

## BARIUM AND STRONTIUM CONCENTRATIONS IN PACIFIC AND MEDITERRANEAN SEA WATER PROFILES BY DIRECT ISOTOPE DILUTION MASS SPECTROMETRY

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The determination of barium and strontium directly from sea water by isotope dilution mass spectrometry proves to be an efficient, precise, and virtual blank free procedure. Results for an eastern Pacific profile confirm a regularly increasing barium concentration from 5 to 23  $\mu\text{g}/\text{kg}$  at 2500 m, but strontium concentrations appear to be nearly homogeneous below 50 m at  $7.6 \pm 0.1 \mu\text{g}/\text{kg}$  with a single low value for the surface water. Results for a western Mediterranean profile show uniform concentrations for both barium and strontium, similar to the Atlantic. There appears to be a nearly conservative strontium-to-salinity ratio of  $0.218 \pm 0.002$  for sea waters below mixed surface zones. The barium salinity ratio for the Mediterranean and Atlantic is  $(0.30 \pm 0.01) \times 10^3$  but the integrated Pacific profile shows a ratio almost twice as great.

### 1. Introduction

Barium, and perhaps strontium, are two elements of particular interest in sea water because they seem to display short residence times and depth gradients due to their reactive natures. Accurate and precise analysis of these elements is important for both an understanding of their controlling reactions in the marine environment, and use as chemical tracers for oceanic circulation.

The analysis of barium in sea water poses serious problems arising from its low concentration (10–30  $\mu\text{g}/\text{kg}$ ) and vulnerability to contamination during chemical processing. Isotope dilution mass spectrometry (IDMS) has been more reliably applied than flame photometry, atomic absorption, and neutron activation of lesser sensitivity or precision. Even in its most successful application [1], IDMS retains some persistent disadvantages in use of rather large samples (100 g), time consuming chemical separation and instrumentation, and significant blank corrections.

Strontium at 7–8 mg/kg is five hundred times more concentrated in sea water than barium and presents fewer problems of sensitivity or blank contamination. However, the demands for higher precision are evident in the reports of significant but small (2–7%) variations of the Sr/salinity ratio for different ocean waters [2] and for the top 500 m of an eastern Pacific profile [3]. Again IDMS appears more suited for high quality analysis than the alternative methods which use external standardization or corrections for interferences.

The objective of this work is to simply analyze Ba and Sr together and directly from small amounts of sea water by IDMS, utilizing the inherent advantages of high precision in internal standardization, element selectivity, and sensitivity in a technique which is rapid and virtually blank free. The method is applied to sea water profiles from the Pacific ocean and Mediterranean sea.

### 2. The technique

In principle, the technique involves just adding by weight a known amount of  $^{135}\text{Ba}$  and  $^{85}\text{Sr}$  spike solutions to a small amount of sea water, directly deposit-

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ing this solution on a decontaminated mass spectrometer filament, measuring the peak intensity ratio of the spike and normal masses by ion multiplication, and calculating the concentration of Ba and Sr in the sea water by dilution formulas.

The experimental details are as follows:

### 2.1. Sample collection

The sea water is sampled using standard teflon-lined hydrographic Nadson bottles, and stored unfiltered and unacidified in polyethylene bottles that have been extensively washed in warm reagent grade 2 N HNO<sub>3</sub> and triple quartz distilled water and dried dustfree. Salinity data for the Pacific was gathered by shipboard salinometry of aliquots, and for the Mediterranean by chloride titration.

### 2.2. Sample preparation and blank control

An accurately weighable but small amount of sea water (in this case about 2 g) is mixed with an equivalent amount of Ba and Sr spikes ( $2.4 \times 10^{-8}$  g <sup>135</sup>Ba;  $1.5 \times 10^{-6}$  g <sup>85</sup>Sr). The vessels used are small teflon or TPX beakers which have been extensively washed in warm reagent grade 5 N HNO<sub>3</sub>, triple quartz-distilled water, and dried dust free. The whole spiking procedure is performed in a clean laboratory with filtered air, and the extent of evaporation is controlled. The spiked mixture is allowed to equilibrate for several hours before analysis.

