

# ISOTOPIC STRONTIUM, CARBON AND OXYGEN STUDY ON NEOPROTEROZOIC MARBLES FROM SIERRA DE UMANGO, ANDEAN FORELAND, ARGENTINA

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**Keywords:** Isotope geochemistry, Marbles, Neoproterozoic, Andean Foreland, Argentina

## INTRODUCTION

The Umango Hill (La Rioja Province, 29°00'S-68°40'W) is one of the mountain blocks of Sierras Pampeanas Occidentales (Caminos, 1979), bounded by thrust faults and surrounded by Upper Devonian to Tertiary marine and continental sedimentites (Fig.1).

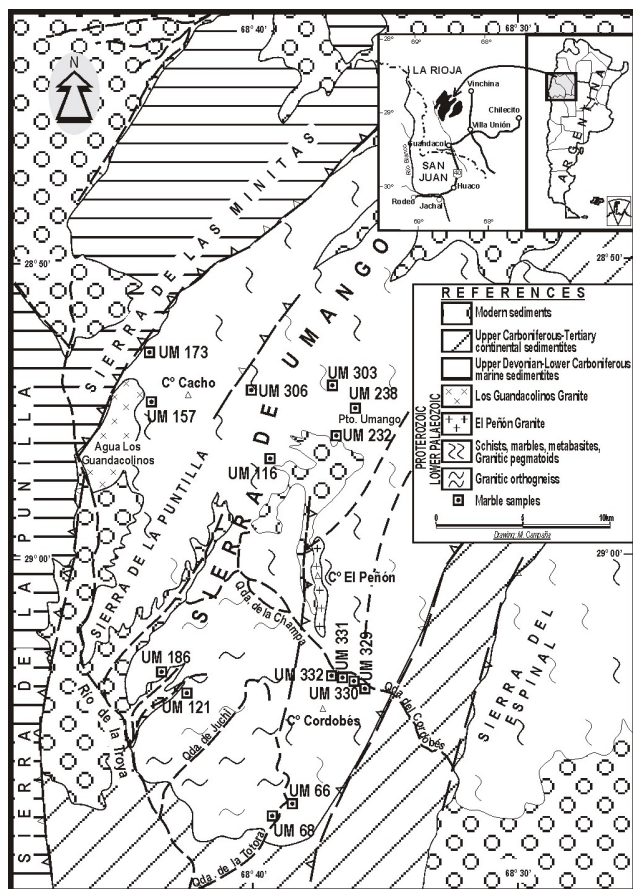


Figure 1. Geological map of the Sierra de Umango showing the sample locations.

The exposed crystalline basement is composed of basic igneous rocks and a siliciclastic-limestone sequence, both affected by amphibolite facies metamorphic peak. In the southern area (Juchi creek), the metamorphic complex carries relics of granitic orthogneisses, with Rb/Sr and U/Pb dates of ~1000 Ma (Varela et al., 1996). These ancient inliers were assigned to a Mesoproterozoic Grenville Orogenic Cycle. Granitic bodies, intrusives at different ages in the Metamorphic Complex, have also been distinguished. The most ancient is El Peñón Granite, with  $469 \pm 9$  Ma Rb/Sr age (Varela et al., 2000) and  $523 \pm 26$  Ma U/Pb zircon age (unpublished data).

In this way it is possible to point out broadly that the siliciclastic-limestone sequence belongs to the Neoproterozoic-Early Palaeozoic times. It was a platform cover over grenvillian cratonic basement. The metamorphism and deformation, we understand, took place in the Early Palaeozoic, related to the Pampean-Famatinian Orogenic Cycle.

In this work, compositional and isotopic data of Strontium ( $^{87}\text{Sr}/^{86}\text{Sr}$ ), Carbon ( $\delta^{13}\text{C}_{\text{VPDB}}$ ) and Oxygen ( $\delta^{18}\text{O}_{\text{VPDB}}$ ) of the marbles derived from the siliciclastic-limestone sequence are presented. The results are interpreted and correlated with the temporal variation curves of  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $\delta^{13}\text{C}$  from Neoproterozoic marine carbonates (Jacobsen and Kaufman, 1999).

