PRELIMINARY CHEMOSTRATIGRAPHIC INSIGHTS ON CARBONATE ROCKS FROM NICO PÉREZ TERRANE (URUGUAY).

K Kawashita[1], C. Gaucher[2], P. Sprechman[2], W. Teixeira[1] and R. Victória.[3]

1-Inst. de Geociências, USP. R. do Lago 562, CEP 05508-900, S. Paulo, Brazil. kaka@usp.br
2-Depto. de Paleontologia, Facultad de Ciencias. Montevideo, Uruguay. gaucher@mailer.um-marburg.de
3-CENA-USP. Av. Centenário,303, CEP 13400, Piracicaba, S. Paulo, Brazil. reyna@cena.usp.br

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Limestones and carbonate rocks, under certain circunstances, can be dated successfully by radiometric methods (Moorbath *et al.*, 1987; Thoulkerids *et al*, 1994; Kawashita *et al.*, 1997). When using "ages" derived from $^{87}Sr/^{86}Sr$ ratios, a secular variation of Sr composition on marine carbonates is relatively well known for Phanerozoic Eon oceans. Precambrian carbonates, however, show an irregular curve ascending from ca. 0.702 to the value of 0.709. However (Ghorokov *et al.* 1995), shows that this approach is applicable to Neoproterozoic carbonate rocks, although there is some limitation due to the lack of biostratigraphic criteria to erect a well-defined curve.

This paper deals with the the possibilities of applying chemostratigraphy concept on two carbonate formations of Nico Pérez Terrane, Uruguay. 1- The Polanco Formation belongs to the Arroyo del Sodado Group and contains a low-diversity microfossil-assemblages (Gaucher *et al.*, 1998; Gaucher and Sprechmann, 1999). The microfilaments and acritarchs found in the Polanco Limestone Formation and elsewhere in the Arroyo del Soldado Group have been assigned to the Upper Vendian (Valdaian), on the basis of low diversity, small size of spheromorphs (<150μm), absence of acantomorphs and abundance of Bavlinella faveolata. Similar assemblages have been found in Namibia (Nama Group), Brazil (Corumbá Group) and East European Platform (Valdai Series, Kotlin Horizon). The age of the Polanco Formation is constrained by Cloudina riemkeae GERMS occurring in the underlying Yerbal Formation (Gaucher *et al.*, 1998; Gaucher and Sprechmann, 1999). 2- The Cerro de Villalba Carbonate Formation belongs to the informal Basal Group (Gaucher *et al.*, 1996), for which the geochronological evidences suggest a Meso-proterozoic age (Teixeira *et al.*, 1999). The whole unit, including stromatolites, stromatolitic breccias and thick intercalations of carbonate rocks, was afffected by two deformational events, and the paragenesis indicate a low-to medium grade of metamorphism. Conversely, the overlying Arroyo del Soldado Group was deformed only by the younger tectonism, implying a younger age for this rock unit.

The $^{87}Sr/^{86}Sr$ and δ‰ determinations performed on 4 limestones (see Table 1) from Polanco Formation at two different localities and 6 dolomitic carbonate rocks from Cerro Villalba Formation. As we expected, among 4 limestones from Polanco Formation, the samples from Puntas de Yerbal with around 1400 ppm of Sr exhibit lower and concordant ratios compared to those from two samples of the Cierro de las Cuentas that shows Sr contents otherwise lesser than 600 ppm. According to the criteria suggested by some of above cited works, the ratio of 0.70780 can be accepted as the probable or maximum value for the coexistent sea. According to the data available for the interval 610 - *ca.* 540 Ma (Vendian) and the curve proposed by Kaufman et al, 1983, the ratio of 0.70780 signs an age of *ca.* 590 Ma (Fig.1), which is more compatible with Lower Vendian than Upper Vendian, as it has been stated in terms of Vendian microfossil assemblages. This ratio, with a possible trend for a lower ratio, suggests to be more concordant with the 0.70740 ratio assumed by Kawashita et al., 1993, for Bambuí and Una limestones (Neoproterozoic São Francisco Basin) or reported by Kawashita *et al.*, 1996, for Araras Group limestones (Neoproterozoic Paraguay Belt). The $^{87}Sr/^{86}Sr$ ratios found in Nama, Witvley and Corumbá Group limestones are significantly higher, in the range 0.70813 to 0.70892 pointing to an age interval of around 590 to 550Ma. These examples reported by Kawashita *et al.* (1993), Derry *et al.* (1992) and Kawashita *et al.* (1996), have Sr contents higher than 1000 ppm. Moreover, a Rb/Sr age of 532 ± 11 Ma (Fig.2) based on 4 samples from the Guazunambí Granite that cuts the Polanco Formation implies for a minmimum depositional age for it.