Each mass spectrometer filament is constructed from ultra-high purity tantalum ribbon and outgassed against a potential of 0.3 kV at about 2 000°C in a special vacuum system. As an additional check for mass spectrometer memory and blank filament control, it proved necessary to check each filament for minute amounts of Ba between runs and before sample mounting by running them in the mass spectrometer at high electron multiplication until no Ba signal is observed ( $10^3$  Ba<sup>2+</sup>/sec). Then about two drops (20λ) of the spiked sea water (about 15 ng Sr and 0.3 ng Ba) are slowly evaporated on the filament under clean laboratory conditions. The initial crystallites of sea salt contain most of the Ba and Sr, and these may be gathered to the center of the filament, the excess sodium-rich supernatant fluid removed with the acid washed plastic tip of the transfer micropipette, and the residual mush oxidized by brief fusion to red temperatures.

### 2.3. Mass spectrometry

Each sample filament is introduced under cover into a 30 cm solid source mass spectrometer (THOMSON HOUSTON 206, modified) and the filament slowly heated at pressures  $< 10^{-7}$  torr until all traces of Rb disappear. Stable Sr and Ba emission is obtained at about 1 000°C, and data is gathered by the electron multiplication of the ion current ( $10^4$ – $10^7$  ions/sec) on a strip chart recorder whose linearity and shunts are calibrated to 0.1%. The period of analysis is about one hour.

## 3. Results

Table 1 presents the concentrations of Ba and Sr in sea water from a 4500 m profile in the Eastern Pacific (9° 13'N; 119° 18'W), a 2500 meter profile in the Western Mediterranean (41° 59'N; 6° 45'E), and a single deep Atlantic water [4]. The sequence of analysis was completely a random function of their depth in the profile so as to cancel any time bias in spike or calibration. These concentrations are computed with a standard formula for isotope dilution which includes terms for (a) the concentration and isotopic composition of the spike solution (b) the weights of spike and sample solutions and (c) the recorded signal ratio of spike and normal masses, which in the case of Sr is corrected for small mass discriminations using the standard normalization of  $^{88}\text{Sr}/^{86}\text{Sr} = 8.3452$ .

The relative precision of analysis is noted in table 1 which utilized single spike solutions and several sample replicates for each profile. Strontium may be measured to  $< 1\%$ , which reflects the inherent combined precision to weigh the sample and spike solutions to  $< 0.3\%$ , and to measure the sample/spike mass signal ratio with correction to  $< 0.5\%$  for any one run. Barium was not analyzed as precisely ( $\approx 3\%$ ) due to lack of correction for mass discrimination ( $\delta(^{135}\text{Ba}/^{138}\text{Ba}) = 1$ – $2\%$ ) and more importantly due to the sensitive blank contamination to the minute amounts (0.3 ng) of Ba on the spectrometer filament.

The blank for the procedure, which is much more severe for Ba than Sr, is evaluated in two ways. First, there seems to be a lesser relative precision of the order of 0.2–0.3 μg/l for sea water samples of lower concentration or 0.01 ng on the filament. Second, about 1 ng

Table 1

Barium and strontium concentrations in profiles of the Pacific Ocean and Mediterranean sea, as measured simultaneously by direct isotope dilution mass spectrometry of sea water. The data normalized to salinity are given for comparison.

Depth (m)	Salinity	Temp. (°C)	Pacific (9° 13' N-119° 18' W).		Sr(mg/kg)	Sr/S × 10 <sup>3</sup>
			Ba(μg/kg)	Ba/S × 10 <sup>6</sup>		
0	33.83	28.36	4.9 ± 0.3	127	7.21	213
64	34.67	15.98	6.2	179	7.66	221
119	34.77	12.08	6.7	193	7.65	220
275	34.72	10.13	8.3	239	7.58	218
499	34.63	8.36	10.3	297	7.62	220
724	34.57	5.95	11.6	336	7.59	220
1112	34.58	4.14	14.7 ± 0.7	442	7.60	220
1410	34.60	3.20	18.4	532	7.54	218
2012	34.65	2.16	21.1	609	7.59	219
2514	34.68	1.86	22.7	655	7.56	218
3017	34.68	1.66	23.0 ± 0.2	669	7.52	217
3519	34.70	1.55	23.0 ± 0.7	651	7.53	217
4020	34.69	1.47	22.7	654	7.52 ± 0.01	217
4506	34.71	1.50	23.6	680	7.58	218
Mean				530 (integrated)		219 ± 1
Mediterranean (41° 54' N-6° 45' E)						
0	38.1	No record	10.0	262	8.24	216
100	38.2		11.5	301	8.30	217
200	38.4		11.5	289	8.35	217
400	38.2		12.1	317	8.28	217
600	38.2		11.3 ± 0.6	296	8.32	218
700	38.3		11.4	298	8.21	214
800	38.4		11.6	302	8.35	217
1000	38.2		11.3	296	8.32	218
1100	38.2		11.6	304	8.36	219
1200	38.1		11.3	297	8.36	219
1700	38.0		11.9	313		
1900	38.1				8.25 ± 0.01	217 ± 1
Mean				298 ± 7		217 ± 1
Atlantic (Woods Hole Interlaboratory Calibration No. 3-40) [4]						
	34.97		10.1	289	7.72	221

