

C AND Sr ISOTOPIC EVOLUTION OF CARBONATE SEQUENCES IN NW ARGENTINA: IMPLICATIONS FOR A PROBABLE PRECAMBRIAN-CAMBRIAN TRANSITION

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ABSTRACT: Upper Precambrian-Lower Cambrian sequences in the Tucuman, Salta and Jujuy provinces, NW Argentina, comprise sandstone, slate, conglomerate and black limestone (Las Tienditas/Volcan Fms.) with abundant Vendian/Tommotian trace fossils in the clastic facies rocks. The Precordillera basin, San Juan province, represents a continuous carbonate sequence belonging to the Lower to Middle Cambrian La Laja Fm. The Pie-de-Palo Range, Pampean Range, characterized by carbonates intercalated with greenschist/amphibolite facies metaclastic rocks, forms a part of the Precordillera basement. The $\delta^{13}\text{C}$ values in carbonates of the Las Tienditas Fm. show a gradual decrease from the base (+3.4 ‰_{PDB}) to the top with a minimum of -1.6‰ observed at ~15m from the top, the latter having a higher clay content. Carbonates in a 700m thick section within La Laja Fm. is marked by a slightly positive $\delta^{13}\text{C}$ values at the base (marly) with a negative anomaly (-2.0‰) at ~20 m above, followed by a small positive anomaly (+0.5‰) ~100 m from the base. All the values above this point are around -0.5‰ with a negative anomaly (-2.0‰) recorded at ~240m above the base.

Seawater $^{87}\text{Sr}/^{86}\text{Sr}$ values define a non-monotonic increase (0.70870 - 0.71082) through the carbonates in Las Tienditas Fm. while the La Laja Fm carbonates vary from 0.70926 to 0.71030, with higher values at the base. C and Sr isotopes, thus suggest that the Las Tienditas carbonates record the Precambrian-Cambrian transition (~15m from the top of studied section). The same is also evident at ~30 m from the base of the La Laja Fm. The narrow range of $\delta^{13}\text{C}$ variation (-1.4 to +1.3‰) and $^{87}\text{Sr}/^{86}\text{Sr}$ in the 0.709-0.710 range for the Caucete Group carbonates of the Pie-de-Palo Range, although unequivocally, appear to be in consonance with a Vendian to Tommotian age, reinforced by the presence of the trace fossils *Didymaulichnus* and *Gordia*.

KEY WORDS: C & Sr isotopes, carbonates, Neoproterozoic-Cambrian, Argentina.

INTRODUCTION

C-isotope stratigraphy is one of the most powerful tools in Precambrian chronostratigraphy, especially when sediments lack recognizable animal fossils (Kaufman 1998). The $\delta^{13}\text{C}$ secular variation curves for marine carbonates in the Neoproterozoic-Cambrian interval show strong positive-negative excursions, several of them interpreted as the stratigraphic position of ancient ice ages (Hoffman et al. 1998; Kha et al. 1999; Shields 1999; Walter 2000; Montañez et al. 2000). The Sr isotope composition of the seawater for this age interval is characterized by a continuous increase of $^{87}\text{Sr}/^{86}\text{Sr}$ that is interrupted, several times, by sharp rises that represent important changes in the Earth history (Montañez et al. 2000).

Only limited data on the behavior of C and Sr isotopes in carbonates are available in South America. We examine here carbonate sequences from the Argentine Precordillera, San Juan province, and from other carbonate sequences in NW Argentina that could be, potentially, proxies for the Precambrian-Cambrian transition. We have studied their $\delta^{13}\text{C}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ chemostratigraphy and compare it to global C and Sr isotope secular variation curves for this time span. This study aims to improve the relatively coarse stratigraphic resolution provided only by the study of the fossil record in some of the carbonate successions under consideration.

GEOLOGICAL SETTING

Upper Precambrian and Lower Cambrian metasedimentary rocks, affected by very low grade metamorphism, occur in three areas in Argentina (Fig. 1): (1) in the northwest, as a sequence of greywackes, slates, conglomerates and limestones; (2) in the Precordillera, as a sequence of limestones and marlstones and (3) in the northern Sierras of Buenos Aires (Tandilia) with quartzites and limestones (Aceñolaza and Miller 1982).

In northwestern Argentina, the oldest among these rocks are in the provinces of Salta and Jujuy (the Puncoviscana Formation of Turner 1972; and the Lerma Group of Salfity et al. 1975). The Lerma Group sedimentary rocks are exposed in the Lerma Valley, in Salta province, and in the Toro and Humahuaca Gorges, in Jujuy province. This Group comprises unmetamorphosed shales of the Sancha Formation which are overlain by limestones of the Las Tienditas Formation, slates and quartzites of the Puncoviscana Formation, and by intraformational conglomerates of the Carralito Formation. Las Tienditas limestones were probably deposited contemporaneously with the Puncoviscana Formation sediments during the Pampean orogeny.

The 400km long Precordillera is an elongated north-south geological province located between the Andes belt to the west

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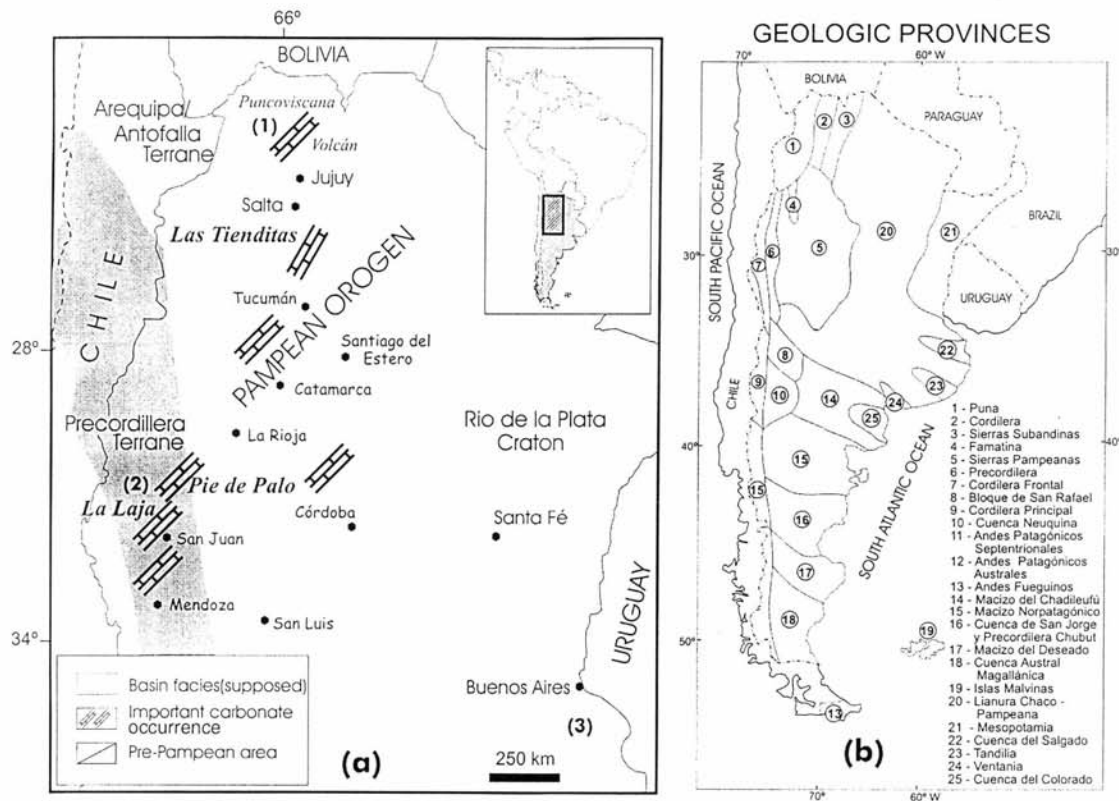


Figure 1. (a) Summary of the Late Neoproterozoic-Early Cambrian paleogeography in southern South America (modified from Aceñolaza and Miller, 1982). The Precambrian-Cambrian transition has been, potentially, recorded in carbonate rocks in Argentina: (1) Salta and Jujuy provinces, northwest Argentina; (2) Precordillera sequence of carbonate rocks and (3) northern Sierras of Buenos Aires (Tandilia). (b) Geologic Provinces of Argentina.

and the Pampean Ranges to the east, and is formed by mountain ranges which are high and relatively inaccessible. It is a unique province throughout the Andes because it contains a complete thick sequence of Early Paleozoic rocks, closely linked to the foreland craton, and exposed by tectonic movements which resulted in the evolution of the Andes (Baldis et al. 1984). In the Precordillera basin, San Juan province, a continuous sequence of carbonates with regressive characteristics developed from the Lower Cambrian (Ollenelus zone) to the base of the Ordovician, at which point a transgressive stage started (Baldis et al. op. cit).

