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Proposal for consensus $^{87}Sr/^{86}Sr$ values for reference samples NBS-987 and Sr_N(E & A)

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A consensus value for normalized $^{87}Sr/^{86}Sr$ in NBS-987 strontium carbonate has not yet been achieved, contrary to what happened with SrN (E & A), established as one of the first reference samples for Rb/Sr studies. Some laboratories have used the provisional value of 0.71014 suggested by NIST (ex-NBS) for the $^{87}Sr/^{86}Sr$ ratio, while others have used values as high as 0.71031. Consensus values for both reference samples are critical for studies requiring exact and very precise determinations, as in the case of chemostratigraphy. Based on recent dynamic multicollection mode determinations the values of 0.71025 and 0.70802 for this ratio are proposed as consensus values for NBS-987 and Sr_N (E & A) respectively.

Adjusting of published $^{87}Sr/^{86}Sr$ results in seawater and in modern biogenic marine carbonates is used in evaluating the consistency and adequacy of the present proposal.

Introduction

Accurate and precise $^{87}Sr/^{86}Sr$ ratios in marine carbonates, specially from the Tertiary, are of fundamental significance in chemostratigraphic studies and absolute dating purposes. Although these ratios are corrected internally for fractionation effects, they could be affected by systematic internal instrumental errors. Among these errors could be included factors linked to relative collector gains, ionic transmission, and with minor effect, to plating of Faraday cups ("cup effects") in multicollector mass spectrometers. The internal error for a single analysis is usually ca. 0.002%, +/- 0.000014 for a reference sample as NBS-987 strontium carbonate. Such error, may not be real because of factors mentioned above, besides the errors qualified as external or inherent to the analysed natural sample. Thus, the mass spectrometer must be calibrated adequately and checked using an interlaboratorial reference sample, such as Eimer and Amend $SrCO_3$[Sr_N(E&A] or a well known NBS-987 $SrCO_3$ from NIST (ex-NBS). Alternatively seawater strontium or modern marine shells can be used, for which a value1 of 0.70907+/-0.000004 (1σ) is recommended, assuming 0.71014 for NBS-987 $SrCO_3$. Unfortunatelly, this provisional value for this reference sample is known not to be the most probable value, as a consequence of the use of modern multicollector instruments.

$^{87}Sr/^{86}Sr$ Ratios on Reference Samples NBS-987 and Sr_N(E&A)

In Table 1 $^{87}Sr/^{86}Sr$ normalized results obtained on NBS-987 carbonate from five different laboratories are presented, including three obtained by dynamic multicollection technique. As advocated by VG, in this technique "the individual gain factors and other characteristics of the collector channels cancel out of the calculations and produce the ultimate in external precision".

Table 1: Some of the $^{87}Sr/^{86}Sr$ results obtained in NBS-987 $SrCO^3$

Instrument/ Laboratory	Analysis Mode	Number of analysis	$(^{87}Sr/^{86}Sr)_n$	Error (1σ)	Ref.:
VG-Sector/ Aveiro-94	Dyn. multic.	8	0.710250	0.000007	
VG-Sector/ Aveiro-95	Dyn.multic.	8	0.710242	0.000002	
VG-Sector/ Fisons Inst.	Dyn.multic.	57	0.710249	0.000011	2
VG-Sector/ Fisons Inst.	Stat. multic.	15	0.710272	0.000006	2
Nier(Lunatic)/Caltech	single collector	?	0.71031	?	3
VG-354/CPGeo	Single collector	81	0.710261	0.000026	
MAT-261/NIST	stat.multic.	85	0.710240	0.000011	4
Shields/NIST	single collector	24	0.71014	-	5

Among these results, the most significative is 0.710249+/-0.000011 (1σ) which was obtained in 57 separated loadings[2]. The two results from Aveiro obtained also by dynamic multicollection mode agree within experimental errors, whereas the others are in a broad range between 0.71014 to 0.71031, stressing possible internal errors. Based mainly on the dynamic multicollection data, a consensus value of 0.71025 is proposed.