The carbonate samples from Cerro de Villalba Formation (Basal Group), sampled in two extreme stratigraphic positions (base and top), were not wholly analysed because the samples were dolomitic and showed low Sr contents. The Sr ratios for two dolomitic stromatolites from top with unusual ratios of ca. 0.725 clearly indicate the high contribution of radiogenic ^{87}Sr. This process probably took place during either metamorphism or dolomitization of the Formation.

Because of scarcity of $\delta^{13}C$ and $\delta^{18}O$ data performed, we cannot make firm conclusions derived from these results. Based on the 4 data available for Polanco Formation, it seems that the most probable primary values for $\delta^{13}C$ and $\delta^{18}O$, both versus PDB, would be close to +2.8‰ and -12.3‰, respectively. These values are in accordance with the reported values for Nama and Witvley groups. It is noteworthy that the results available for Bambuí and Una Group limestones fall into three distinct domains (Fig.3). We can argue that the data from Polanco, Nama and Witvley limestones are fiting better because of similar paleogeographical and paleotectonic situations during Neoproterozoic times. More global studies and additional data have to be performed in order to confirm this argument. The other δ‰ results obtained on Villalba Formation and illustrated in the same diagram plot in two separate fields, showing that they are uncorrelatable with the limestones from Polanco Formation. It is proposed that the two tectonic events mentioned above lead to disturbance of the C and O primary isotope ratios of these carbonates, as is supported by the Sr ratios.

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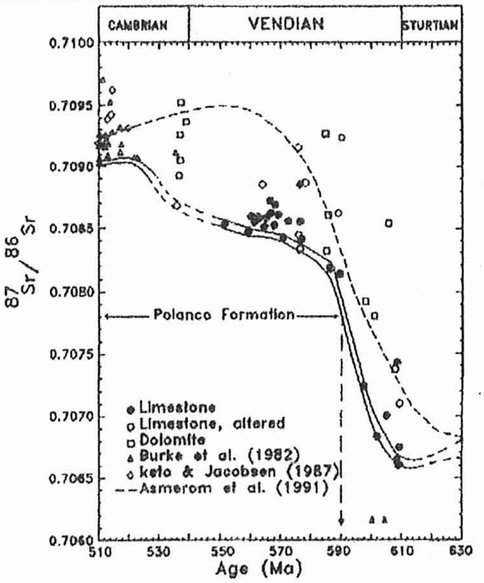

Fig.1. Estimated age for Polanco Formation based in secular variation in $^{87}Sr/^{86}Sr$ of vendian and cambrian seawater suggest by Kaufman et al. (1993) from preserved limestones.

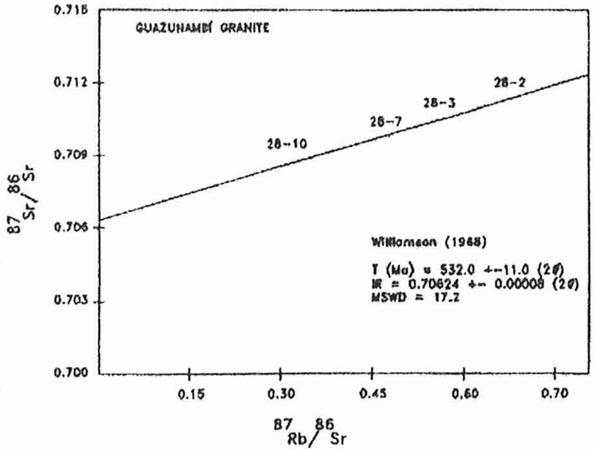

Fig.2. Rb–Sr isochron for intrusive Guasunambí granite in the Arroyo del Soldado Group.