La Laja Formation (Borello 1962) is the oldest unit of the carbonate platform succession and consists of several large-scale sedimentary successions which have two main components, a siliciclastic interval and a calcareous interval (Keller 1999). The name of this Formation is derived from the Quebrada de La Laja and the type section is located in the Quebrada de Zonda, from the western flank of the Sierra Chica de Zonda to the Quebrada de Juan Pobre (Borello 1962). The lower boundary of this Formation is poorly known due to tectonic disturbance (usually cut by thrust; Peralta 2000). The

upper boundary is drawn at the transition from limestones to the dolomites of the Zonda Formation (Bordonaro 1980).

Siliciclastic intervals have been used by Bordonaro (1980) as marker horizons to define the members of this Formation and, in consequence, four limestone-sandstone cycles have been recognized. These cycles were formed in an open, shallow platform, with clean and warm water with free circulation, by fluctuation of the sea level, which suffered an important lowering during the deposition of the high portion of the La Laja Formation, with the development of oolitic bars and supratidal dolomitic facies (Baldis and Bordonaro 1982). The areal extent of outcrop of this Formation is restricted to the San Juan subbasin where they are observed in a single belt parallel to the paleodepositional strike (Keller 1999). In many places, thrust planes developed in the lowermost beds of the La Laja Formation during the Andean orogeny.

The origin of the Argentine Precordillera is surrounded by controversy, and it has been proposed by some workers (e.g. Kay et al. 1996, Dalziel 1997, Keller 1999) that it represents a Laurentian crustal fragment in South America, while for some

other researchers it seems to be of Gondwanic strike-slip parautochthonous origin (Aceñolaza and Toselli 1999).

The Pie-de-Palo Range, east San Juan town, westernmost Pampean Ranges, has been regarded as part of the Precordillera basement. The western sector of this range is characterized by carbonate-dominated shallow sediments (Caucete Group; Ragona et al. 1995) intercalated with metaquartzites and calciferous schists, metamorphosed in the greenschist to amphibolite facies. Well-preserved klippe are observed in the rocks of the crystalline basement that corresponds to an ancient seafloor that has been displaced underneath a platformal sequence of clastics and carbonates. The present erosional level exposed the corresponding fault zone (Ragona et al. op. cit.).

A Neoproterozoic age for the Pie-de-Palo complex has been suggested (although U-Pb zircon data indicate a Grenville age; Kay et al. 1996), based on the presence of trace fossils (Bordonaro et al. 1992) found in carbonate rocks of the Angaco Formation (Caucete Group) in the occidental flank of the Pie de Palo Range. This ichnofauna is not very abundant and, sometimes, structural cleavages obscure it. The presence of Gordia (cosmopolitan form ascribed to the action of worms) and Didymaulichnus (a cosmopolitan form found in a large variety of sedimentary environments, ascribed to mollusk displacement), suggest that a Vendian to Tommotian age for the deposition of the Caucete Group sedimentary rocks is, in the present case, more likely.

CARBON AND STRONTIUM ISOTOPE COMPOSITION

Sampling and Analytical Methods

Table 1. Chemical analyses of representative samples from Las Tienditas, La Laja and Caucete Group carbonate rocks in the Pie-de-Palo Range.

(a) Las Tienditas Formation										
	TIEND-1	TIEND-3	TIEND-5	TIEND-10	TIEND-12	TIEND-15	TIEND-18	TIEND-20	TIEND-23	
SiO ₂	1.92	0.55	1.15	1.89	9.84	13.54	9.07	21.94	41.32	
Al ₂ O ₃	0.17	0.12	0.10	0.32	0.43	0.66	0.42	2.40	1.35	
Fe ₂ O ₃	0.10	0.09	0.06	0.13	0.18	0.36	0.19	0.97	0.83	
MgO	0.16	0.15	0.11	0.20	0.36	0.44	0.37	0.80	0.93	
CaO	55.20	55.66	55.85	55.01	49.17	46.20	49.69	38.23	26.43	
Na ₂ O	0.11	0.49	0.10	0.10	0.08	0.12	0.18	0.10	0.12	
K ₂ O	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.61	0.13	
TiO ₂	0.01	0.01	0.01	0.02	0.02	0.04	0.03	0.11	0.07	
P ₂ O ₅	0.18	0.12	0.09	0.28	0.02	0.21	0.03	0.05	0.06	
MnO	0.01	0.02	0.02	0.04	0.04	0.07	0.08	0.11	0.09	
Sub-Total	57.86	57.21	57.49	57.99	60.14	61.65	60.06	65.32	74.33	
(b) La Laja Formation										
	LAJAS-1	LAJAS-3	LAJAS-6	LAJAS-9	LAJAS-12	LAJAS-15	LAJAS-18	LAJAS-21	LAJAS-24	LAJAS-27
SiO ₂	1.14	9.62	12.97	6.31	10.84	4.10	5.14	3.34	1.94	7.17
Al ₂ O ₃	0.39	2.43	3.25	1.29	3.29	1.35	1.13	0.90	0.94	2.94
Fe ₂ O ₃	0.56	0.64	0.93	0.38	1.20	0.53	0.85	0.65	0.31	0.99
MgO	2.89	1.33	1.34	1.00	1.14	0.99	0.91	1.34	0.82	1.05
CaO	51.74	44.46	41.42	48.75	42.81	49.83	49.34	50.85	53.05	45.60
Na ₂ O	0.32	1.12	1.48	0.90	1.37	0.27	0.79	0.37	0.12	0.11
K ₂ O	0.06	0.69	1.02	0.15	1.09	0.47	0.21	0.25	0.30	1.34
TiO ₂	0.02	0.10	0.14	0.05	0.16	0.05	0.05	0.04	0.04	0.09
P ₂ O ₅	0.00	0.02	0.03	0.02	0.01	0.02	0.06	0.03	0.02	0.04
MnO	0.02	0.03	0.04	0.02	0.02	0.02	0.05	0.03	0.02	0.03
Sub-Total	57.14	60.44	62.62	58.87	61.93	57.63	58.53	57.80	57.56	59.36
(c) Caucete Group, Pie-de-Palo Range										
	PPALO-2	PPALO-5	PPALO-10	2 PPALO-5	PPALO-15	2 PPALO-9	3 PPALO-1	3 PPALO-5	2 PPALO-1	3 PPAL-0-9
SiO ₂	0.63	0.81	0.25	0.16	1.46	0.00	0.05	0.46	0.49	0.19
Al ₂ O ₃	0.21	0.29	0.15	0.08	0.26	0.06	0.06	0.18	0.16	0.10
Fe ₂ O ₃	0.27	0.21	0.33	0.06	0.31	0.15	0.05	0.06	0.19	0.09
MgO	1.20	0.58	19.41	1.04	3.52	19.78	3.14	3.97	14.65	5.55
CaO	53.96	55.06	55.51	55.51	50.70	54.46	52.95	52.10	40.07	51.32
Na ₂ O	0.18	0.25	0.20	0.12	0.21	0.10	0.22	0.29	0.19	0.3
K ₂ O	0.11	0.06	0.07	0.00	0.12	0.00	0.00	0.09	0.00	0.01
TiO ₂	0.02	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.03	0.02
P ₂ O ₅	0.01	0.01	0.00	0.00	0.01	0.00	0.00	0.00	0.03	0.01
MnO	0.09	0.04	0.05	0.01	0.02	0.02	0.01	0.01	0.02	0.01
Sub-Total	56.68	57.33	55.98	56.99	56.62	54.58	56.49	57.17	55.83	57.53
Si	3141	4132	1304	946	7230	0	379	2448	2555	1062
Ca	38.55	39.28	25.33	39.57	36.13	24.57	37.89	37.27	28.54	36.18
Mn	716	331	402	2	98	120	12	0.006	70	39
Mg	0.80	0.33	11.68	0.72	2.19	11.82	1.99	2.47	8.80	3.39
Sr	246	280	166	292	461	193	366	273	643	209
Rb	3	1	2	1	4	1	1	2	1	4
Fe	1805	1390	2186	417	2073	1016	303	402	1239	608
Ba	0	0	0	0	0	0	0	0	0	0
Mg/Ca	0.021	0.011	0.461	0.018	0.061	0.481	0.052	0.066	0.310	0.094

