Sr ISOTOPIC COMPOSITION AND Pb-Pb AGE OF NEOPROTEROZOIC-LOWER PALEOZOIC CARBONATE SEQUENCES AT SALINAS HILL AND PIE DE PALO RANGE, WESTERN ARGENTINA

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INTRODUCTION

It is well known that isotope stratigraphy is one of the most powerful tools in Upper Precambrian to Lower Paleozoic chronostratigraphy. The Sr isotope composition of seawater for this age interval is characterized by a continuous increase of $^{87}Sr/^{86}Sr$ that is interrupted, by sharp rises, which represent important changes in the Earth history. During Late Cambrian to Early Ordovician time the $^{87}Sr/^{86}Sr$ seawater ratio is high and close to the modern value of 0.70907 (Kaufman et al., 1993; Veizer et al., 1997; Jacobsen & Kaufman, 1999; Montañez et al., 2000). The Pb-Pb isotopic dating technique have been refined and successfully applied to a variety of geological problems (Jahn & Cuvellier, 1994, Babinski et al., 1999). We examine in this paper carbonate sequences from the Precordillera or Cuyania Terrane that are located at the Salinas Hill and Pie de Palo Range (Fig. 1), as a part of the "Angaco Belt" (Vujovich & Ramos, 1994). Also for comparison, we use two samples from the fossiliferous Lower to Middle Cambrian carbonates in the Eastern Precordillera (La Laja Fm.). We have studied their $^{87}Sr/^{86}Sr$ composition and compare it to global Sr isotope secular variation curves and we present new Pb-Pb isotope analyses on carbonate samples from Salinas Hill. The aims of the study were to constrain the timing of deposition/diagenesis and of subsequent metamorphism/deformation of the carbonate levels from the Caucete Group.

GEOLOGICAL SETTING AND PREVIOUS ISOTOPIC DATA

The study area encompasses the eastern side of the Precordillera from San Juan and the western foothills of the Western Pampean Ranges (Fig. 1) as a part of the Precordillera or Cuyania composite Terrane. Lower Cambrian-Ordovician platform limestones characterize eastern Precordillera. The western sector of Pampean Ranges at Pie de Palo area has a low to high metamorphic basement with two different sequences: the Pie de Palo Complex that consists of an ophiolitic assemblage, schists and gneisses of Grenvillian-age and the low grade metamorphic rocks "Angaco Belt" represented by the Caucete Group, that is characterized by platform clastic to carbonate sequence of uncertain age between Neoproterozoic to Lower Paleozoic (Ramos & Vujovich, 2000). The contact between both units is tectonic. Pioneer work on this region was produced by Schiller (1912) who mentioned the limestone rocks as a Lower Paleozoic belt. The Caucete Group (Puntilla Blanca, Angaco, Pie de Palo and El Quemado Fms.) was defined by Borrello (1969) as an 'Infracambrian' sequence. Linares et al. (1982) using statistical methods on C and O data found a similar isotopic composition that suggests a same depositional environment for the precordilleran "Zonda Limestones" and "Pie de Palo Limestones". Dalla Salda and Varela (1984) mentioned these carbonates as a Vendian age rocks. The "Angaco Belt" outcrops are extended from western Pie de Palo Range to Salinas Hill towards the South, where were defined by Vujovich and Ramos (1994). Ramos & Vujovich (2000) mapped part of the Pie de Palo Range, and discussed the possibility that the Caucete Group could be Neoproterozoic to Lower Paleozoic in age. Bordonaro et al. (1992) on the basis of trace fossils suggest a Neoproterozoic-Cambrian age for the Angaco Fm. Sial et al. (2001) studied C and Sr isotopic composition on some carbonate rocks of the Caucete Group and suggest a Vendian to Cambrian time of deposition. Finally, SHRIMP U-Pb detrital zircon ages comprise two populations that fall between c. 1.2 and c. 0.67 Ga, from El Quemado quartzites, were obtained by van Staal et al. (2002).