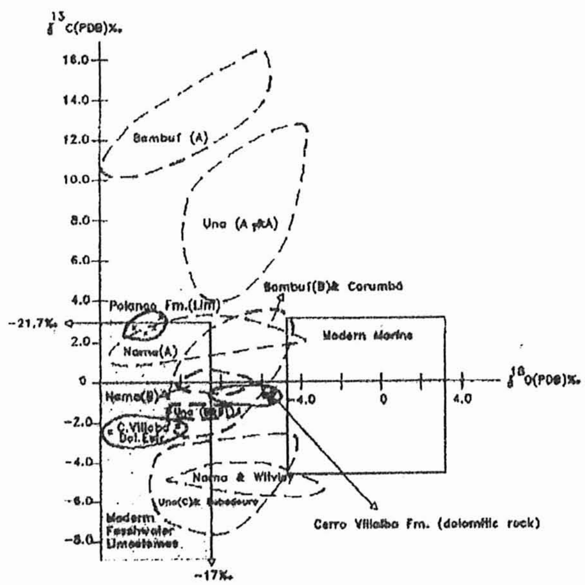

Fig.3. Crossplot of $\delta^{13}C$ and $\delta^{18}O$ for the carbonate rocks from Nico Pérez Terrane. Also included the field values for Nama and Witvley, groups (Nama and South Africa) compiled from Kaufman et al. (1977) and Derry et al. (1993), and for Bambuí, Una and Curumbá groups (Brazil), compiled from Kawashita et al. (1994). Torquato and Misi (1977) and Kawashita et al. (1996) respectively. The domains for modern and freshwater limestones are also plotted for comparison.

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Table 1. Analytical Data and $^{87}Sr/^{86}Sr$ Values of Carbonate Rocks from Nico Pérez Terrane (Uruguay).

Field N.	Sample Type	Group/Form & local	Rb (ppm)	Sr (ppm)	$^{87}Sr/^{86}Sr$	$\delta^{13}C$ (PDB)	$\delta^{18}O$ (PDB)
PYE-32/1	Limestone	Polanco F., P.Yerbal	4	1380	0.70780	2.82	-12.3
PYE-32/2	Limestone	Polanco F., P.Yerbal	14	1460	0.70785	2.86	-11.0
CCU-4/12	Limestone	Polanco F., C.Cuentas	3	575	0.70801	2.56	-11.4
CCU-4/13	Limestone	Polanco F., C.Cuentas	6	580	0.70816	2.60	-11.3
MIN-31/5	Dolomitic rock	Basal G., C. del Umbú	17	40	n.a.	-0.71	-5.2
MIN-31/6	Dolomitic rock	Basal G., C. del Umbú	8	40	n.a	-0.89	-5.7
MIN-31/7	Dolomitic rock	Basal G., C. del Umbú	4	55	n.a	-0.09	-8.5
MIN-31/8	Dolomitic rock	Basal G., C. del Umbú	≤3	40	n.a	-0.45	-5.8
AFL-85/1	Stromatolite	Basal/C.de Villalba	≤3	165	0.72365	-2.18	-9.8
AFL-85/2	Stromatolite	Basal/C.de Villalba	≤3	105	0.72531	-2.55	-13.5

* All determinations were performed on soluble fractions using 1N HCl acid for Sr/Sr ratio determinations or 100% phosphoric acid for CO_2 extraction to obtain δ‰ values versus PDB. The Sr isotopic compositions were obtained in a single collector VG-354 instrument whereas the $\delta^{13}C$ and $\delta^{18}O$ were get in a multiple collector Delta E mass spectrometer. The external error for Sr/Sr ratios is estimated as 0.00003, based on 9 analyses done on the standard NBS-987 which yield an average value of 0.71025 ± 0.00002 (1σ). The estimated error for δ determinations is better than 0.3‰.