Over 100 samples were collected along traverses, perpendicular to the strike of limestone layers, at a metric scale, from carbonates of the Las Tienditas Formation, La Laja

Formation, Precordillera basin, and from three metasedimentary carbonate lenses in the Pie-de-Palo Range complex.

Carbon and oxygen isotope analyses were carried out at the Stable Isotope Laboratory (LABISE) of the Department of Geology, Federal University of Pernambuco (UFPE), Brazil. CO₂ gas was extracted from powdered carbonates in a high vacuum line after reaction with 100%

phosphoric acid at 25°C for one day (three days allowed, when dolomite was present). The CO₂ released, after cryogenic cleaning, was analyzed in a double inlet, triple collector SIRA II mass spectrometer and results are reported in δ notation, PDB scale, in permil (‰). The uncertainties of the isotope measurements were 0.1‰ for carbon and 0.2‰ for oxygen, based on multiple analyses of an internal laboratory standard (BSC).

Ten samples from Las Tienditas, eight from La Laja Formations and seven from carbonate lenses from the Pie-de-Palo Range complex that had C and O isotopes determined in this study, were selected for ⁸⁷Sr/⁸⁶Sr analyses. For determination of the Sr isotopic ratios, the samples were leached in 5M acetic acid and centrifuged to separate the dissolved from the insoluble fraction. Rb and Sr were separated from leached solutions by standard

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Table 2. $^{87}\text{Sr}/^{86}\text{Sr}$, C and O isotope analyses of representative samples from Las Tienditas and La Laja Formations and some major and trace chemistry (ppm).

(a) Las Tienditas Formation

Sample	Height* (m)	$\delta^{18}\text{O}$ PDB	$\delta^{13}\text{C}$ PDB	Ca%	Mg%	Mg/Ca	Si (ppm)	Fe (ppm)	Mn (ppm)	Sr (ppm)	Rb (ppm)	$^{87}\text{Sr}/^{86}\text{Sr}$ (1 σ)
TIEND 1	0	-6.9	3.4	39.22	0.17	0.004	9459	662	68	3062	2	0.70870(06)
TIEND 2	2.40	-11.5	0.5	-	-	-	-	-	-	-	-	-
TIEND 3	2.45	-10.3	2.9	39.60	0.17	0.004	2709	567	100	3098	3	0.70875(09)
TIEND 4	3.70	-10.1	2.9	-	-	-	-	-	-	-	-	-
TIEND 5	4.90	-8.8	3.11	39.70	0.14	0.004	5655	426	110	2538	0	0.70877(08)
TIEND 6	2.75	-10.9	2.14	-	-	-	-	-	-	-	-	-
TIEND 7	5.20	-11.3	1.91	-	-	-	-	-	-	-	-	-
TIEND 8	6.20	-9.9	2.93	-	-	-	-	-	-	-	-	0.70890(09)
TIEND 9	4.45	-8.8	1.81	-	-	-	-	-	-	-	-	-
TIEND 10	7.20	-6.9	1.23	39.06	0.19	0.005	9145	855	271	1887	0	0.70878(09)
TIEND 11	5.90	-7.68	1.96	-	-	-	-	-	-	-	-	-
TIEND 12	5.80	-6.86	1.01	34.86	0.23	0.007	46771	1211	279	1336	0	0.70912(09)
TIEND 13	6.10	-5.60	-0.23	-	-	-	-	-	-	-	-	-
TIEND 14	5.90	-5.87	0.55	-	-	-	-	-	-	-	-	-
TIEND 15	2.80	-6.60	0.19	32.78	0.23	0.007	63818	2382	564	940	0	0.70928(08)
TIEND 17	6.00	-7.31	0.69	-	-	-	-	-	-	-	-	-
TIEND 18	2.20	-6.60	0.45	35.28	0.23	0.006	43249	1229	679	369	0	0.70993(12)
TIEND 19	4.90	-6.83	0.05	-	-	-	-	-	-	-	-	-
TIEND 20	4.20	-5.55	-1.57	27.15	0.34	0.012	102386	6508	935	536	20	0.70948(04)
TIEND 21	4.70	-6.93	-0.41	-	-	-	-	-	-	-	-	-
TIEND 22	4.20	-7.39	0.35	-	-	-	-	-	-	-	-	-
TIEND 23	5.00	-6.44	-1.01	18.78	0.29	0.015	206826	5520	739	229	9	0.710819(12)

* Stratigraphic position in relation to the previous sample of the section.

(b) La Laja Formation

Sample	Height* (m)	$\delta^{18}\text{O}$ PDB	$\delta^{13}\text{C}$ PDB	Ca%	Mg%	Mg/Ca	Si (ppm)	Fe (ppm)	Mn (ppm)	Sr (ppm)	Rb (ppm)	$^{87}\text{Sr}/^{86}\text{Sr}$ (1 σ)
Lajas-1	0	-8.88	0.79	37.13	1.81	0.049	5.651	3724	153	745	1	0.71006(07)
Lajas-2	0.78	-10.25	0.82	-	-	-	-	-	-	-	-	-
Lajas-3	0.9	-8.74	0.75	31.97	0.77	0.024	45.888	4298	204	606	15	0.70962(10)
Lajas-4	4	-8.88	0.38	-	-	-	-	-	-	-	-	-
Lajas-5	2.6	-8.67	0.11	-	-	-	-	-	-	-	-	-
Lajas-6	3.4	-8.98	0.7	29.80	0.74	0.025	61.605	6257	276	532	18	0.70955(10)
Lajas-7	2	-8.69	0.37	-	-	-	-	-	-	-	-	-
Lajas-8	2.25	-8.54	0.06	35.11	0.62	0.018	30.268	2567	116	661	2	-
Lajas-9	2.8	-8.5	0.29	-	-	-	-	-	-	-	-	0.70941(11)
Lajas-10	5.8	-8.57	0.4	-	-	-	-	-	-	-	-	-
Lajas-11	2.4	-8.78	-1.36	-	-	-	-	-	-	-	-	-
Lajas-12	13	-8.22	-1.87	30.80	0.62	0.020	51.645	7.997	138	577	21	-
Lajas-13	38.2	-7.1	-0.36	-	-	-	-	-	-	-	-	-
Lajas-14	4.3	-7.18	-0.56	-	-	-	-	-	-	-	-	-
Lajas-15	2.6	-7.46	0.42	35.83	0.62	0.017	20.000	3.572	144	930	12	0.70926(07)
Lajas-16	14.4	-7.67	-0.49	-	-	-	-	-	-	-	-	-
Lajas-17	25	-8.73	0.29	-	-	-	-	-	-	-	-	-
Lajas-18	25	-7.57	-0.65	35.47	0.58	0.016	24.828	5.661	377	937	8	-
Lajas-19	24	-7.47	-0.93	-	-	-	-	-	-	-	-	0.70958(07)
Lajas-20	23.3	-8.02	-0.92	-	-	-	-	-	-	-	-	-
Lajas-21	20	-7.84	-1.03	36.58	0.85	0.023	16.197	4.330	0.03	526	9	0.70958(15)
Lajas-22	19	-8.12	-1.29	-	-	-	-	-	-	-	-	-
Lajas-23	25	-8.82	-1.92	-	-	-	-	-	-	-	-	-
Lajas-24	100	-8.04	-0.54	38.08	0.56	0.015	9.566	2.078	92	674	7	0.70985(59)
Lajas-25	50	-7.75	-0.69	-	-	-	-	-	-	-	-	-
Lajas-26	20	-7.96	-1.01	-	-	-	-	-	-	-	-	-
Lajas-27	50	-7.9	-0.9	32.76	0.60	0.018	34.299	6.674	165	577	25	-
Lajas-28	50	-7.72	-0.5	-	-	-	-	-	-	-	-	-
Lajas-29	50	-7.88	-0.49	-	-	-	-	-	-	-	-	-
Lajas-30	14	-4.66	-0.56	25.12	11.25	0.448	5.680	1.970	41	288	3	-
Lajas-31	16	-4.67	-0.44	-	-	-	-	-	-	-	-	-
Lajas-32	100	-7.88	-0.49	-	-	-	-	-	-	-	-	-
Lajas-33	12.2	-5.46	-0.47	22.10	10.97	0.496	20.575	4.295	67	183	8	-
Lajas-34	10	-4.2	-0.12	-	-	-	-	-	-	-	-	-
Lajas-35	7	-4.35	-0.29	-	-	-	-	-	-	-	-	-