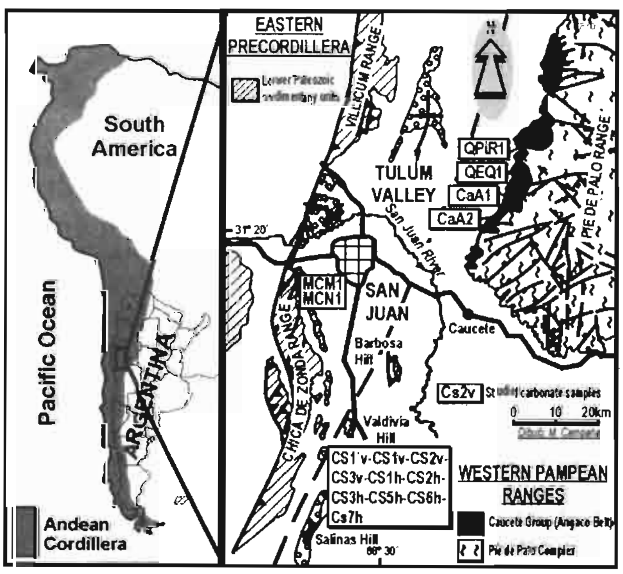

Figure 1. Regional geological map showing the sample locations.

ANALYTICAL PROCEDURES

Sr sample preparations were carried out at the Centro de Investigaciones Geológicas (CIG), University of La Plata. All whole-rock carbonate samples were crushed and dissolved in HCl 0.5N for no more than 5'. After that the Sr was concentrated in cationic exchange columns. The mass spectrometer measurements and Pb/Pb analyses were carried out at Laboratório de Geologia Isotópica, UFRGS, Porto Alegre, Brazil. For Pb-Pb method, nearly 1 gr of sample were weighed and leached with HCl 0.1N. The residue was leached again with HCl 1.0 N and 5 ml of the leached solution were used to determine the Pb/Pb isotopic ratios. Pb was separated with AG1X8 anion exchange column with 0.6 HBr and extracted with 6M HCl. Isotopic analyses were carried out with a multicollector VG Mass spectrometer at UFRGS. The Pb isotopic composition ratios were corrected to a fractionation factor based on successive determinations of NBS 981 Standard. Isochron regressions were done using the ISOPLOT program of Ludwig (1990).

RESULTS

Sr ISOTOPIC DATA

Major and trace element distribution and XRD analyses are used to identify carbonates that are most likely to have retained the original seawater $^{87}Sr/^{86}Sr$ (Denison et al., 1994, Jacobsen & Kaufman, 1999). The accurate definition of the $^{87}Sr/^{86}Sr$ in seawater with time depends on three major factors: analytical accuracy, retention of the original ratio and the precision of the biostratigraphic assignment. Diagenetic or metamorphic alteration is clearly a major cause of scatter and this increase with time. Twenty two carbonate samples from Angaco Fm. outcropped in the western side of Pie de Palo Range were stratigraphically collected (in vertical and horizontal profiles) from La Petaca, El Gato, El Quemado and Pirquitas creeks and twenty carbonate samples from the Salinas Hill as a southern end of the Angaco Fm. (Fig. 1). Based on the Fe, Sr, Mn contents (Table 1) determined by XRF in compacted powdered samples using international reference standards (INGEIS, University of Buenos Aires) and excluded samples with high dolomitic contents detected by XRD (CIG, La Plata), we finally selected four samples from Pie de Palo (CaA1, CaA2, QEQ1 and Qpir1), and ten from Salinas Hill (CS'1v, CS1v, CS2v, CS3v, CS1h, CS2h, CS3h, CS5h, CS6h, CS7h). For comparison two carbonate samples from La Laja Fm. at the Zonda Creek classical eastern Precordillera Lower to Middle Cambrian outcrop (MCM1, MCN1) has been studied. As we can see on the Fe/Sr vs. Mn/Sr diagram (Fig.2) only two samples (CaA2, QEQ1) both from Pie de Palo Range, are far from the recommended values for primary isotopic studies (Jacobsen & Kaufman, 1999). As shown in Table 1 the $^{87}Sr/^{86}Sr$ ratios of the Angaco Fm. outcropped at Pie de Palo area, range from 0.7089 to 0.7091, only the QEQ1 sample with high Mn and Fe content goes up to 0.7094. At the Salinas Hill the southern end of the Angaco Fm. yield ratios from 0.7091 to 0.7099. For comparison, the two samples from the unmetamorphosed Cambrian fossiliferous La Laja Fm. (Precordillera) range in between 0.7088-0.7089, in agreement with seawater curve (Veizer et al., 1997).

The values of $^{87}Sr/^{86}Sr$ were plotted versus Mn/Sr ratio according to the fluid-rock interaction models proposed by Jacobsen & Kaufman (1999). It is shown (Fig. 3) that the samples are outside of the primary sector and in coincidence with diagenetic open system.