## COMPOSITION AND RESULTS

The study is based on the results obtained over 35 samples of marbles, which came from 15 localities (Fig. 1). In some of those locations a several number of samples were taken. These do not correspond to a

stratigraphic order, nor it is possible to time-correlate the levels of marbles in different locations.

Sample	% Mineralogical composition					Sr	Mn	Fe	Mn/Sr	<sup>87</sup> Sr/ <sup>86</sup> Sr	Error	δ <sup>13</sup> C	δ <sup>18</sup> O
	Cal	Dol	Qz	Fel	Other	ppm	ppm	ppm				‰	‰
UM 116 A	40	53	4	<1	2	253	460	5100	1.82	0.708179	0.000021	6.7	-12.3
UM 116 B	12	85	1	1	1	159	70	700	0.44	0.708264	0.000057	7.7	-9.0
UM 116 D	47	45	4	Tr	4 (m:3)	194	910	3600	4.69	0.711362	0.000043	7.1	-12.3
UM 116 E	25	70	2	1	2	151	290	1800	1.92	0.710385	0.000028	7.8	-9.8
UM 116 F	32	64	2	1	1	123	300	1300	2.44	0.709668	0.000028	7.6	-10.9
UM 116 G	23	72	4	Tr	1	161	290	1000	1.80	0.710104	0.000043	6.5	-12.9
UM 116 H	7	89	Tr	1	3	107	70	800	0.65	0.708669	0.000028	7.6	-10.4
UM 121 A	95	2	2	Tr	<1	967	230	1100	0.24	0.708444	0.000050	0.2	-9.9
UM 121 B	90	6	3	Tr	1	758	540	1000	0.71	0.708497	0.000028	0.6	-15.3
UM 121 C	1	90	3	2	4 (c:2)	56	290	2200	5.18	0.709273	0.000035	0.3	-9.6
UM 121 D	75	22	1	Tr	2	677	180	600	0.27	0.708612	0.000071	-0.5	-11.4
UM 121 E	77	20	1	Tr	2	462	80	300	0.17	0.708682	0.000035	-0.5	-12.7
UM 121 F	94	3	2	Tr	<1	523	130	500	0.25	0.708283	0.000028	0.3	-10.7
UM 157 A	96	Tr	3	Tr	<1	1754	80	1100	0.05	0.707429	0.000050	3.0	-8.5
UM 157 B	97	-----	<1	Tr	2	1235	130	800	0.11	0.707426	0.000042	3.2	-7.9
UM 173 A	34	58	4	Tr	4	156	530	2000	3.40	0.711721	0.000028	1.3	-13.1
UM 173 B	73	18	6	1	2	41	460	8000	11.22	0.709878	0.000035	-0.9	-4.7
UM 66	<1	95	1	1	2	116	240	1500	2.07	0.709953	0.000050	0.9	-6.7
UM 68	6	89	3	1	1	43	300	2300	6.98	0.707992	0.000028	0.3	-11.5
UM 186 B	86	10	1	1	2	985	120	600	0.12	0.708712	0.000050	-0.5	-10.2
UM 232 A	2	95	<1	<1	1	65	2330	5700	35.85	0.708895	0.000050	2.9	-13.9
UM 232 B	5	91	Tr	<1	3	94	840	7400	8.94	0.707745	0.000035	-0.1	-14.2
UM 238 A	92	<1	Tr	2	5	1306	470	17300	0.36	0.707753	0.000092	1.8	-18.9
UM 238 B	85	2	Tr	10	3	990	580	21700	0.59	0.707990	0.000057	-2.0	-17.4
UM 238 C	91	<1	2	3	3	1504	400	12000	0.27	0.707874	0.000071	2.4	-14.5
UM 238 D	91	-----	Tr	Tr	4 (m:3)	1275	160	2600	0.13	0.707299	0.000035	10.2	-10.9
UM 303 A	91	9	-----	-----	-----	1927	110	300	0.06	0.708695	0.000043	2.7	-10.4
UM 303 B	99	-----	1	-----	-----	1281	40	400	0.03	0.708349	0.000050	0.0	-9.5
UM 306	98	2	-----	-----	-----	498	380	2300	0.76	0.709353	0.000057	-1.2	-11.8
UM 329 A	-----	98	2	-----	-----	68	680	2400	10.00	nd	nd	-0.9	-22.1
UM 329 B	-----	99	1	-----	-----	77	1590	4400	20.65	nd	nd	-0.8	-22.2
UM 330	95	4	-----	-----	1	537	360	15200	0.67	0.709626	0.000043	-1.6	-25.7
UM 331	96	-----	4	-----	-----	795	120	5800	0.15	0.709611	0.000071	-0.6	-23.6
UM 332 A	97	1	2	-----	-----	999	150	5900	0.15	0.709129	0.000043	-0.6	-20.8
UM 332 B	94	5	1	-----	-----	558	130	700	0.23	0.709067	0.000050	-0.8	-15.5