* Stratigraphic position in relation to the previous sample of the section.

ion-exchange techniques. Sr isotope analyses were performed on a seven-collector Mat 262 instrument at the University of Brasilia, Brazil. The isotopic ratios have been normalized to a $^{86}\text{Sr}/^{88}\text{Sr}$ value of 0.1194.

The same samples analyzed for Sr isotopes had major elements and some trace elements analyzed by X-ray fluorescence, using fused beads and an automatic RIX-3000 (RIGAKU) unit available at the LABISE (UFPE). Fused beads were prepared using Li fluoride and Li tetraborate. The whole-rock major element analyses are found in Table 1 and C, O and Sr isotope analyses with some trace elements, in Tables 2 and 3.

Evaluating Sample Quality

Alteration, neomorphic recrystallization, diagenesis and metamorphism can lead to post-depositional changes in the isotopic composition of sedimentary carbonates. Therefore, the use of C, O and Sr isotopes as tools in chemostratigraphy requires precaution and screening samples with primary isotopic values becomes imperative.

With this purpose, a certain number of geochemical and petrological tests have been adopted by several authors to evaluate the degree of alteration of individual samples and are discussed in details, among others, in Kaufman and Knoll (1995) and Kha et al. (1999). The knowledge of the behavior of Rb, Sr, Mn and Fe helps selecting samples that have undergone little or no alteration. Among all the parameters used to make such an evaluation, it seems that the simplest and one of the most effective is the Mn/Sr ratio. Limestones or dolostones with Mn/Sr < 10 commonly retain near primary $\delta^{13}\text{C}$ abundances according to these authors. The knowledge of Mg contents helps precisising dolomitization while SiO_2 contents help to assure the presence of siliciclastics.

It is well-known that oxygen isotopic compositions are sensitive indicators

Table 3. Carbon and oxygen isotope analyses for carbonate samples from three carbonate lenses (Caucete Group) in the Pie-de-Palo Range, near San Juan, NW Argentina.

Caucho Venado											
Sample	Height* (m)	$\delta^{18}\text{O}$ PDB	$\delta^{13}\text{C}$ PDB	Ca%	Mg%	Mg/Ca	Si (ppm)	Fe (ppm)	Mn (ppm)	Sr (ppm)	$^{87}\text{Sr}/^{86}\text{Sr}$
PPalo 1	0	-7.8	-0.92								
PPalo 2	0.20	-7.64	-0.55	53.96	1.20	0.021	3141	1805	716	246	0.71020
PPalo 3	0.80	-7.83	-0.92								
PPalo 4	1.00	-8.17	-1.28								
PPalo 5	2.00	-7.49	-0.81	55.06	0.58	0.011	4132	1390	331	280	0.70955
PPalo 6	1.50	-7.62	-0.54								
PPalo 7	2.00	-6.9	-0.46								
PPalo 8	2.10	-8.24	-0.85								
PPalo 9	2.30	-8.20	-1.30								
PPalo 10	3.80	-7.92	-0.24	35.5	19.41	0.461	1304	2186	402	166	0.71056
PPalo 11	1.40	-8.40	-0.65								
PPalo 12	1.90	-6.61	-0.29								
PPalo 13	0.70	-6.11	-0.16								
PPalo 14	1.00	-8.34	-0.33								
PPalo 15	0.40	-8.00	0.98	50.70	3.52	0.061	7230	2073	98	461	0.70946
El Pozo											
2PPalo 1	0	-7.6	-0.09	40.07	14.65	0.310	2555	1239	70	643	1
2PPalo 2	1.2	-10.84	0.1								
2PPalo 3	3	-7.77	-0.04								
2PPalo 4	0.8	-9.20	0.12								
2PPalo 5	0.2	-8.92	0.04								
2PPalo 6	0.8	-9.65	0.32	55.51	1.04	0.018	946	417	2	292	0.70973
2PPalo 7	0.8	-8.2	0.07								
2PPalo 8	1	-7.69	0.72								
2PPalo 9	2	-9.33	-0.07								
2PPalo 10	0.2	-8.08	0.82	34.46	19.78	0.481	0	1016	120	193	1
3PPalo 1	0.3	-7.59	0.37	52.95	3.14	0.052	379	303	12	366	0.70999
3PPalo 2	3	-7.56	0.4								
3PPalo 3	0.8	-8.13	-0.48								
3PPalo 4	0.2	-7.35	-0.27								
3PPalo 5	0.6	-7.23	-0.12	52.10	3.97	0.066	2448	402	13	273	2
3PPalo 6	0.3	-8.6	0.46								
3PPalo 7	2	-7.82	-0.18								
3PPalo 8	1.2	-8.77	-0.41								
3PPalo 9	0.5	-8.15	-0.18	51.32	14.65	0.094	1062	608	39	209	0.70960
San Ceferino											
Sample	Height* (m)	$\delta^{18}\text{O}$ PDB	$\delta^{13}\text{C}$ PDB	Ca%	Mg%	Mg/Ca	Si (ppm)	Fe (ppm)	Mn (ppm)	Sr (ppm)	$^{87}\text{Sr}/^{86}\text{Sr}$
SANCEF-1	0	-8.93	-0.81	33.33	2.13	0.064	22,170	6471	592	244	8
SANCEF-2	0.2	-11.22	-0.92								
SANCEF-3	0.5	-8.96	-1.03	31.10	4.33	0.139	15080	4595	443	301	9
SANCEF-4	10.5	-7.65	1.33								
SANCEF-5	2	-9.05	0.07								
SANCEF-6	2	-8.95	0.89	32.87	3.65	0.111	18263	1516	273	374	9
SANCEF-7	12	-8.77	0.39								
SANCEF-8a	10	-8.57	1.07	28.99	8.31	0.287	1194	996	170	166	1
SANCEF-8b	10	-9.23	0.79								
SANCEF-9	10	-9.62	-0.06								
SANCEF-10	0.2	-8.34	0.17	38.33	0.34	0.009	8541	872	145	225	3

*Stratigraphic position in relation to the previous sample of the section.

of diagenesis with a decrease in $\delta^{18}\text{O}$ values often resulting from isotopic exchange with meteoric or hydrothermal fluids. In most cases, crossplots of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ commonly show no variation of $\delta^{13}\text{C}$ with decreasing $\delta^{18}\text{O}$ indicating that fluid volumes sufficient to re-equilibrate O-isotopic composition are too small to have a significant effect on $\delta^{13}\text{C}$.

