphy suggests a Middle to Late Neoproterozoic age (580–720 Ma). Isotope similarities with other Neoproterozoic carbonate rocks in Brazil, which form part of cover sequences to the Archean and Paleoproterozoic cratons, suggest that they could likewise be part of the same general cover sequence and therefore autochthonous to Gondwana. This hypothesis is reinforced by the absence of an equivalent Neoproterozoic carbonate-bearing cover sequence along the Appalachian margin of Laurentia. Moreover, the Grenville-age basement of the Sierra de Pie de Palo cannot necessarily be correlated with the unexposed Grenvillian basement of the Argentine Precordillera, but could be an autochthonous/paraautochthonous part of the Gondwana margin.

- (3) Caucete Group carbonates. These are of Cambrian age and could be correlated with isotopically equivalent rocks of the carbonate platform of the Precordillera (and probably the Sierra del Gigante) implying that this carbonate platform extends much further east than previously estimated. Therefore, the boundary between the Precordillera terrane and the Western Sierras Pampeanas has to be located along the thrust system between the Caucete Group and the complex basement composed of Grenville-age rocks and its Neoproterozoic carbonate-bearing metasedimentary cover sequence.

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