Abbreviations: P. = Puntas de; C. = Cerro (de las); G. =Group ; F. = Formation
n.a.= not analysed

GEOCHRONOLOGY AND CHEMOSTRATIGRAPHY OF "LA TINTA" NEOPROTEROZOIC SEDIMENTARY ROCKS, BUENOS AIRES PROVINCE, ARGENTINA.

K. Kawashita[1], R. Varela[2], C. Cingolani[2], E. Soliani Jr.[3], E. Linares[4], S.A. Valencio[4], A.V. Ramos[4] and M. Do Campo[4]

1 Instituto de Geociências, USP. Rua do Lago, 562; 05508-900, S. Paulo, Brasil. kaka@usp.br
2 Centro de Investigaciones Geológicas, UNLP-CONICET. Calle 1 N° 644. 1900 La Plata, Argentina. varela@cig.museo.unlp.edu.ar; ccingola@cig.museo.unlp.edu.ar
3 Instituto de Geociências, UFRGS. Av. Bento Gonçalves, 9000, Poa, RS, Brasil. soliani@if.ufrgs.br
4 INSTITUTO DE GEOCRONOLOGIA Y GEOLOGIA ISOTOPICA (INGEIS). Pabellón INGEIS, Ciudad Universitaria. 1428 Buenos Aires, Argentina. linares@ingeis.uba.ar; susana@ingeis.uba.ar; adriana@ingeis.uba.ar; marga@ingeis.uba.ar

Keywords: La Tinta Group, Chemostratigraphy, Geochronology, Rio de la Plata cratonic region.

INTRODUCTION

The Tandilia (Buenos Aires Province) Neoproterozoic sedimentary cover largelly known as La Tinta Group (Amos *et al.*, 1972) was redefined (Iñiguez *et al.*, 1989; Poiré, 1993) to integrate a lower section as Sierras Bayas Group and the upper part as Cerro Negro Formation. These Neoproterozoic units represents a Southern portion of the Rio de la Plata cratonic region (Fig.1), in the Southwestern Gondwana (Dalla Salda *et al.*, 1988). In an attempt to obtain better constrained ages for Sierras Bayas Group, new whole rock Rb/Sr determinations on argillites and strontium isotopic measurements on limestones were carried out in order to compare with previous fine fractions Rb/Sr isochronic ages and also with inferred secular variation curve proposed by Gorokhov *et al.* (1995). $\delta^{13}C$ and $\delta^{18}O$ measurements were also performed on the same carbonates with the purpose to compare with others of similar ages reported in the literature and to constrain the $^{87}Sr/^{86}Sr$ determinations.

PREVIOUS WORKS

The Sierras Bayas Group in Olavarria area is well described by Poiré (1993). The three transgressive-regressive sedimentary sequences reported by Iñiguez *et al.* (1989) comprise from base to top by Villa Mónica, Cerro Largo and Loma Negra Formations. The Loma Negra Formation is overlain unconformably by Cerro Negro Formation, which is followed, also unconformably, by quartzites of Ordovician Balcarce Formation. The Cerro Negro Formation was previously studied by Bonhomme and Cingolani (1980) and Cingolani and Bonhomme (1982), who obtained an isochronic Rb/Sr age of 723 ± 21 Ma, established on fine fractions separated from Cerro Negro quarry argillites. This age was tentatively assumed as early diagenesis time. Other two siliciclastic Cerro Largo and Villa Mónica Formations of Sierra Bayas Group were also studied by Rb/Sr method on fine fractions (Bonhomme and Cingolani, 1980; Cingolani and Bonhomme, 1988). Their respective ages of 769 and 797 Ma, consistent with the stratigraphic positions, were interpreted as the minimum ages for sedimentation. Among the Sierras Bayas Group, only the uppermost carbonate sequence, the Loma Negra Formation, was not dated by radiometrically methods, until the present. Carbon and oxygen isotopic data in limestone rocks were obtained by Valencio *et al.* (1985).