In Figure 2, Mn/Sr ratios for carbonate rocks from Las Tienditas and La Laja Formations and from Pie-de-Palo Range carbonates are much lower than 10. In the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ crossplots for both Formations as well as for carbonates in the Pie-de-Palo Range complex, apparently scattering rather than

co-variance seems to predominate. These observations have led us to believe that the $\delta^{13}\text{C}$ values in most of the analyses reported here are primary values.

Stratigraphic Variation in $\delta^{13}\text{C}$ and $^{87}\text{Sr}/^{86}\text{Sr}$

(a) *Las Tienditas Formation.*-- Twenty three representative, dark gray, carbonate samples were stratigraphically collected from a 100m-thick section about 31 km SE from Salta in the Lerma Valley (Fig. 3). In this section, dark limestones occur in the first 50m from the base of the section, next 30 m being characterized by marly limestones and, finally, the uppermost

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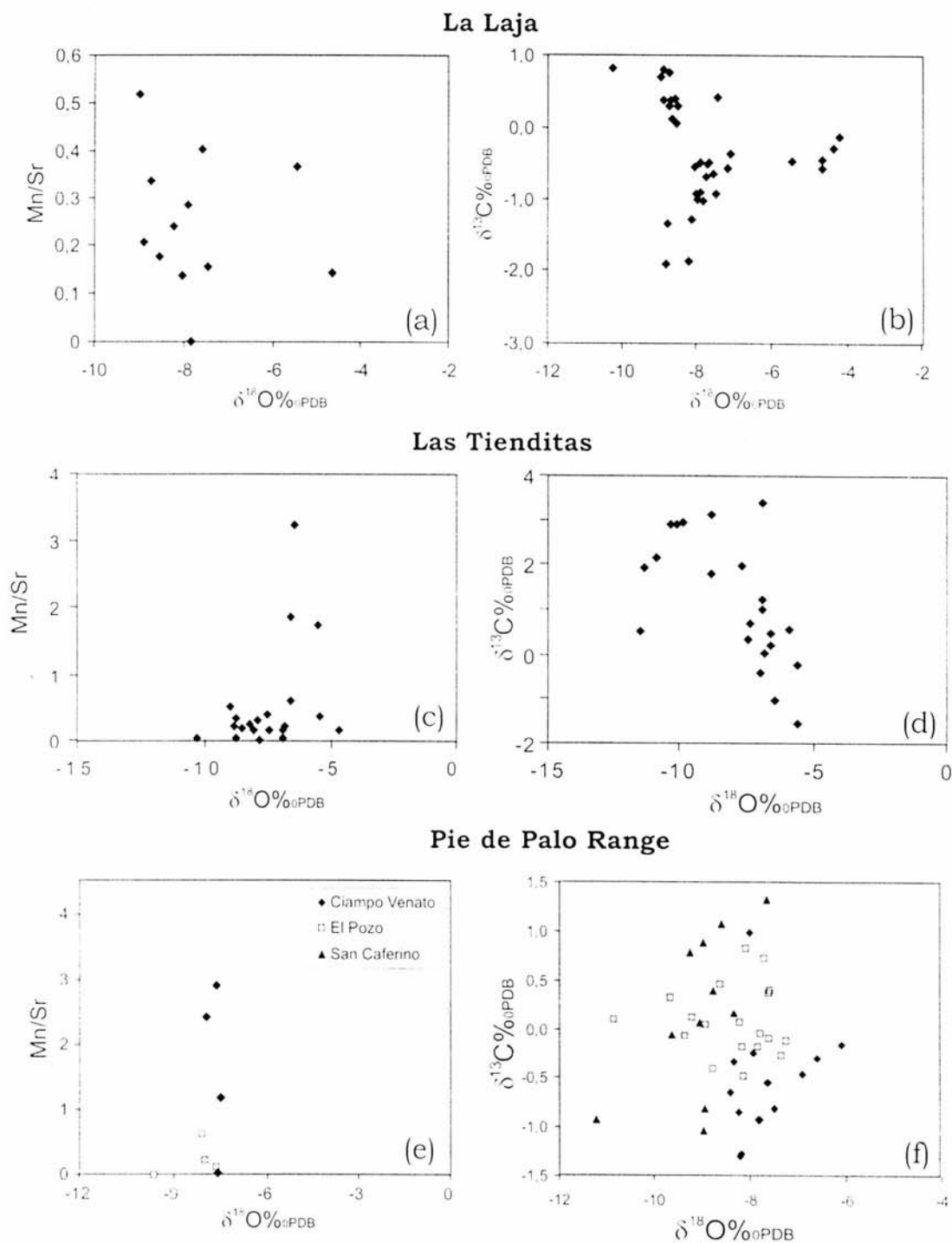


Figure 2. Mn/Sr ratios for carbonates of La Laja Formation in the Chica de Zonda Valley at (a) and at (c) for Las Tienditas Formation near Salta. $\delta^{13}\text{C}$ vs $\delta^{18}\text{O}$ (‰ PDB) from La Laja carbonate rocks at (b) and for Las Tienditas Formation at (d). $\delta^{13}\text{C}$ vs $\delta^{18}\text{O}$ (‰ PDB) for limestone lenses (Caucete Group) in the Pie-de-Palo Range at (e).

20m by marlstones, the whole-section becoming more clay-enriched towards the top. Limestones in this Formation show sparitic calcite with recrystallized organic matter, pyrite grains, and lithic fragments (plagioclase, chlorite, quartz)

These samples yielded $\delta^{13}\text{C}$ values between -1.6 and $+3.4$ ‰_{PDB}, the highest positive values observed at the base of the section, gradually decreasing towards the top (Fig. 3). About 15 m from the top, a negative excursion (-1.6) is then observed. Oxygen isotopes tend to exhibit opposite behavior with strong oscillations at the base of the Formation, gradually increasing up section, reaching a maximum of -5 ‰ around 15 m from the top of the section. The C-isotope curve of this Formation when compared to the one across the Precambrian-Cambrian transition elsewhere suggests that Las Tienditas carbonates have registered such a transition about 15m from the top at the studied section.

In this section, carbonates show $^{87}\text{Sr}/^{86}\text{Sr}$ values (Fig. 4)

defining a non-monotonic increase ($0.70870 - 0.71082$) as seen in Figure 4 with a rise around 15m from the top of the section. SiO_2 increases dramatically in the upper 40m of this section where it varies from 10 to 40% per volume, a reflection of the substantial incorporation of clay and, in minor amounts, other terrigenous sediments (plagioclase, chlorite, quartz) to these carbonates. Fe and Mn as well as Mg/Ca ratio vary sympathetically with SiO_2 from the base to the top of the section, gradually increasing up section while Sr displays an opposite behavior, decreasing gradually up section. About 15 m from the top all elemental variation curves examined show an enhancement of values, although maintaining the same general trend (Fig. 4).