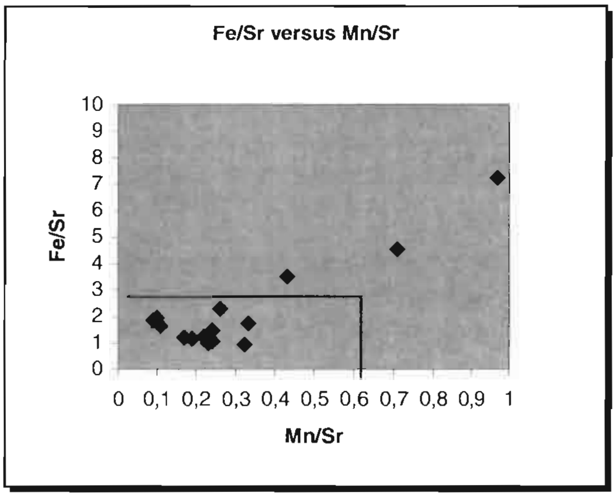

Figure 2. Fe/Sr vs. Mn/Sr diagram.

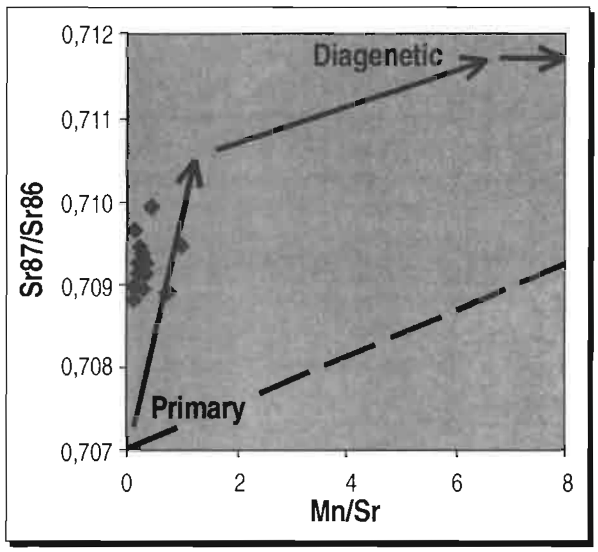

Figure 3. Sr^{87}/Sr^{86} vs. Mn/Sr diagram. Arrows indicate the trends between Primary and Diagenetic end-members (Jacobsen & Kaufman, 1999).

Table 1. Some major element ratios and Sr isotopic data.

Field N°	Fe2O3 (%)	MnO (%)	Fe (ppm)	Mn (ppm)	Sr (ppm)	Mn/Sr	Fe/Sr	$(^{87}Sr/^{86}Sr)_0$*	*Error (%)*
			ANGACO Formation (Pie de Palo Range)						
Ca A 1	0.040	0.006	280	46	193	0.24	1.45	0.709112	0.0013
Ca A 2	0.134	0.019	937	147	207	0.71	4.53	0.708919	0.0022
QEQ 1	0.486	0.059	3399	457	471	0.97	7.22	0.709471	0.0020
Qpir 1	0.112	0.005	783	39	428	0.09	1.83	0.708986	0.0018
			ANGACO Formation (Salinas Hill)						
CS' 1 v	0.046	0.006	322	46	272	0.17	1.18	0.709247	0.0021
CS 1 v	0.037	0.006	259	46	212	0.22	1.22	0.709448	0.0015
CS 2 v	0.046	0.008	322	62	187	0.33	1.72	0.709294	0.0019
CS 3 v	0.133	0.015	930	116	267	0.43	3.48	0.709929	0.0012
CS 1 h	0.047	0.003	329	23	202	0.11	1.63	0.709661	0.0022
CS 2 h	0.025	0.008	175	62	191	0.32	0.92	0.709163	0.0018
CS 3 h	0.043	0.009	301	70	287	0.24	1.05	0.709376	0.0017
CS 5 h	0.028	0.006	196	46	202	0.23	0.97	0.709213	0.0020
CS 6 h	0.035	0.006	245	46	204	0.23	1.2	0.709280	0.0013
CS 7 h	0.033	0.005	231	39	201	0.19	1.15	0.709150	0.0016
			LA LAJA Formation (Precordillera)						
MCN 1	0.234	0.006	1637	46	719	0.26	2.28	0.708958	0.002
MCM 1	0.177	0.008	1238	62	639	0.1	1.94	0.708837	0.002

Mean of ±100 isotopic ratios, static mode, 1.0 V ionic intensity and multicollector, with 86 in axial collector.
*Normalized from 86Sr/87Sr: 0.1194 and adjusted for bias.
$SrCO_3$ NBS-987 assumed $(^{87}Sr/^{86}Sr)$ n=0.71025.

