FORAMNIFERA AS RECORD FOR PRESENT–DAY OCEAN WATER Sr COMPOSITION ; PROCEDURES AND MASS SPECTROMETRY

Machado M. C.[1], Kawashita, K.[2],Chemale Jr, F.[3], K. B. Costa and Toledo F.[4]

1. Laboratório de Geologia Isotópica, IG-UFRGS, CP 15001, Porto Alegre, 91501-970, Brazil. machado.mc@ig.com.br
2. Laboratório de Geologia Isotópica, IG-UFRGS, CP 15001, Porto Alegre, 91501-970, Brazil. farid.chemale@ufrgs.br
3. Laboratório de Geologia Isotópica, IG-UFRGS, CP 15001, Porto Alegre, 91501-970, Brazil. koji@usp.br
4. Laboratório de Paleoceanografia do Atlântico Sul, IO-USP, São Paulo, Brazil. karen.costa @io.usp.br, and felipe.Toledo@io.usp.br

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Procedures and results on planktonic foraminifers from Campos-Espírito Santo Basin

One of most important requirements to obtain reliable $87Sr/^{86}Sr$ on marine carbonates is to select pristine shells or fresh samples without posthumous processes such as diagenesis. As the older the samples more are the chances to be submitted to diagenetic alteration and, in situ radiogenic Sr generated could be influence the original Sr composition. To determine the state of preservation a series of experimental procedures are known and commented with good detail by MacArthur (1994) for example. Among various possible methods we mention: scanning electron microscopy (SEM), X-ray diffraction (XRD), examination of thin sections, O and C del determinations, cathode luminescence, and chemical analysis including few trace elements, specially Fe, Mg, Sr, and Mn. Special care has also been observed on sample dissolution, specially because detrital silicate phase or contaminant could obliterate the original Sr composition. Dilute HCl or acetic acid (0.1 N) and ion- exchange technique (Kralik, 1984) are been chosen with the intention of minimizing the dissolution of extraneous Sr. With regard to this last question, little attention has been made by the most of users. Generally the samples should be pre-leached appropriately and discarded as pointed out by, for example, Gorokhov et al. (1996) In the present work, some additional experiments, including studied recent foraminifers species, one cretaceous belemnite and one example from silicic limestone from Bambuí Group (Fig 1) illustrate the importance of such procedure specially when use old carbonate samples. In the first extraction using only warm water (ca. 60^0 C) radiogenic Sr is visibly removed together with presumed primary Sr. Thus, is recommended to use only the second extraction using dilute acid to evaluate the Sr isotope composition. It seems that this procedure is not essential for well-preserved modern shells as is illustrated in our studied samples, despite Sr of possible existence of impurities in the micro-shells. The main reasons are: high Sr content estimated as more than 20 nanograms/specimen, similar and homogeneous Sr isotope composition of the environment, and negligible amount of in situ generated radiogenic Sr.

The Sr isotope composition obtained for three planktonic foraminifers separated from sample core (< 6m depth) collected by Petrobras at Campos-Espírito Santo Basin are presented in table 2. The $^{87}Sr/^{86}Sr$ ratios were obtained using minimum of 10 specimens, then pre-leached, and Sr from second extraction passed through cation exchange resin column. The VG Sector TIMS provided with 9 faraday collectors was used in a static mode of analysis. Generally, minimum of hundred ratios in 10 blocks was systematically adopted and signal intensity for ^{88}Sr was in general in the range 1-2 x 10^{-11} A. The 12 different runs (3 of them by dynamic mode) performed on NIST SRM-987 gave a mean ratio 0.710273 ± 0.000011 (σ). Assuming 0.710247 (mean of 20 independent determinations chosen in our compilation) as consensus value for this reference sample the respective bias value is + 0.000026. This factor was used to adjust the obtained $^{87}Sr/^{86}Sr$ data in the table 2.

The both benthic species assumed as being modern because were collected near surface (< 6 ms depth) in Campos-Espírito Santo Basin are exhibiting, with one exception, distinct range values and clearly lower than expected for modern ones. The mean ratio of 0.7082 for C. wuellestorf is more coherent to Late Oligocene age (ca. 27Ma.). while the more homogeneous ratios for U. peregrina with a mean of 0.70911 would be younger and an age of 3.0 ± 0.5 Ma could be assigned if adopt in both cases the suggested curve by DePaolo and Ingram (1985) for Cainozoic marine carbonates. These unexpected ratios and probable ages are illustrating the inadequacy of previous assumption and some hypotheses to explain the discordances, including sampled area, could be raised, but it is out of the scope of the present work.