(b) *La Laja Formation (Precordillera).*-- Thirty five representative samples have been stratigraphically collected for approximately 700m of carbonates in this Formation along the Zonda Valley in the Chica de Zonda Range, west of San Juan town (Fig. 5). Carbonate rocks in this section are

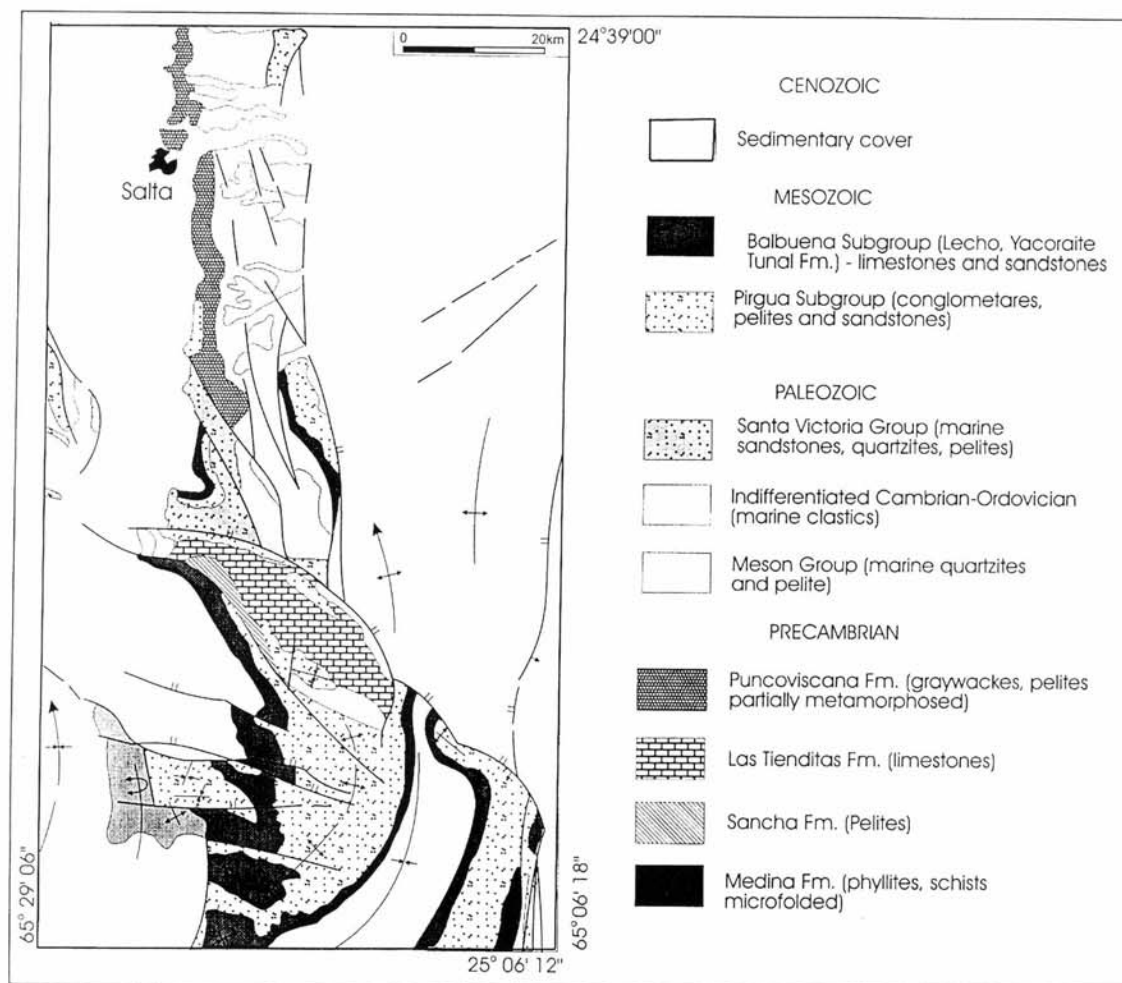


Figure 3. Geologic map of an area near Salta town, where carbonate rocks of Las Tienditas Formation limestones crop out (source: Salfity et al. 1998. Geologic map of Salta Province).

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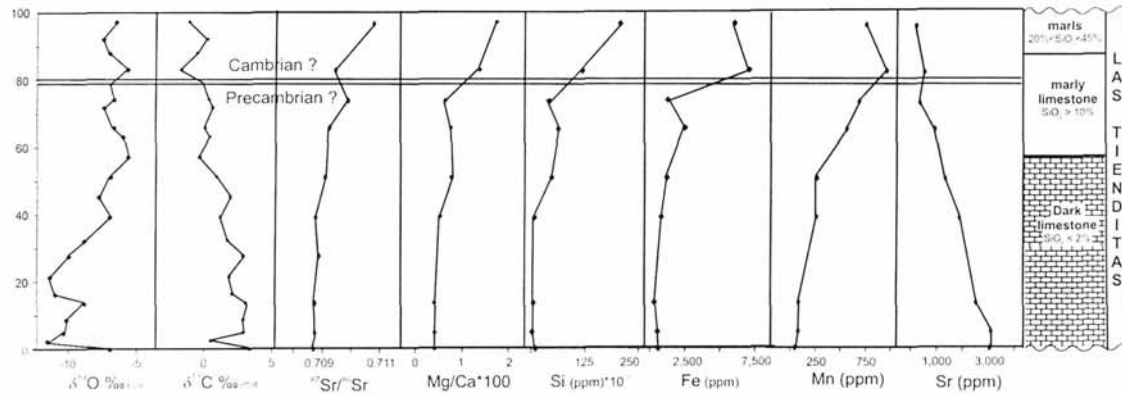


Figure 4. Chemostratigraphy including $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ (‰ PDB) and $^{87}\text{Sr}/^{86}\text{Sr}$ and some major and trace elements in carbonate rocks along the stratigraphic column of Las Tienditas Formation in a section about 31 km southeast of Salta, NW Argentina.

characterized by dark limestones with intercalations of layers of less than one-meter thick, fine-grained sandstones, in the base of the La Laja Formation (for about 120m). This situation is followed by about 100m of pure limestones (SiO_2 content decreases while CaO increases towards the top). The next 200m are characterized by marly limestones (distal facies) and that are followed in the uppermost portion of this section by 160m-thick fossiliferous (with bioturbation) buff dolomitic limestones, deposited in open sea. Black chert is eventually intercalated in this height of the section. In some portions of this section, rocks show well-developed cleavage caused by pervasive faults and mesoscale drag folds whose axes dip almost vertically. As the structural perturbations make the precise stratigraphic position of samples difficult, sampling from these portions has been omitted to avoid ambiguities.

This section displays an overall $\delta^{13}\text{C}$ variation from -2‰ to $+1\text{‰}_{\text{PDB}}$ (Fig. 6). The C-isotope curve for the lowermost portion of the profile (limestones/sandstone intercalations) shows much stronger oscillations, with values varying from $+1\text{‰}$ to -2‰_{PDB} . For the next 100m upsection, this C-isotope chemostratigraphic profile is characterized by progressively more negative $\delta^{13}\text{C}$, reaching a minimum of about -2‰ about 250m from the base of the section. For the next 350 m upsection, $\delta^{13}\text{C}$ values are around -0.5‰ . This C-isotope profile for La Laja Fm., when compared to profiles for carbonates that registered the Vendian-Tommotian transition elsewhere (e.g. Magaritz 1989; Magaritz et al. 1991; Brasier et al. 1994), suggests that such a transition was recorded at the base of this Formation.

There is always a potential for isotopic alteration during dolomitization (Sheppard and Shwarcz 1970) but, apparently, in the uppermost portion of this section, dolomitic limestones do not show any substantial change in the C-isotopic composition in relation to the underlying marly limestones.

Eight samples from the lower 350m of this carbonate section

were also analyzed for Sr isotopes and $^{87}\text{Sr}/^{86}\text{Sr}$ values vary from 0.70926 to 0.70950 (Table 2) with exception of one sample (>0.710). The higher $^{87}\text{Sr}/^{86}\text{Sr}$ value is recorded on the base of the section which coincides with sandstone intercalations. In the lowermost 80m of the section, Sr isotope ratios drop from an initial value slightly higher than 0.71000 to 0.70926 and, thereafter, it rises to 0.70985. Such differences in the carbonate Sr isotopic signatures between the lowermost and upper portions of the section indicate a significant variation in the depositional environment and can be correlated with possible Precambrian-Cambrian transition that the La Laja Formation carbonates appear to have recorded.