RESULTS AND DISCUSSION

In order to evaluate the possible age of sedimentation for Cerro Negro and Loma Negra Formations and to check the validity of the concept of mechanical mixing (Cordani *et al.*, 1978) whole rock Rb/Sr analysis were performed on argillites sampled from two different localities in Olavarría area (Fig. 2). The first set of 7 selected greenish argillites from Cerro Negro Formation supplied a well aligned

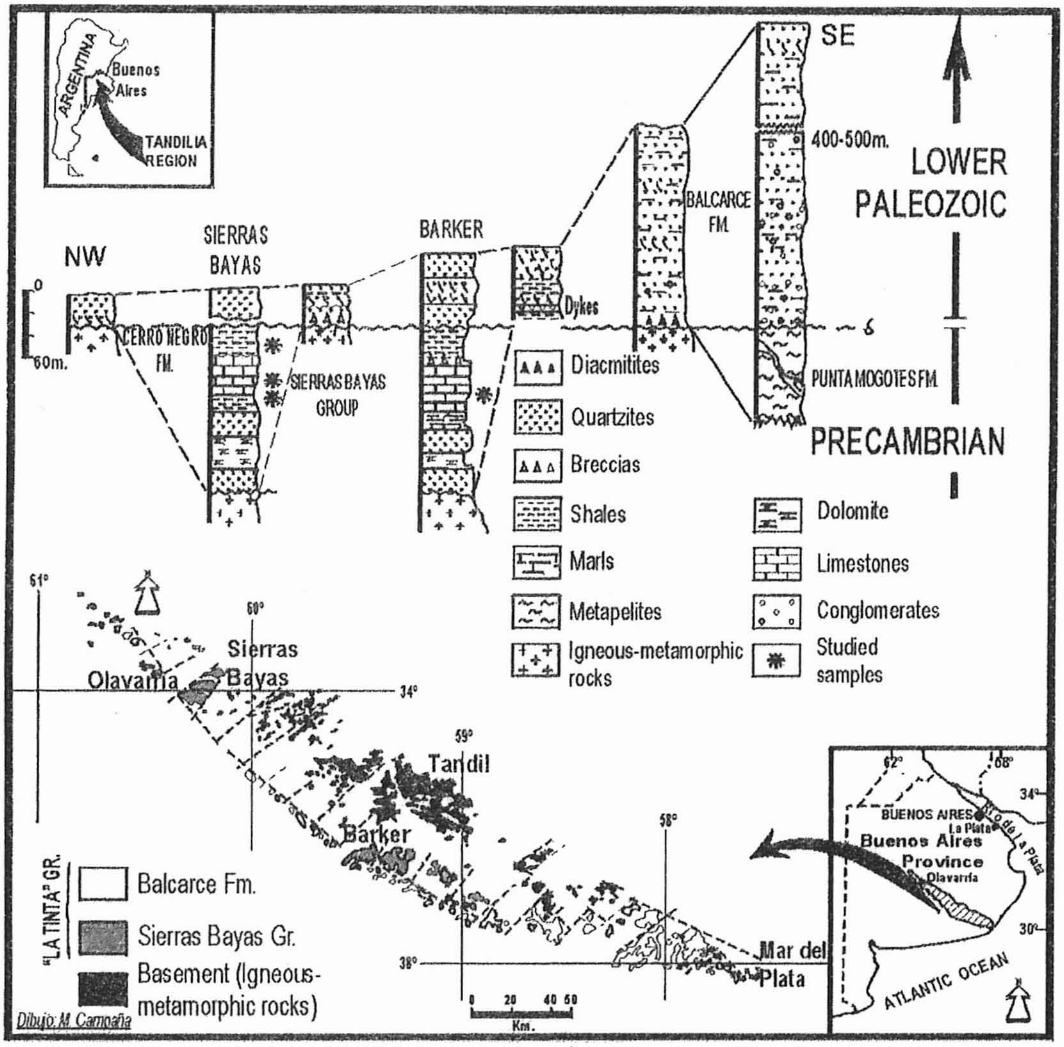

Figure 1 : Geological sketch map from Tandilia Region. Correlation of the units.