Table 2. $^{87}Sr/^{86}Sr$ results on 4 different species on planktonic foraminifers collected from Campos Basin

Foram. (Species)	Sample N.#	$^{87}Sr/^{86}Sr$	SE(abs)	ratios	($^{87}Sr/^{86}Sr$)adj.
	1Brp	0.709111	0.000012	97	0.709085
Globiligerinoid	2Brp	0.709195	0.000017	97	0.709169
ruber	3Brp	0.709193	0.000013	94	0,709173
	5Brp	0.709189	0,000014	96	0.709163
	6Brp	0.709203	0.000013	96	0.709177
	7Brp	0.709041	0.000022	96	0.709015*
	8Brp	0.708371	0.000081	91	0.708345*
	9Brp	0.709241	0.000015	97	0.709215
	10Brp	o.709248	0.000016	97	0.709222
Globoratalia	1Am	0;709191	0.000009	116	0.709165
menardii	2Am	0.709177	0.000009	127	0.709151
	3Am	0.709188	0.000013	95	0.709162
	4Am	0.709184	0.000008	114	0.709158
	5Am	0.709157	0.000009	113	0.709131
	6Am	0.709239	0.000008	105	0.709215
	7Am	0.709228	0.000009	123	0.709202
	8Am	0.709190	0.000011	124	0.709164
	9Am	0.709214	0.000008	105	0.709188
	10Am	0.709210	0.000009	115	0.709184
Globorotalia	1At	0.709163	0.000008	95	0.709137
Truncalinoids	2At	0.709127	0.000032	48	0.709101*
	3At	0.709170	0.000009	95	0.709144
	4At	0.709133	0.000009	95	0.709107*
	5At	0.709216	0.000007	92	0.709190
Orbulina	1Ao	0.709195	0.000023	112	0.709169
Universa	2Ao	0.709201	0.000006	97	0.709175
	3Ao	0.709189	0.000009	96	0.709163
	4Ao	0.709191	0.000007	96	0.709165
	5Ao	0.709168	0.000013	111	0.709142
	6Ao	0.709200	0.000007	116	0.709174
	7Ao	0.709227	0.000018	110	0.709201
	8Ao	0.709179	0.000013	119	0.709153
	9Ao	0.709250	0.000014	18	0.709224
	10Ao	0.709198	0.000014	113	0.709172
Mean (n=30)		0.709196	0.000027 (σ)		0.709172

- excluded (2σ criteria); # different bedding planes

In a general way, the most of results are agreeing within 2σ error limit. Only one result is higher than expected of around 0.709175, while four others are lower, not discarding the hypothesis that these 4 samples could not recent. This idea is supported by anomalous and remarkable lower ratios obtained on two species of benthic foraminifers separated from the same area (see Table 2).

Table 2 $^{87}Sr/^{86}Sr$ ratios in two species of benthic foraminifers shells supposedly as recent and co-existent with planktonic species.

Foram. (species)	sample n.	$^{87}Sr/^{86}Sr$	SE (abs.)	ratios	$(^{87}Sr/^{86}Sr)_{adj.}$
Cibicidoides	1Ac	0.707688	0.000011	125	0.707667
Wuellestorfi	2Ac	0.708213	0.000085	123	0.708192
	3Ac	0.707695	0.000008	126	0.707674
	4Ac	0.709262	0.000011	125	0.709241
	5Ac	0.708492	0.000011	124	0.708471
	6Ac	0.708626	0.000012	126	0.708625
	7Ac	0.708607	0.000013	104	0.708586
	8Ac	0.708579	0.000013	125	0.708558
	9Ac	0.708307	0.000013	125	0.708286
	10Ac	0.707599	0.000011	123	0.707578
Uvigerina	1Au	0.709157	0.000006	94	0.709136
Peregrina	2Au	0.709102	0.000011	114	0.709081
	3Au	0.709137	0.000009	115	0.709116
	4Au	0.709130	0.000011	112	0.709109
	5Au	0.709181	0.000012	114	0.709160
	6Au	0.709057	0.000013	115	0.709036
	7Au	0.709115	0.000012	114	0.709094
	8Au	0.709124	0.000008	112	0.709103
	9Au	0.709165	0.000013	112	0.709144
	10Au	0.708979	0.000009	113	0.708958

Sr MASS SPECTROMETRY AND ITS ROLE IN FINE STRATIGRAPHY

Modern mass spectrometers equipped up to 9 faraday collectors for simultaneous measurements of Sr isotope intensities, allied to dynamic mode of analysis, have permitted $^{87}Sr/^{86}Sr$ ratios with high precision as 5ppm error (0.000004). Notwithstanding, such accurate results obtained, for example, in standard sample NIST SRM-987, in general don't agree within their respective errors. The main reason is that each instrument has own technical characteristics. The best alternative is to normalise the obtained results for some consensus value. Many authors are preferentially normalizing their results adopting a value close to 0.71025, instead of the provisional value of 0.71014 proposed by NIST. Other results are not normalized but results on this standard carbonate or in an old reference one called Sr_N (E&A) are usually presented, permitting in these cases the comparison of the results. As an example, our results on modern planktonic foraminifers and some accurate results on modern carbonates samples which are listed by McArhur (1994) and all them adjusted for 0.710247 is shown in Table 3.