**Table 1.** Mineralogical and isotopic compositions of the Sierras de Umango marbles. GPS sample location available on request to R. Varela. Tr: traces; m: mica; c: clays.

Petrographic studies allowed to identify Calcitic marbles, Calcitic-dolomitic marbles, Dolomitic marbles and Calcsilicate rocks. The marbles are white to brownish, fine to medium grained rocks. The

prograde metamorphic assemblages vary from upper greenschist facies up to upper amphibolite facies with granoblastic arrangement. The main assemblages are 1) calcite + dolomite + talc  $\pm$  quartz  $\pm$  accessory minerals, 2) calcite + tremolite-actinolite  $\pm$  quartz  $\pm$  accessory minerals, and 3) calcite + diopside  $\pm$  quartz.

The marble compositions were obtained by X ray diffraction. The Sr, MnO and  $\text{Fe}_2\text{O}_3^T$  concentrations were determined by X ray fluorescence spectrometry in compacted powdered samples using international reference standards (Table 1). The main components, calcite and dolomite, are found together with lower percentages of quartz, feldspar, mica and clays. The samples containing high percentages of calcite (>85%; 17 samples), are those which have higher contents of Sr, which varies between 498 and 1927 ppm. They also have the lowest contents of Mn (40-580 ppm), while the Fe contents are in correspondence of the mineralogical composition of the different metamorphic facies. With these, the Mn/Sr relationship gets to values between 0.03 and 0.76. So, we think that these samples might have constituted "closed systems" and could have kept the original isotopic composition, which corresponds to the seawater from they were deposited.

To determine the isotopic composition of Sr, samples were crushed and dissolved in HCl 0.5 N for no more than 5 minutes. After that the Sr was concentrated in cationic exchange columns at the CIG laboratories. The mass spectrometer measurements were performed in the CPGeo (Brazil). C and O isotope ratios were determined as described in Panarello et al. (1980) at INGEIS.

The values of  $^{87}\text{Sr}/^{86}\text{Sr}$  were plotted versus Mn/Sr and  $\delta^{18}\text{O}$  values according to the fluid-rock interaction models proposed by Jacobsen and Kaufman (1999). It is shown (Figs. 2a, b) that 3 samples lay close to the "Primary System" end. They are distinguished as UM157A, UM157B and UM238D. For these samples the isotopic ratios  $^{87}\text{Sr}/^{86}\text{Sr}$  are 0.707429 (average of two values), 0.707426 (average of two values) and 0.707299, respectively.

According to these, carbonates of the Umango Hill, were formed in a seawater with a Sr isotopic composition between 0.7072 and 0.7075. In the curve of  $^{87}\text{Sr}/^{86}\text{Sr}$  in the Neoproterozoic time (Fig. 2c), compiled by Jacobsen and Kaufman (1999), we can see that the values of the Umango Hill samples fall between 640 and 580 Ma.

The  $^{13}\text{C}$  content of the analyzed samples varies between -2.0 ‰ and +10.2 ‰ and the  $^{18}\text{O}$  between -25.7 ‰ and -4.7 ‰ (Table 1 and Fig. 3).