(MSWD = 0.10) points in an isochron diagram with an age of 734 ± 48 Ma and initial ratio of 0.7330 ± 0.008 (Fig.3). This age performed on whole rock samples would support the previous interpretation of early diagenesis for the age of 723 Ma obtained in fine fractions. Nevertheless, the sedimentation of Cerro Negro Formation could started earlier, around 770 Ma because of large uncertainty of 48 Ma in the age. The whole rock analysis performed on 10 varied assortment of argillites (pinky to greenish) sampled at Loma Negra quarry, Olavarría area, suggest an isochronic age of 725 ± 36 Ma and estimated initial ratio of 0.707 (Fig. 3). Although the points are not well aligned (MSWD = 7.55), this calculated age is coherent with two other estimated ages for overlying Formation. Thus, these ages support an hypothesis that the Loma Negra and Cerro Negro Formations were deposited at *ca.* 770 Ma and, at around 730 Ma ago, the clay minerals were homogeneized during diagenesis. Both examples confirm the validity of using total rock analyses on diagenetic rocks to evaluate the probable age of sedimentation, and the present data sign the possible age limit of *ca.* 730 Ma for Sierras Bayas Group. This means that the Cerro Negro Formation was deposited during or later Sturtian glacial epoch, established as around 780 Ma by Knoll *et al.* (1986).

The micritic black limestones sampled in Olavarría and Barker area, at Loma Negra and El Infierno quarries, respectively, are exhibiting $^{87}Sr/^{86}Sr$ in a wide range, between 0.70584 and 0.71409 (Figure 4). Using the criteria currently adopted (Kaufman *et al.*,1993; Kawashita *et al.*, 1994), the most probable ratios can be assumed as 0.7059 or 0.7068, inferred respectively from El Infierno and Loma Negra black limestones. Based in the Rb content, the best estimate for Loma Negra Sr "sea" would be 0.70584 ± 0.00010. This value points to two possible ages, 800 and 1100 Ma, when plotted in the secular $^{87}Sr/^{86}Sr$ ratio variation curve in the Neoproterozoic and Early Cambrian seawater proposed by Gorokhov and collaborators. The first inferred age of *ca.* 800 Ma is more compatible and is in accordance with the above mentioned Rb/Sr ages for overlying Cerro Negro Formation, whose minimun age was estimated by

Lab.N°	Field N°	Rb (ppm)*	Sr (ppm)*	87Rb/86Sr**	87Sr/86Sr***
SPR12952	CN0-12A	229.7	48.8	13.85	0.87833
SPR12953	CN0-12C	230.6	47.1	14.42	0.88448
SPR12954	CN0-12D	190.4	53.0	10.54	0.84410
SPR12955	CN0-12E	157.0	52.5	8.75	0.82433
SPR13109	CN0-12B	209.2	53.0	11.60	0.85475
SPR13110	CN0-12F	221.8	56.5	11.53	0.85197
SPR13111	CN0-12I	221.6	48.1	13.55	0.87342
CIG 845	LN0-1B	229.3	39.1	17.28	0.88904
CIG 846	LNO-1C	229.6	40.9	16.54	0.89116
CIG 847	LN0-1D	227.4	37.6	17.86	0.91277
CIG 848	LN0-1E	224.2	38.0	17.37	0.88314
CIG 849	LN0-1F	220.3	51.8	12.45	0.82453
CIG 850	LN0-1G	228.0	39.4	17.04	0.88600
CIG 851	LN0-2A	221.3	45.6	14.22	0.83568
CIG 852	LN0-2B-1	229.7	41.6	16.23	0.86541
CIG 853	LN0-2B-7	223.3	44.4	14.77	0.85428
CIG 854	LN0-2C	223.1	39.8	16.50	0.88264

Figure 2. Rb/Sr whole rock analytical data; CN0 (Cerro Negro Formation); LN0 (Cerro Largo Formation); *X-ray fluorescence, error ± 2%; **Error ± 2.8%; ***Error ± 0.00010