(c) *Pie-de-Palo Range (Precordillera basement)*.-- Carbonate rocks of the Caucete Group in the occidental portion of this Range have been sampled in three localities: Ciampo Venato, El Pozo (abandoned quarry), and a third one, in the San Ceferino locality, next to the southernmost extension (Fig. 5). In all three localities, rocks show a slightly higher degree of metamorphism (greenschist facies) than that exhibited by Las Tienditas and La Laja Formation metasediments.

In the Ciampo Venato locality, white saccharoidal carbonates form a 20m-thick limestone layer that dips 30° to the south and is in sharp contact with a finely-laminated orthoquartzite. Iron-rich concretions, one-cm in diameter, are observed along the contact with the orthoquartzite. There are intercalations of four thin siliciclastic layers in the uppermost 2m of this lens.

In the El Pozo quarry locality, about 35 km east of San Juan town, finely-granular carbonate metasediments dip around 10° to the south and are intercalated in greenschist-facies metapelites. In this quarry that once was exploited for refractory mineral industry, five levels of dolomitic carbonates (one-meter thick or less) can be observed within the major carbonate layer. At the San Ceferino locality, carbonate lenses are intercalated in quartzites and garnet-schists. Small pyrite cubes are present in these carbonates. The whole set of strata

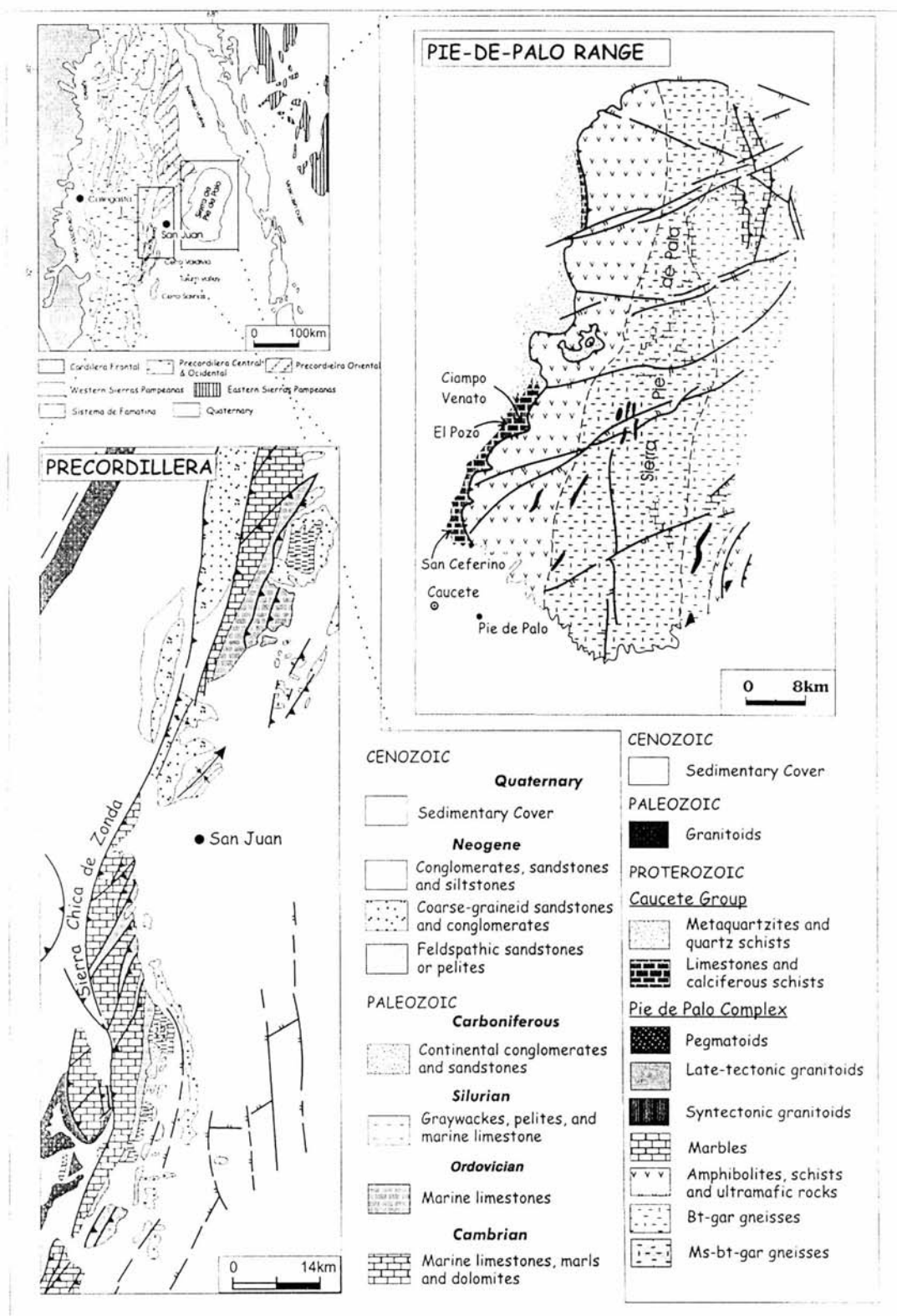


Figure 5. Geology of the area of the Precordillera carbonate sequence and its basement, the Pie-de-Palo Range, near San Juan, Argentina (source: Ragona et al. 1995. *Geologic Map of San Juan Province*), showing sample localities.

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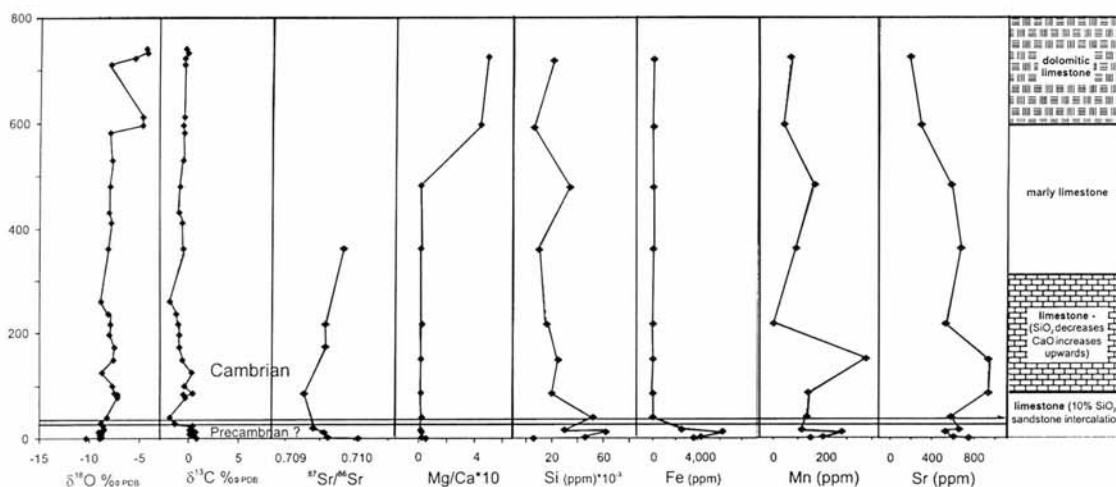


Figure 6. Chemostratigraphy including $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ (‰ PDB), $^{87}\text{Sr}/^{86}\text{Sr}$ and some major and trace elements in carbonate rocks along the stratigraphic column of La Laja Formation in a section in the valley along Chica de Zonda Range west of San Juan town, NW Argentina.

has been deformed into tight isoclinal folds, with southward dipping axial planes.

Carbonate rocks of these three localities display $\delta^{13}\text{C}$ chemostratigraphic profiles similar to each other (Fig. 7). $\delta^{13}\text{C}$ in 10 carbonate samples from the El Pozo locality display very little variation and are very close to 0.0‰_{PDB}, while 15 carbonate lens samples from Ciampo Venato yielded $\delta^{13}\text{C}$ values between -1.0‰ and 0.0‰_{PDB}. At San Ceferino, 11 carbonate samples exhibit $\delta^{13}\text{C}$ values from -1.4‰ to +1.3‰_{PDB}. Values of $\delta^{13}\text{C}$ reported by Linares et al. (1982) are

mostly around 0‰_{PDB}, in agreement with C isotope values reported here.