Geochemical and isotopic criteria used to select those samples that preserve their primary marine isotopic compositions are not so rigorous for C as are for Sr. This is related to the fact that the volume of fluids that may easily alter minor elements could have not affected major element chemistry in carbonatic rocks (Kaufman and Knoll, 1995). Although, we have taken into account the same screening parameters:  $\text{Mn}/\text{Sr} < 2$  and  $\delta^{18}\text{O} < -10\text{‰}$ . Hence, dealing only with those samples that fulfill the first requisite, we can distinguish 3 conspicuous groups of samples on the basis of their  $\delta^{13}\text{C}$  compositions:  $-2.0\text{‰} < \delta^{13}\text{C} < 3.2\text{‰}$  and  $6.5\text{‰} < \delta^{13}\text{C} < 7.8\text{‰}$  and  $10.2\text{‰}$  (only one sample: UM238D). In the first 2 groups, the primary isotopic contents are more closely reflected by the samples with the most enriched C isotopic compositions (Derry et al., 1992; Frank et al., 1997). They are UM157A and UM157B ( $\delta^{13}\text{C}_{\text{average}} = 3.1\text{‰}$ ) and UM116B and UM116E ( $\delta^{13}\text{C}_{\text{average}} = 7.8\text{‰}$ ) respectively. On the other hand, these selected samples have  $\delta^{18}\text{O}$  values ranging between -7.9‰ and -9.8‰, fulfilling with the second stipulated requisite, while UM238D does not (Fig. 3).

Plotting  $\delta^{13}\text{C}_{\text{average}}$  of both groups on the secular variation curve for the Neoproterozoic seawater (Jacobsen and Kaufman, 1999) and taking into account the  $^{87}\text{Sr}/^{86}\text{Sr}$  results, we could assign an age ranging between 600 and 590 Ma to the Umango Hill selected carbonates.

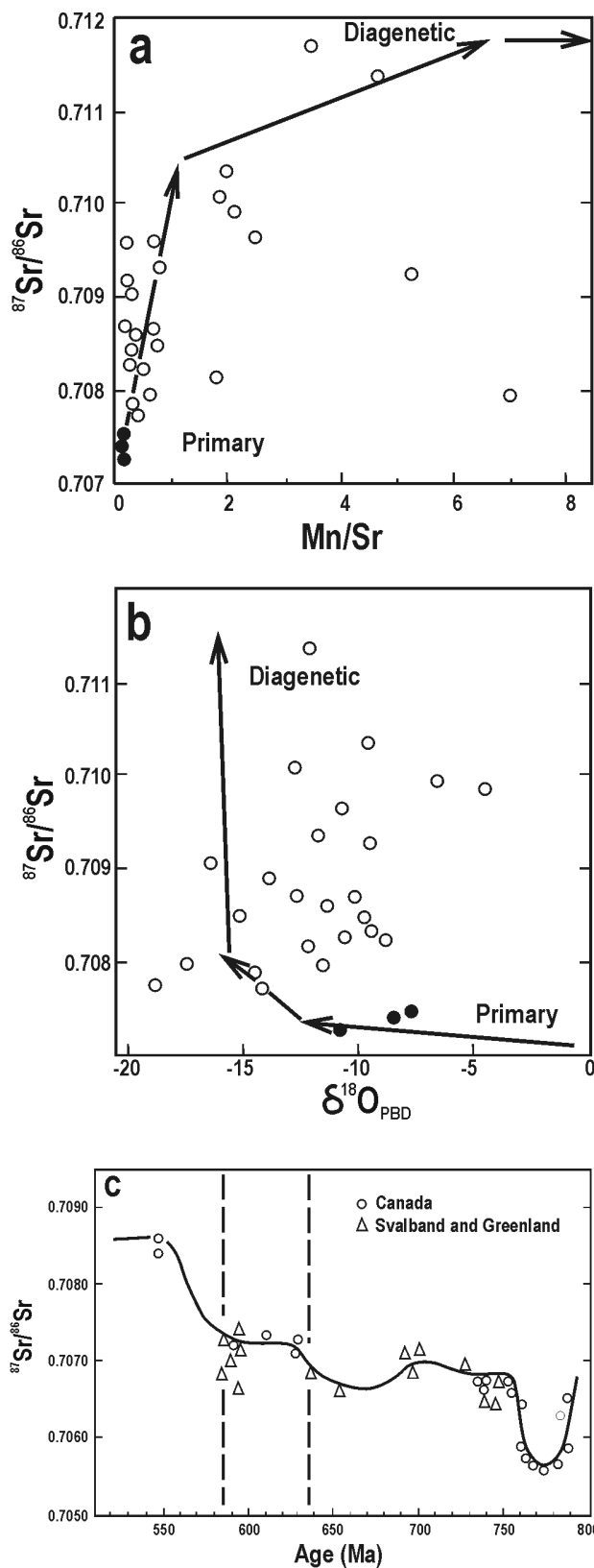
The strongly positive  $\delta^{13}\text{C}$  values of groups 2 and 3 are characteristic of the late Cryogenian interval (730-590 Ma) (Kaufman and Knoll, 1995) and the time between 730 and 600 Ma reported by Jacobsen and Kaufman (1999).