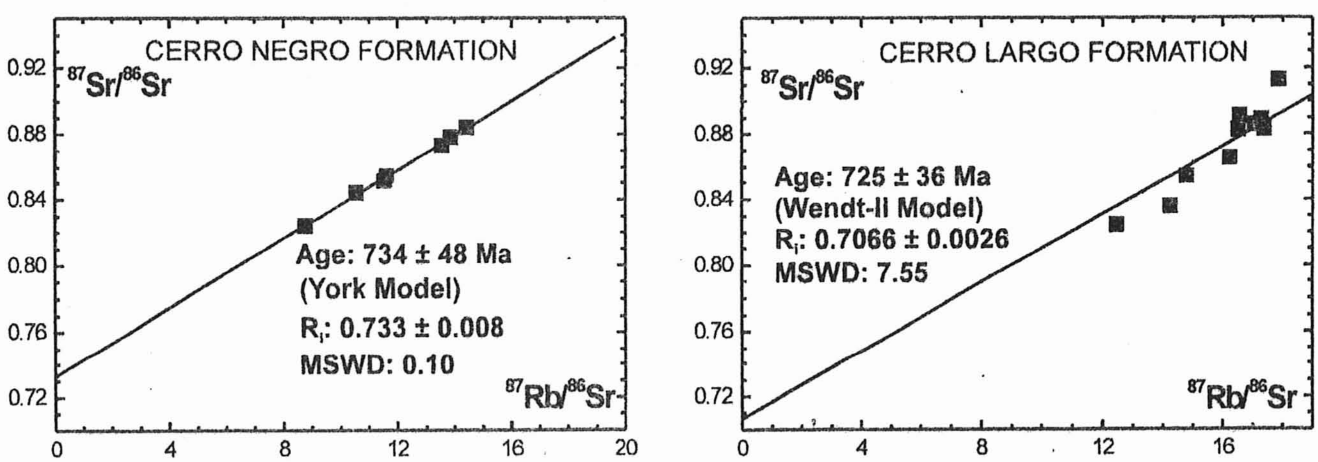

Figure 3: Isochron diagrams from argillites of Olavarría.

Bonhomme and Cingolani (1980) as 769 ± 12 Ma. Assumption of the age of 800 Ma for Loma Negra Formation implies that either this age or 793 ± 32 Ma obtained by Cingolani and Bonhomme (1988) for the lowermost Villa Mónica Formation are relatively younger or concordant, respectively, with the probable expected age of sedimentation.

Despite some restrictions to use the stable isotope data (C and O) on Neoproterozoic limestones, because both elements can be more affected than modern ones by post-depositional processes, most of the limestones were analized for carbon and oxygen isotopic composition. The $\delta^{13}C_{PDB}$ ‰ determinations performed on the Loma Negra Formation limestones (Fig. 4) show no significant variations as is usually observed in the Neoproterozoic basins (Kaufman *et al.* ,1991; 1995). With one exception, the results are in the range 3.0 – 4.6 ‰. It is noteworthy to observe that in the lower $^{87}Sr/^{86}Sr$ ratios limestones, the respective $\delta^{13}C$ values are lower than 4.0‰. Conversely, in the limestones exhibiting $\delta^{18}O \leq -9.0$‰ the $^{87}Sr/^{86}Sr$ ratios are significantly higher, denoting influence of diagenetic process or effect of meteoric fluid. Anyway, it seems that the same process was responsable for changing the primary isotope signatures. Since, there is facies control in carbon isotopic carbonate composition within the basin and, oxygen isotopes are also sensitive indicators of diagenesis. is not easy to evaluate the primary isotope compositions.

One key to infer the possible values is to use the $^{87}Sr/^{86}Sr$ ratios as support. It seems that either in Barker and Olavarría area, the primary $\delta^{13}C$ would be 3.4 ± 0.3 ‰, while the primary $\delta^{18}O_{PDB}$ would be different in these studied areas. A value of -8.0 ‰, an average value on four similar black limestones from El Infierno quarry, is suggested through cross plot with $^{87}Sr/^{86}Sr$ ratios. Using the same proceeding for Loma Negra Formation limestones, a primary value of around –5.0‰ can be suggested. This is the minimum value recorded on one profile sampled at Loma Negra quarry, Olavarria. The samples with lower values must be influence of post-depositional effect. This affected the $^{87}Sr/^{86}Sr$ ratios and is well evident on greenish and brownish limestones that constitute the base of LNO (Loma Negra, Olavarría) profile. They show a negative correlation: decreasing in $\delta^{18}O$ values and increase in the $^{87}Sr/^{86}Sr$ ratios, in response to increasing alteration.