pure spike solution was processed identically to the entire sample procedure. These results in terms of isotopic composition are presented in table 2, and the excellent agreement within error to those provided by Oak Ridge National Laboratories translates to < 0.01 ng of Ba on the filament. Thus the Ba blank or irreproducibility for the technique is less than 1–3%, depending on the concentration of the particular sea

water analyzed. The results of table 1 are uncorrected for this.

The absolute accuracy of analysis is evaluated from the accuracy of terms used in the formula for isotope dilution, and by running several sea water analyses using more than one independently calibrated spike solution. The accuracy of weighting 2 g of sample and spike solutions is < 0.2%. The accuracy in isotopic

Table 2

The isotopic composition for the  $^{135}\text{Ba}$  spike provided by Oak Ridge National Laboratories, and the isotopic composition measured in 1 ng of  $^{135}\text{Ba}$  spike solution processed and run identically to the sea water samples. The excellent agreement demonstrates the accuracy of the mass spectrometric measurements and the undetectable contributions of blank barium to the procedure.

Ba Isotope	Atomic % (ORNL)	Atomic % (This work)
134	$0.35 \pm 0.05$	$0.35 \pm 0.07$
135	$92.82 \pm 0.1$	$93.90 \pm 0.0$
136	$1.47 \pm 0.05$	$1.48 \pm 0.08$
137	$0.73 \pm 0.05$	$0.72 \pm 0.08$
138	$3.62 \pm 0.05$	$3.54 \pm 0.10$

composition of the spike solution was demonstrated in table 2 to be  $< 0.1\%$  of the atomic percentages provided. The accuracy of the measured isotopic ratio may be evaluated as  $< 0.2\%$  by the ability of the mass spectrometer to measure the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of (1) the standard Eimen and Amend  $\text{SrCO}_3$  as 0.7083 for an accepted value of 0.70803, and (2) sea water itself as a ratio of  $0.709 \pm 0.001$  for an accepted value of 0.7091. The accuracy of the spike solution concentration may be evaluated by calibration against several normal solutions constructed gravimetrically from dried high purity nitrate salts of an assumed molecular weight. The results of such a calibration (table 3) show

Table 3

The cross calibration of spikes used for this work with normal solutions of barium and strontium nitrate. An accuracy of 1–2% is estimated for the accuracy of the absolute spike concentrations.

	Spike No.	Spike Concentration ( $\mu\text{g}/\text{g}$ )		
		MBS-1	SS-2	SS-3
Sr standard	NS-1	2.44	0.723	1.48
	NS-2	2.46	0.732	—
	NS-3	2.54	0.723	1.50
	NS-4	2.31	0.714	$1.46 \pm 0.01$
			SB-1	SB-2
Ba standard	NB-1	0.122	0.344	0.0799
	NB-2	0.124	$0.343 \pm .001$	0.0799

the accuracy in spike solution concentration as 1–2% for Sr and 1% for Ba.

The use of an absolute volumetric calibration of the normal solutions would have improved any further bias in the absolute Ba and Sr concentrations of table 1 that may arise from the composition of a gravimetric standard. Table 3 shows the results for replicate sea water analyses against more than one spike and confirms a 1–2% limit in the accuracy for analysis.

### 3. Discussion

The results are presented graphically in fig. 1.

Barium concentration in the eastern Pacific are observed to increase from  $4.9 \mu\text{g}/\text{kg}$  to  $23 \mu\text{g}/\text{kg}$  by 2500 meters, remaining quite constant at this concentration to the bottom. The blank corrected IDMS results taken at the Geosecs I station some 1100 miles to the north three months later are also plotted in fig. 1. The excellent agreement between the two independent sets