In summary, the Sr and C isotope signature for the Umango marbles suggests a Neoproterozoic age for the sedimentation of the siliciclastic-limestone sequence.  $^{87}\text{Sr}/^{86}\text{Sr}$  values (ca. 0.7072-0.7075) point out the time between 640 and 580 Ma.

## ACKNOWLEDGEMENTS

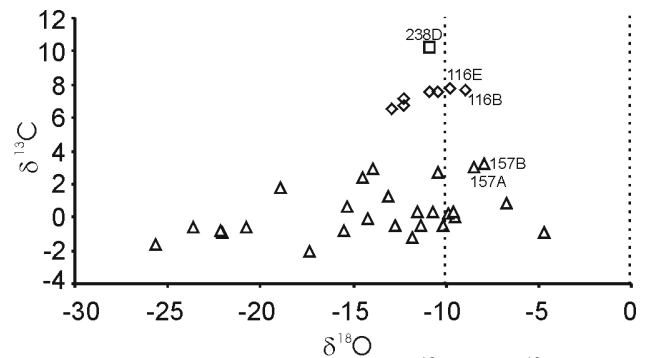
This research was supported by the Project PICT 00742, ANPCyT, Argentina, and is a contribution to IGCP 436 "Pacific Gondwana Margin".

We are grateful to Dr. D. Poiré and Lic. J. Maggi for the X-Ray Diffractograms.



**Figure 2.** a) and b), Isotopic relation for Umango marbles. The arrows indicate the trends between Primary and

Diagenetic end-members after Jacobsen and Kaufman (1999); c) Temporal variations of  $^{87}\text{Sr}/^{86}\text{Sr}$  in Neoproterozoic carbonates, compiled by Jacobsen and Kaufman (1999). Dashed vertical lines represent the estimated plot for Umango marbles ( $^{87}\text{Sr}/^{86}\text{Sr}$  range: 0.7072-0.7075).



**Figure 3.** Isotopic relation between  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  from the Sierra de Umango marbles.

## REFERENCES

- Camino, R., 1979. Sierras Pampeanas Noroccidentales. Salta, Tucumán, Catamarca, La Rioja y San Juan. 2° Simposio de Geología Regional Argentina, 1: 225-291.
- Derry, L., Kaufman, A. and Jacobsen, S., 1992. Sedimentary cycling and environmental change in the Late Proterozoic: Evidence from stable and radiogenic isotopes. *Geochimica et Cosmochimica Acta*, 56: 1317-1329.
- Frank, T., Lyons, T. and Lohmann, K., 1997. Isotopic evidence for the paleoenvironmental evolution of the Mesoproterozoic Helena Formation, Belt Supergroup, Montana, USA. *Geochimica et Cosmochimica Acta*, 61: 5023-5041.
- Jacobsen, S. and Kaufman, A., 1999. The Sr, C and O isotopic evolution of Neoproterozoic seawater. *Chemical Geology*, 161: 37-57.
- Kaufman, A. and Knoll, A., 1995. Neoproterozoic variations in the C-isotopic composition of seawater: stratigraphic and biogeochemical implications. *Precambrian Research*, 73: 27-49.
- Panarello, H., García, C., Valencio, S. and Linares, E., 1980. Determinación de la composición isotópica del carbono en carbonatos, su utilización en Hidrogeología y Geología. *Revista Asociación Geológica Argentina*, 35: 460-466.
- Varela, R., López de Luchi, M., Cingolani, C. and Dalla Salda, L., 1996. Geocronología de gneises y granitoides de la sierra de Umango, La Rioja. Implicancias tectónicas. 13° Congreso Geológico Argentino, 3: 519-527. Buenos Aires.
- Varela, R., Roverano, D. and Sato, A.M., 2000. Granito El Peñón, sierra de Umango: descripción, edad Rb/Sr e implicancias geotectónicas. *Revista Asociación Geológica Argentina*, 55 (4): 407-413.