These three C-isotope profiles show a very narrow range of variation around 0.0‰_{PDB}, which is in consonance with the behavior of carbon isotopes in carbonates of Vendian age of the 580-550 Ma interval (see Narbonne et al.1994, for example). A total of seven carbonate samples from Ciampo Venato and El Pozo quarries had Sr isotopes analyzed and show $^{87}\text{Sr}/^{86}\text{Sr}$ from 0.70939 to 0.71080 (Table 3) which are values that are a little too high for Late Mesoproterozoic (age

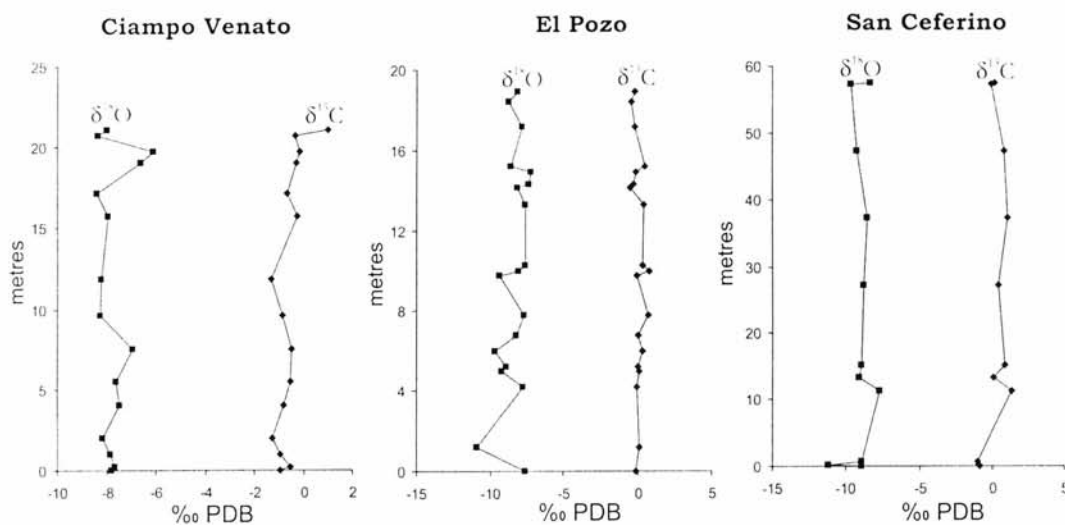


Figure 7. $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values(‰PDB) of limestones along the stratigraphic column of three lenses from three different localities (Ciampo Venato, El Pozo and San Ceferino) in the Pie-de-Palo Range complex, east of San Juan Town, NW Argentina.

proposed by Kay et al. 1996) carbonate rocks (values in the 0.706 - 0.707 range would be anticipated for that age interval; Veizer and Compston 1976; Veizer et al. 1983).

Three possible interpretations for this Sr isotope behavior are: (a) samples underwent important secondary alteration; (b) less likely, Late Mesoproterozoic carbonates could eventually show $^{87}\text{Sr}/^{86}\text{Sr}$ in that high range; (c) these carbonates are of Vendian to Early Cambrian age.

The bulk chemistry of these carbonate rocks suggest that they might have undergone only minor secondary alteration, and a Mesoproterozoic age for the Pie-de-Palo complex is challenged by the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios encountered in this study. This way, the third hypothesis seems to be the most acceptable one in the light of our present C, Sr isotope data. This contention finds further support in the work by Bordonaro et al. (1992) where trace fossils (*Dydimaulichnus* and *Gordia*) found in carbonate rocks from the occidental flank of the Pie de Palo Range have been described by the first time. Similar fossils are found in the Puncovicana Formation in Northwestern Argentina which is regarded as of Late Vendian to Early Cambrian age.

CONCLUSIONS

The data presented here raise the possibility that carbonate rocks of the Las Tienditas Formation have recorded the Vendian-Tommotian transition in the uppermost part of the studied section. Besides, we also raise the possibility that the La Laja Formation carbonates have also recorded this transition at the basal part the studied section. The $\delta^{13}\text{C}$ and the $^{87}\text{Sr}/^{86}\text{Sr}$ profiles for the uppermost portion of Las Tienditas Formation and for the lowermost portion of La Laja Formation are closely comparable. Such an overlap of isotopic profiles would imply that carbonates in the base of the La Laja Formation were deposited synchronously with carbonates in the top of the section sampled in Las Tienditas. This contention finds further support in the similarities of the whole-rock chemistry (major and trace elements) of the corresponding carbonate rocks.

Minor $\delta^{13}\text{C}$ variation displayed by carbonate lenses of the Caucete Group carbonates of the Pie-de-Palo Range complex (0 ‰_{PDB}) coupled with high $^{87}\text{Sr}/^{86}\text{Sr}$ (0.709 to 0.710) ratios and the observed ichnofauna raise the possibility this Group is probably of Vendian age rather than Mesoproterozoic.

The Sr isotopic ratio values observed in this study are among the highest reported in the stratigraphic record. The $^{87}\text{Sr}/^{86}\text{Sr}$ peak values are, probably, related to the nature of the continental crust being eroded during the time of deposition of these carbonates successions. An upper continental crust (high Rb/Sr) or ancient crust (high $^{87}\text{Sr}/^{86}\text{Sr}$), or both, was responsible for these high Sr isotope ratio values. The seawater with which carbonates equilibrated was likely in contact with the western margin of the Gondwana

supercontinent where Paleoproterozoic terrains, likely with high Sr isotope ratios, dominated.

The isotopic evolution of the Precambrian-Cambrian transition in Argentina shows a moderate shift to negative ^{13}C values in contrast with strong shifts to negative values reported from other continents (e.g. Magaritz 1989). Apparently, the C isotopic behavior of these carbonates in Argentina does not seem to be anomalous, as equivalent moderate shift has been documented elsewhere (e.g. in Siberia; Magaritz et al. 1991). In northwestern India, a negative excursion of ^{13}C during phosphoric activity at the base of the Birmania succession is followed by positive excursion close to the Precambrian-Cambrian transition and a swing back to less positive values in the Early Cambrian (A. Maheshwari, written communication). Friedman et al. (1996) reported a sharp drop of $\delta^{13}\text{C}$ from +5 ‰_{PDB} to +2.7 ‰_{PDB} in the top of Bhander and Sirbu limestones in the Vindhyan basin in India, that potentially recorded the Precambrian-Cambrian transition. This demonstrates a nonuniform behavior of $\delta^{13}\text{C}$ in the Precambrian-Cambrian transition, at least in some of the continents that were once part of Gondwanaland.

The debate on the origin of the Argentine Precordillera has been kept alive for the last 5 years and has been discussed in detail in the recent publication by Keller (1999). The Precordillera basin has been regarded as a conjugate rift pair of the Appalachians, part of an exotic terrane detached from the Ouachita embayment of the southern Appalachians (Astini et al. 1995), as supported by stratigraphic, faunal and chemical arguments (Kay et al. 1996). Other hypotheses proposed that the Argentine Precordillera is an exotic terrane detached from Gondwana western side, by strike-slip movement, from a region between South America, Africa and Antarctica (SAFRAN; Aceñolaza and Toselli 1999) or its incorporation to South America resulted from a collisional event between Occidentalia terrane and South America plate (Dalla Salda et al. 1992).

Our inferences call for reexamination of the status of matching of the Cordillera basin in its earliest stage of development, to the North American counterpart in the Appalachians, as well as their basement (Pie-de-Palo Range complex in South America and the basement of the Ouachita Mountains in southern Appalachians).

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