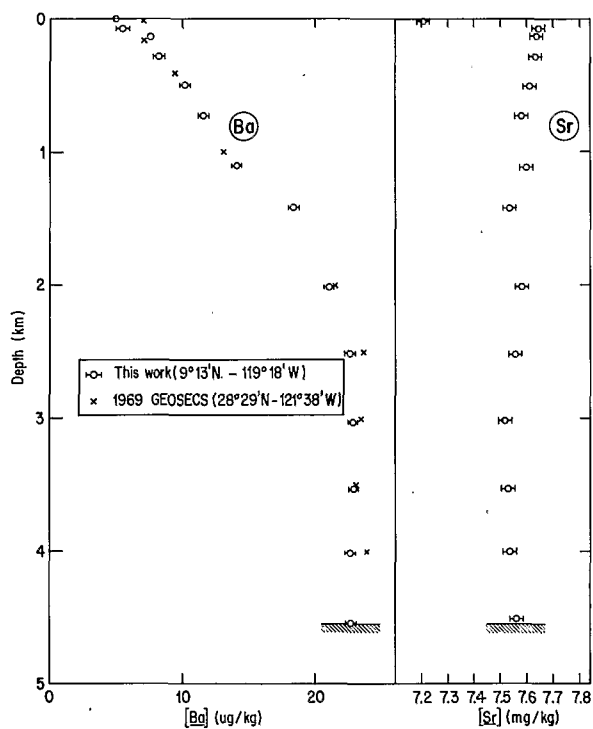


Fig. 1a. Barium and strontium concentration profiles in sea water from Pacific Ocean ( $9^{\circ}13'N$ – $119^{\circ}18'W$ ).

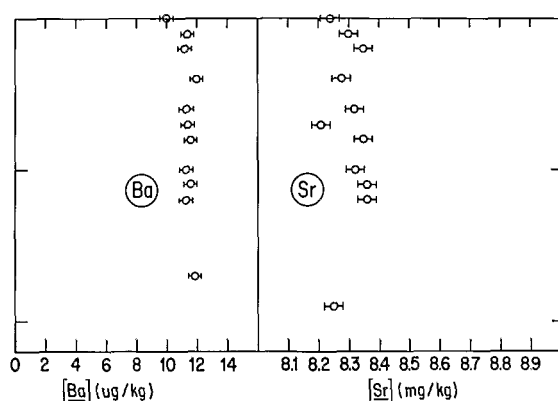


Fig. 1b. Barium and strontium concentration profiles in sea water from Mediterranean Sea ( $41^{\circ}54'N-6^{\circ}45'E$ ). The analyses were performed directly and simultaneously from spiked sea water solutions by isotope dilution mass spectrometry. For comparison the IDMS barium results for the neighboring Geosecs I station are included [4], and an expanded scale is utilized for strontium.

of Ba data supercedes the non-blank corrected results [5] for the same station, and the irradically increasing Ba concentrations (to some  $60 \mu\text{g}/\text{kg}$ ) reported for the original IDMS analyses in the eastern Pacific [6]. The barium concentrations in the Mediterranean are quite constant with depth ( $11 \pm 1 \mu\text{g}/\text{kg}$ ), and closely resemble the constant depth profile for the Atlantic [5, 7] whose deep water values are confirmed by this work at  $10 \mu\text{g}/\text{kg}$ . Both oceans display a similar barium-salinity ratio of  $0.30 \pm 0.01$ . However the eastern Pacific sea water profile has an integrated barium-salinity ratio almost twice as great. This barium enrichment probably reflects the deep Pacific as an accumulative reservoir for the downward flux of barium-rich particulates [5, 6] as the Pacific deep water ages generally from the southwest to the northeast [8]. However, the details of this process and exact sources must await many more detailed and accurate profiles from the whole Pacific basin.

Strontium concentrations in the eastern Pacific are remarkably constant at  $7.58 \pm 0.04$  below 64 m, with perhaps a slight (1%) trend to lower concentrations toward the bottom that approximates the precision of analysis. The IDMS result of this work value is significantly lower and more precise than the  $8.18 \pm 0.13 \mu\text{g}/\text{kg}$  mean concentration below 500 m obtained at the Geosecs I station [3] using atomic absorption and

neutron activation. However the IDMS value is higher than the  $7.34 \pm 0.14 \mu\text{g}/\text{kg}$  mean Sr concentration obtained earlier using X-ray fluorescence for thirteen waters below 400 m in the Pacific [9]. The difference in absolute values for different methods could arise in a systematic bias of standardization or instrumentation. This is emphasized in the bias between a Sr concentration of  $7.72 \pm 0.15 \text{ mg}/\text{kg}$  obtained for the deep Atlantic sample by IDMS, and a value of  $8.07 \pm 0.36 \text{ mg}/\text{kg}$  for the same sample obtained by the original inter-laboratory calibration using a variety of atomic absorption and neutron activation techniques [4]. While the absolute calibration used by IDMS is probably no more accurate than other methods, the inherent selective qualities of IDMS instrumentation (internal standardization, mass selectivity, mass fractionation and ratio control) would seem superior.