In Table 2 results for six separate loadings of the salt Sr_N (E&A), used until the last decade, are shown. The users of this salt adopted 0.7080 as the most probable value for $^{87}Sr/^{86}Sr$. The average of 0.708013+/-0.000005 (1σ) obtained at Aveiro confirms the adopted value. The respective adjusted value for 0.71025, suggested for NBS-987, is 0.70802.

Table 2: The $^{87}Sr/^{86}Sr$ results obtained in Sr_N (E & A) with VG-Sector mass spectrometer and using dynamic multicollection mode

Date (volts)	(µg)	$(^{87}Sr/^{86}Sr)_n$	error (1 σ)
Ap/25/95 (3V)	~ 0.5	0.708017	0.000011
Ap/28/95 (3V)	~ 1.0	0.708006	0.000007
Ap/28/95 (2V)	~ 1.0	0.708020	0.00004
Ap/28/95 (2V)	~ 1.0	0.708007	0.000005
Ap/28/95 (2V)	~ 1.0	0.708013	0.000004
Ap/28/95 (2V)	~ 1.0	0.708015	0.000005
mean (6)		0.708013	0.000005
mean (adjusted for 0.71025 on NBS-987		0.708021	0.000005

Adequacy and Consistency for a Consensual Value

While a consensus value for NBS-987 has not been established, we belive that all studies involving high resolution stratigraphy based in $^{87}Sr/^{86}Sr$ must indicate the ratio obtained on this reference sample. This is important, since where a sample is measured on an instrument which yields a ratio of 0.71031 for the standard, it will suffer a ratio shift of 0.00017 if a provisional standard value of 0.71014 is used for normalization. This fact could explain the reason why some very precise ratios for marine strontium (Table 3) or modern biogenic carbonates (Table 4) are in disagreement.

Table 3: Normalized (n) and adjusted (adj) $^{87}Sr/^{86}Sr$ ratios for NBS-987 and Sr_N(E & A) respectively

Location	$(^{87}Sr/^{86}Sr)_n$	NBS-987	Sr_N(E&A)	$(^{87}Sr/^{86}Sr)_{adj}$	N	Ref.
Campos Basin (Atl.)	0.70923+/-3	0.710261	-	0,70922+/-3	3	
NE Atl. Ocean (IAPSO)	0.709187+/-38	0.71026	-	0.709177+/-38	23	2
Cont Shelf (NE/USA)	0.70920	-	0.70800	0.70922	1	2
Modern sea water	0.709198+/-20	0.71022	0.7080	0.709228+/-20	9	3
Pacific Ocean	0.709174+/-5	0.710241	-	0.709183+/-5	-	4
Arabian Gulf	0.70911	0.71014	0.70797	0.70922	1	6

As can be seen, the discrepancies virtually disappear after the adjustment. Most of the values in marine Sr are in the range 0.70918 to 0.70922, while in the modern marine shells we can conclude that is close to 0.70918 which is consistent with the I.A.P.S.O. Standard Seawater value

Table 4: 87Sr/86Sr ratios in modern carbonate shells

Sample type	$(^{87}Sr/^{86}Sr)_n$	NBS-987	$(^{87}Sr/^{86}Sr)adj$	n	Ref.
shells & carb. sediments	0.709070+/-40	0.71014	0.709180+/-40	41	1
foraminifera	0.709238+/-29	0.710275	0.709213+/-29	25	5
shells	0.709234+/-9	0.71031	0.709174+/-9	18	3
gastropod shell	0.709182+/-22*	-	-	1	6

Conclusions

The available $^{87}Sr/^{87}Sr$ ratios on seawater strontium and on modern marine carbonate shells demonstrate the adequacy and consistency of correcting observed values adopting 0.71025 for NBS-987 $SrCO_3$ or 0.70802 for Sr_N (E & A), which we are suggesting as consensus values. Adopting this procedure the most probable value for $^{87}Sr/^{86}Sr$ in modern marine strontium is 0.709188 and respective weighted standard deviation is +/- 0.000015 (1σ).

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