Pb-Pb ISOTOPIC AGE

The Pb-Pb isochron method has provided a useful technique for determining ages on carbonate rocks and to obtain ages of sedimentation or metamorphic activity (Jahn et al., 1990). Ten analyses from Angaco Fm. at Salinas Hill outcrop, define a good linear trend in the $^{207}Pb/^{204}Pb$ vs. $^{206}Pb/^{204}Pb$ diagram (Fig. 4) that corresponds to an age of 546±74 Ma (MSWD=11,8). The isotopic data of Pb-Pb analyses of Angaco Fm. are presented on Table 2. $^{206}Pb/^{204}Pb$ values have a range between 20 to 31. If we consider the isochron error range, the age could be from Upper Neoproterozoic to Lower Ordovician time.

Table 2. Pb/Pb isotopic data.

Field N°	$^{206}Pb/^{204}Pb$	error (%)	$^{207}Pb/^{204}Pb$	error (%)	$^{208}Pb/^{204}Pb$	error (%)
			Angaco Formation (Salinas Hill)			
CS1'v	20.064	0.019	15.689	0.019	38.106	0.019
CS1 v	21.300	0.023	15.772	0.023	38.173	0.024
CS2 v	30.824	0.018	16.308	0.018	38.130	0.019
CS3 v	27.145	0.023	16.119	0.024	38.321	0.025
CS1 h	21.412	0.016	15.779	0.016	38.191	0.016
CS2 h	20.119	0.026	15.693	0.026	38.071	0.026
CS3 h	20.742	0.017	15.717	0.018	38.102	0.017
CS5 h	19.926	0.019	15.687	0.019	38.073	0.019
CS6 h	19.697	0.017	15.663	0.018	38.147	0.017
CS7 h	20.670	0.018	15.725	0.018	37.959	0.018
	1.002		1.003		1.004	
NBS981·	16.877	0.008	15.421	0.008	36.498	0.008
NBS981·	16.937		15.491		36.721	

NBS 981- 0,001% /u.m.a.

Average of more than 50 isotopic ratios, ionic intensity 0.5 V for ^{206}Pb multicollector with 206 axial collector.
·= LGI/UFRGS. ·· = International

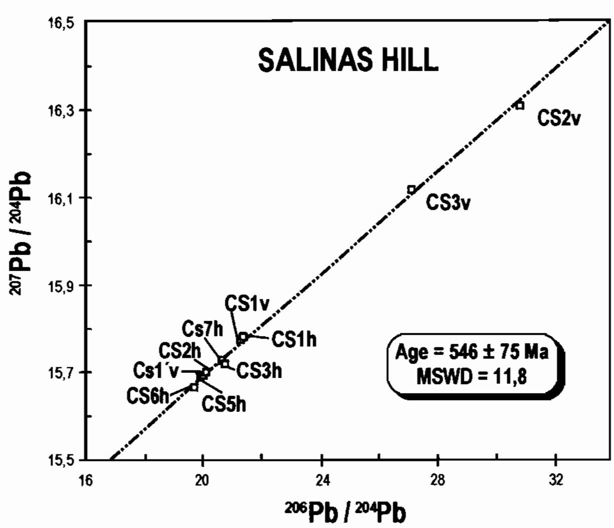

Figure 4. Pb-Pb isochron diagram for Salinas Hill rocks.

DISCUSSION

Many authors have suggested a sedimentation age for the Angaco Fm. as a range in between the Neoproterozoic to the Lower Paleozoic time. The lack of accurate fossils from the Caucete Group, with the exception of trace fossils, was an important stratigraphic limitation. Our $^{87}Sr/^{86}Sr$ isotopic ratios from 0.7089 to 0.7099 are in coincidence with data obtained by Sial et at. (2001) in Pie de Palo Range. Those ratios are rather high for the best-known Neoproterozoic seawater curve but are close to Middle and Late Cambrian $^{87}Sr/^{86}Sr$ values that rose to a maximum 0.7091. However we interpret these high values as a result of secondary alteration (diagenetic or metamorphic events) as we shown in the fluid-rock interaction models, or influence of continent sedimentation in the seawater during the carbonate deposition. The good aligneament on Pb-Pb isochron of c. 546 Ma determined from carbonates is interpreted as a last diagenetic/metamorphic event affecting the Angaco Fm. at Salinas Hill area. This suggests that the depositional àge of this unit could be older, and range the Neoproterozoic time. If we consider the c. 670 Ma U-Pb detrital zircon age obtained by van Staal et al. (2002) in the El Quemado siliciclastic rocks, the deposition age of the Angaco Fm. could be constrained in between 670 and 546 Ma.

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