In summary, the concepts of mechanical mixing and chemostratigraphy applied to siliciclastic rocks and limestones of some of La Tinta neoproterozoic units has revealed as very úseful and valid tools.

Field N°	Type of sample	Local/Area	Rb (ppm)	Sr (ppm)	$^{87}Sr/^{86}Sr$	$\delta^{13}C_{PDB}$ (‰)	O^{18}_{PDB} (‰)
LNO-3A	Greenish limestone	Loma Negra/Olavarria	110	290	0.70981±12	+ 5.0	-10.1
LNO-3B	Greenish limestone	Loma Negra/Olavarria	40	270	0.71153±7	+ 4.6	- 9.7
LNO-3C	Greenish limestone	Loma Negra/Olavarria	25	295	0.71135±7	+ 4.3	- 9.5
LNO-3D	Brownish limestone	Loma Negra/Olavarria	25	305	0.71030±12	+ 4.4	- 9.4
LNO-3I	Black limestone	Loma Negra/Olavarria	9	325	0.70690±12	+ 3.7	- 5.7
LNO-7A	Black limestone	Loma Negra/Olavarria	7	355	0.70717±6	+ 3.7	- 5.5
LNO-7C1	Black limestone	Loma Negra/Olavarria	9	330	0.70697±5	+ 3.1	- 5.1
LNO-7C2	Black limestone	Loma Negra/Olavarria	8	325	0.70752±8	+ 3.1	- 5.5
LNO-7E	Black limestone	Loma Negra/Olavarria	11	325	0.70725±11	+ 3.4	- 5.4
LNO-7G	Black limestone	Loma Negra/Olavarria	10	315	0.70712±8	+ 3.6	- 4.9
LNO-5A	Black limestone	Loma Negra/Olavarria	6	320	0.70680±7	+ 3.9	- 6.6
LNO-5D	Black limestone	Loma Negra/Olavarria	5	330	0.70689±8	+ 4.0	- 6.8
LNO-5G	Black limestone	Loma Negra/Olavarria	8	310	0.70712±6	+ 4.1	-7.0
LNO-5I	Black limestone	Loma Negra/Olavarria	8	325	0.70746±6	+ 4.0	- 7.2
Av-1	Black limestone	Avellaneda/Olavarria	20	320	0.70810±6	(3.8±0.4)	(-10.5±2,5)
Av-2	Greenish limestone	Avellaneda/Olavarria	30	335	0.70873±6	n.a.	n.a.
VC-1(top)	Black limestone	Villa Cacique/Barker	35	560	0.71323±7	(3.4±0.7)	(-9.0±0.7)
VC-2 (base)	Black limestone	Villa Cacique/Barker	15	27o	0.71409±12	n.a.	n.a.
El Inf.1(V)	Black limestone	El Infierno/Barker	5	238	0.70666±13	(3.7±0.7)	(-8.0±1,2)
El Inf.2(V)	Black limestone	El Infierno/Barker	≤ 3	254	0.70584±10	(3.7±0.7)	(-8.0±1,2)
El Inf.3(V)	Black limestone	El Infierno/Barker	≤ 3	281	0.70604±11	(3.7±0.7)	(-8.0±1,2)

Figure 4. Isotopic compositions and Rb and Sr contents on Loma Negra Formation limestones from Barker and Olavarria areas. The $^{87}Sr/^{86}Sr$ ratios were normalized assuming $^{86}Sr/^{88}Sr$ = 0.1194 and were performed on soluble fractions using 1N HCl acid. $\delta^{13}C$ and $\delta^{18}O$ determinations, both versus PDB, were carried out on soluble fractions using 100% phosphoric acid for CO_2 extractions. The $^{87}Sr/^{86}Sr$ ratios were obtained in a single collector VG-354 mass spectrometer, while the $\delta^{13}C$ and $\delta^{18}O$ were obtained in a MM-602 instrument. The estimated errors in δ determinations are ± 0.2 ‰. The δ values in parentheses are those from similar samples from the same locality.