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SEARS FOUNDATION FOR MARINE RESEARCH
Bingham Oceanographic Laboratory, Yale University

Journal of
Marine Research

Volume 20, Number 3

Mass Spectrometric Determination of Lithium in Seawater

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ABSTRACT

Lithium concentrations in Pacific Ocean waters to depths of over 4,000 m have been determined using isotope dilution techniques with a mass spectrometer. Values varied about 170 μg/L and showed a covariance with the salinity.

The reported analyses for lithium in seawater (Table I) have not as yet delimited its concentration range. In fact it is difficult to arrive at a value within a factor of two for its abundance inasmuch as (1) all of the work has been concerned with surface coastal waters, most probably atypical of the marine environment as a whole, and (2) the analytical techniques employed suffer from a number of inadequacies. Thus, the aim of this work is to seek out a representative value for the lithium content of seawater from samples collected at various depths and locations in the eastern Pacific Ocean.

Method. To 50 ml of unfiltered seawater were added 100 μl of Li^6 tracer obtained from the Oak Ridge National Laboratory, Oak Ridge, Tennessee. The isotopic composition of the tracer and common lithium follow:

	Li^6 atom %	Li^7 atom %
Tracer	99.7	0.3
Common	7.5	92.5

The original metallic form of the Li^6 was converted to a sulphate solution which contained 0.1494 μg Li/μl. The combined seawater-tracer solution was passed through a Dowex 50-X16 (100–200 mesh) resin column to separate the lithium from seawater. The resin was initially washed with 8 N HCl (all HCl solutions were prepared by bubbling anhydrous HCl gas into distilled water), packed into a 30 cm × 1 cm column and conditioned with 1 N HCl. After being treated with the seawater solution, the column was rinsed with distilled water to remove the unabsorbed anions. Elution of the absorbed lithium was accomplished with 1 N HCl. The first 20 ml of the eluate were collected in a teflon beaker. The sodium break-through was continuously monitored by flame tests, and the appearance of the characteristic sodium flame indicated the termination of the elution process. By this technique, about 60 % of the lithium (about 15 μg) was separated in a nearly pure form.

The eluate was evaporated to near dryness, and about 5 μg of lithium were transferred to a tantalum filament. The mass spectrometric procedure was similar to that described by Chow and Goldberg (1960). The filament current was slowly raised to 0.9 ampere corresponding to a temperature of 850°C. At this temperature, Li^+ was emitted. The analysis in this mass range is completely specific for lithium, for no other element has a naturally occurring isotope of mass number 6 or 7.

TABLE I. PREVIOUS INVESTIGATIONS OF LITHIUM IN SEAWATER.

Location	Method	Lithium Concentration (μg/L)	Reference
English Channel	Gravimetric isolation of Li_3PO_4	70	Marchand (1855)
North Sea	Emission spectroscopy on sea salts	72	Goldschmidt, *et al.* (1933)
Pacific Coast, U.S.A.	Emission spectroscopy on carbonate precipitate from seawater	100	Thomas and Thompson (1933)
North Sea	Emission spectroscopy on sea salts	140	Strock (1936)
Brittany Coast	Gravimetric isolation of Li_2SO_4	170	Bardet, *et al.* (1937)
Japanese Coast	Gravimetric isolation of Li_2SO_4	200	Ishibashi and Kurata (1939)
Indian Coast	Emission spectroscopy on sea salts	160	Kappanna, *et al.* (1960)

Inghram and Hayden (1954) have pointed out that a correction proportional to the square root of the mass ratio should be applied when a multiplier is used. The correction is critical for lithium analysis since the square root of 6 over 7, that is 0.9258, is significant. This value was acertained by mixing known quantities of tracer and common lithium (0.1686 μg/μl) solutions and by comparing Li^6/Li^7 ratio calculated from the mixture with that determined experimentally.

The results are as follows:

Lithium (μl)		Observed Li^6/Li^7 Ratio			Calculated Li^6/Li^7
Tracer	Common	Atom	Wgt.	0.9258 × Wgt.	Wgt. Ratio
100	100	1.303	1.117	1.034	1.033
100	50	2.536	2.174	2.013	2.101

It is evident from the experiments that the square root of mass ratio correction is necessary and accurate for the lithium analysis. The deviation observed, about 4%, was in the same order of magnitude as the experimental error.