The strontium-salinity ratios for the eastern Pacific show a distinctly low ( $-3\%$ ) value for the surface water. The Geosecs I profile also confirms a strontium-salinity surface minimum ( $-4\%$ ) which extends down to 500 m [3]. Thus anomalously low strontium-salinity ratios seem a distinct possibility for surface ocean water. The nature of the *in situ* Sr extraction seems related to the extent of down-mixing of low salinity surface waters (fig. 2), and likely possibilities include the metabolic cycles of  $\text{SrSO}_4$  bearing Acanthania organisms [10]. In any case, these processes seem distinct from the parallel extraction processes for barium.

Thus, further studies of strontium in sea water should have an analytical resolution of  $< 1\%$ , detailed sampling of the mixed surface layer, and knowledge of the nature of the biomass.

The strontium concentration of the Mediterranean also is quite constant with depth ( $8.30 \pm 0.06 \text{ mg}/\text{kg}$ , with perhaps minimums at 0 and 700 m). When normalized to the increased salinity, there is a good agreement with the deeper Pacific and Atlantic at  $\text{Sr}/\text{S} = 0.218 \pm 0.002$ .

Within the accuracy and range of samples studied by this work, strontium appears to be a remarkably homogeneous and conservative element for sea water below mixed surface zones.

#### 4. Conclusions

The analysis of barium and strontium directly from small amounts of sea water proves to be an efficient

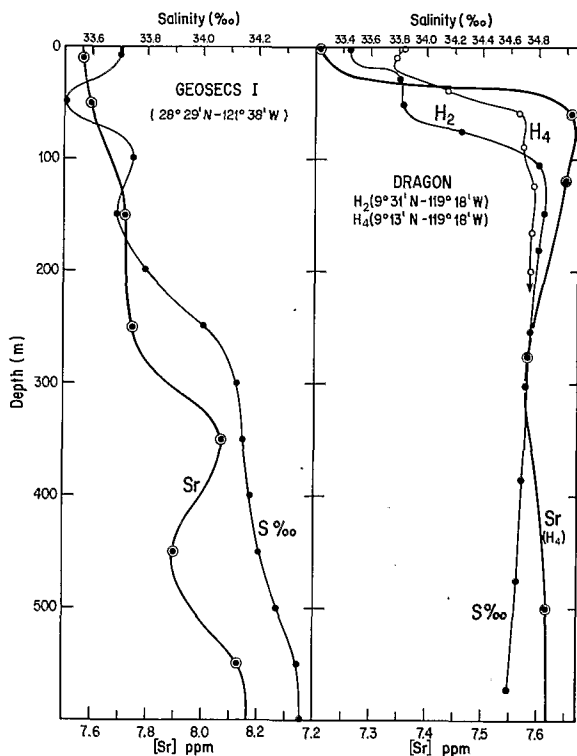


Fig. 2. Strontium and salinity profiles for the surface Pacific waters of (a) this work, (b) the Geosecs I station [3]. The lower salinity mixed zones of both profiles contain Sr-salinity ratios distinctly lower than the remaining water column.

and highly precise technique. The quality of the method is demonstrated in concentration profiles from the eastern Pacific and western Mediterranean. For barium there is excellent confirmation in the Pacific for an increasing gradient with depth from 5 to 23  $\mu\text{g}/\text{kg}$ , while the Mediterranean and the Atlantic display lower homogeneous concentrations of 10–12  $\mu\text{g}/\text{kg}$  with a similar Ba-salinity ratio of  $(293 \pm 5) \times 10^6$ . Strontium, however, is quite constant with depth at  $7.58 \pm 0.04$  mg/kg for the deeper Pacific and  $8.30 \pm 0.06$  mg/kg for the Mediterranean which as the Atlantic displays a remarkably conservative Sr-salinity ratio of  $(218 \pm 2) \times 10^3$ . Confirmed is the possibility for a 3% depletion in the Sr salinity ratio for the mixed surface zones of the Pacific.

Several other trace elements in sea water, such as the lanthanides and transition elements seem amenable to high precision analysis by isotope dilution mass spectrometry, and this laboratory is exploring these possibilities.

#### 4. Acknowledgements

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