Table 3: Some reported $^{87}Sr/^{86}Sr$ ratios on modern seawater Sr and adjusted to 0.710247 for standard $SrCO_3$ SRM 987 from NIST. The errors are absolute values.

Authors #	SRM 987	Modern sea water Sr (σ)	Modern Sr *(adj.)
This work (2006)	0.710273	0.709198 ± 27	0.709172
DePaolo and Ingram,1985	0.710310	0.709234 ± 9	0.709171
Palmer and Elderfield, 1985	0.710275	0.709244 ± 12	0.709216*
Hess et al., 1986	0.710220	0.709185 ± 13	0.709213*
Hodell et al., 1990	0.710235	0.709172 ± 12	0.709184
McArthur et al., 1990	0.710241	0.709166 ± 8	0.709172
Martín and McDougall, 1991	0.710265	0.709175 ± 11	0.709157

Asmeron et al., 1991	0.710241	0.709174 ± 3	0.709180
Nelson et al.,	0.710240	0.709161 ± 13	0.709168
Miller et al., 1991	0.710252	0.709191 ± 13	0.709186
Brand, 1991	0.710231	0.709171 ± 16	0.709187
Carpenter et al., 1991	0.710245	0.709179 ± 17	0.709181
Quinn et al., 1991	0.710245	0.709178 ± 8	0.709180
Dia et al., 1992	0.710244	0.709169 ± 4	0.709175
McArthur et al., 1992	0.710248	0.709175 ± 12	0.709174
Ohde and Elderfield, 1992	0.719232	0.709158 ± 12	0.709173
Anderson et al., 1992	0.710234	0.709159 ± 12	0.709172
Buhl et al., 1991	0.710238	0.709149 ± 17	0.709148*
Capo and DePaolo, 1992	0.710326*	0.709254 ± 3	0.709175
Derry et al., 1992	0.710241	0.709174 ± 5	0.709180
Clemens et al., 1993	0.710150*	0.709066 ± 11	0.709 166
Kaufman et al., 1993	0.710241	0.709174 ± 5	0.709180
Denison et al., 1994	0.71914*	0.709073 ±>30	0.709178
Mean (n=23) and error (σ)	0.710247 ± 23	0.709173 ± 42	0.709178 ± 14
Excluding outliers * (n=20)	0.710247 ± 20	- -	0.709175 ± 8

Selected from compilation by McArthur (1994)

Our results exhibit higher standard error when compared with other determinations. Clearly can not be attributable to mass spectrometry because the standard error on SRM 987 is actually around 0.000010. The most probable reason is the sampling coupled with some inadequate dissolution procedure. According to selective dissolution test performed and described above the higher ratios could be attributable to radiogenic Sr from environment. Anyway, our results is in perfect accordance with the expected value of 0.709175 (Rundberg and Smalley (1989) This value is the same as obtained in our compilation when adjust to SRM 987 as being 0.710247 the mean value of 20 determinations on this reference carbonate involving different laboratories. Thus, in our opinion, no makes difference if ones adjust to this suggested value or adopt 0.709175 ±0.000008 (σ) for MSS.

Conclusions

The two sites elected in the Campos-Espírito Santo Basin to sample recent foraminifers revealed successful only for planktonic species. Despite high dispersion on ^{87}Sr/86Sr the

RESUMO

Composição isotópica precisa do Sr moderno constitui-se em um dos pontos chaves e terminais da curva de variação secular no Per:iodo Cenozóico. Microcarapaças bem preservadas de foraminiferos modernos parecem constituir a melhor escolha para tal propósito. Quatro espécies de foraminiferos plantônicos e três de bentônicos separados de amostras de box core (900 metros de profundidade) coletados em dois cruzeiros oceanográficos realizados na Bacia de Campos e Espírito Santo dentro do Projeto MAPEM foram estudados para se avaliar corretos procedimentos de dissolução do Sr e também levantar a questão das correções das razões ^{87}Sr/^{86}Sr medidas. Determinações nas 4 espécies plantonicas (G. ruber, G. menardii, G. truncatulinoides e O. universa) revelaram certa dispersão nas razões obtidas, mas a média final de 0,709172 (ajustada para 0,710247 na amostra de referencia SRM 987) é muito próxima da razão esperada de 0.709175. As duas espécies bentônicas, Cibicidoides wuellerstorfi e Uvigerina peregrina, revelaram razões mais baixas e não esperadas de 0.7082 e 0.70911, respectivamente, conferindo lhes idades de cerca de 27 e 3 Ma. Estas razões e idades discordantes não poderiam ser explicadas com base nos procedimentos químicos adotados ou a inadequada correção sistemática. Exame estatístico cuidadoso de 23 dados disponíveis na literatura, .incluindo os do presente estudo, aliados aos respectivos resultados obtidos no padrão internacional SRM 987, resulta como sendo de 0.709175 ± 0.000008 (D`P) como mais provável para a razão ^{87}Sr/^{86}Sr marinho atual.