The concentration of lithium in the seawater samples is therefore calculated from the following equation:

$$M = \frac{m\,(Li_s^6 - N \times Li_s^7)}{N \times Li_w^7 - Li_w^6},$$

where M = lithium in the sample (μg);
m = amount of Li^6 tracer added (μg);
N = observed Li^6/Li^7 ratio with atom and square root corrections;
Li_s^6, Li_s^7 = atom % of Li^6 and Li^7 in the tracer, respectively;
Li_w^6, Li_w^7 = atom % of Li^6 and Li^7 in the common lithium respectively.

Results of Analysis. The seawater samples were taken from three areas to depths of over 4000 m. The results of lithium analyses are given in Table II. There appears to be a co-variance of lithium with the salinity. The data show that lithium exists in the ocean in proportion to the chlorinity expressible by the ratio 8.94 ± 0.12 lithium (μg/l) per Cl ‰. The data, also plotted in Fig. 1, show a least square fit of all points.

These results are not surprising. Lithium is probably a relatively inert element in the marine chemical system. The well-known tendency of lithium ion to be strongly hydrated in solution, together with the observation that it is not markedly enriched in the marine biosphere, suggest a long residence time in marine waters. By using a value of 170 μg Li/L as well as the calcula-

TABLE II. LITHIUM CONTENT OF SEAWATER.

Station	Depth (m)	Temp (°C)	S (‰)	Li (µg/L)	Li (µg/L) / (Cl ‰)
Downwind - 1	2	20.64	33.82	165	8.81
29°26′N					
120°26′W	2804	1.70	34.60	171	8.93
Downwind - 14	0	26.66	36.16	178	8.89
19°22′S					
149°21′W	3316	1.59	34.68	176	9.17
Downwind - 22	0	11.54	34.01	159	8.45
45°54′S					
97°08′W	4285	0.94	34.71	174	9.06
29°09′N	50	14.89	33.48	161	8.69
117°40′W	200	8.94	33.92	173	9.21
	937	4.19	34.48	175	9.17
	1943	2.10	34.64	170	8.87
	2954	1.62	34.67	174	9.07
	3775	1.63	34.68	173	9.01
30°27′N	2599	1.73	34.66	170	8.86
117°51′W					
S.I.O. Pier					
32°52′N	0	14.70	33.55	166	8.94
117°15′W					

tions of Goldberg and Arrhenius (1958), a residence time of 20×10^6 years is computed.

Acknowledgements. The authors are indebted to Dr. C. C. Patterson of the California Institute of Technology who provided the stimulation as well as the mass spectrometer used in this work. This work was supported by grants from the National Science Foundation, the Office of Naval Research, and the Atomic Energy Commission, Division of Biology and Medicine.

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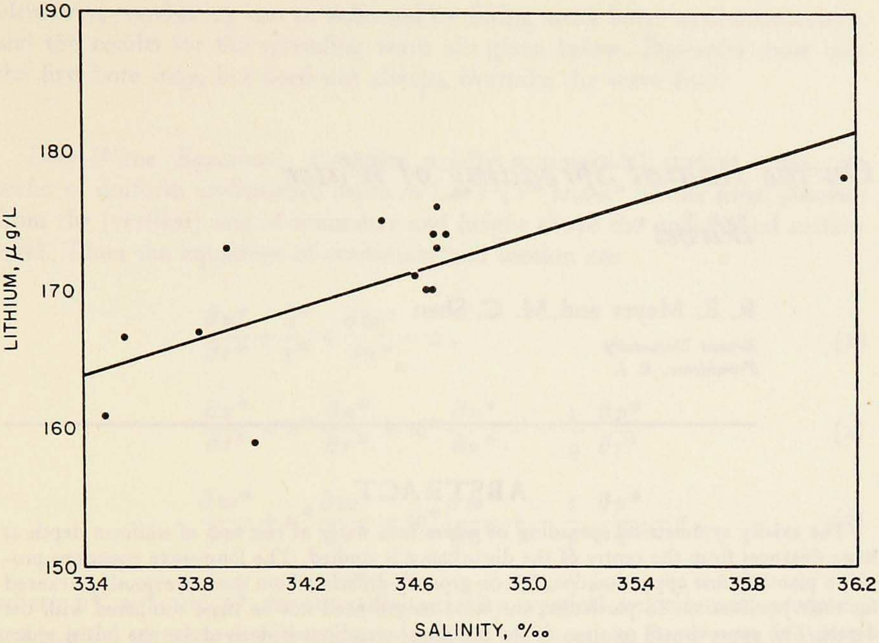

Figure 1. The lithium concentrations in sea water as a function of salinity. The line was fitted by least-squares analysis.

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