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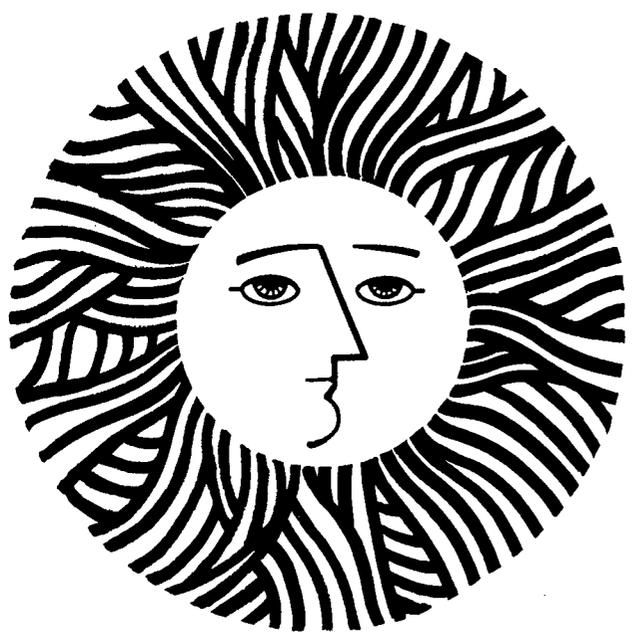
ENERGY & ENVIRONMENT DIVISION

MEASUREMENTS OF ELEMENT ABUNDANCES IN PLANKTON
BY NEUTRON ACTIVATION ANALYSIS

Helen V. Michel and Frank Asaro

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Measurements of element abundances in Plankton by Neutron

Activation Analysis

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Introduction

Six samples of plankton and planktonic fish were received from Dr. A. Russell Flegal of Moss Landing Marine Laboratory and were subjected to neutron activation analysis (NAA).

These samples were treated in a different manner than we normally do in order to increase the sensitivity of measurement for many elements. Pills for the NAA measurement were prepared by mixing the powders with 50 mg of cellulose binder each and compressing in an Al_2O_3 die at a pressure of $\approx 25000 \text{ lbs/in}^2$. Normally a tool-steel die is used, but it can contribute contaminants of Mn, Fe, Cr, W and Co. The Al_2O_3 die should only contribute an Al contamination. After all six samples had been prepared, a pill of the pure cellulose used for a binder was

prepared (49.1 mg in weight). Its purpose was to evaluate possible cross-contamination between samples and to evaluate impurities contributed by the cellulose, the Al_2O_3 die and a polyethylene foil used to seal the samples.

The 6 sample pills, containing 74.3 mg to 101.2 mg of unknown, and the cellulose pill were sealed in polyethylene film and irradiated for 3 minutes at a power level of 11 kilowatts ($\sim 2 \times 10^{11}$ n/sec cm^2). Normally we irradiate for 18 min. The high levels of Na expected in the plankton would give gamma-ray counting rates higher than our equipment would tolerate. With Na abundances of 12%, a 3-4 min. irradiation is optimum.

The samples were counted for 1.00 min. each, 9-15 min. after the end of the irradiation. Al, Ca, and Cl are determined in this measurement. The "apparent" Al may be due to Al in the sample, Si in the sample or Al contamination from the Al_2O_3 die. One hundred percent SiO_2 appears as 0.514% Al. Two Standard Pottery pills are used in each irradiation (with 5 unknowns) for calibration. In addition KCL and CaCO_3 primary standards are used to calibrate Cl and Ca respectively (Standard Pottery does not have Cl and Ca in useful amounts for calibration).

About one hour after the end of irradiation the pills were counted for 12 minutes each, twice the normal counting period. The extended counting period improved the sensitivity for Sr, Mn, Dy, Ba and In. Na is measured with high precision in this measurement. In order to improve the sensitivity for K, Cu and Ga a 2 hour measurement on each sample was made the next day. This also serves to improve the precision of the Na measurement. A high precision Na measurement along with a

high precision Cl measurement is useful in determining if there is any Na present over and above that expected from seawaters.

Sometime later the polyethylene film was removed from the six plankton and one cellulose pills and they were rewrapped in 99.9999% Al (.001" thick) foil. These samples and one of the Al foil by itself were irradiated for 8 hours in the Berkeley Triga reactor at a power level of 1000 kilowatts (2.7×10^{13} n/sec-cm²). One Standard Pottery pill from each short irradiation was also removed from the polyethylene wrapping and rewrapped in the Al foil. Two Standard Pottery pills are used to calibrate each group of 10 unknowns.

About 6.5-6.9 days after the end of the long irradiation the samples were counted for 20 minutes each with a 1 cc high resolution gamma-ray detector. This measurement gives data on rare earths (Sm, La, Lu), U, As, Br, Ba, Au, Ti and W. The count rates for samples with Na in ~12% abundance were too high for the electronic system. If the counts were started ~8.5 days after the end of the irradiation this problem would be avoided. The sensitivities for As and W, however, would become significantly poorer.

About 3 weeks after the end of the irradiation the samples are counted for 60 minutes each with our 7cc detector. This gives data on Sc, Fe, Cr, Ni, Co, Zn, Sb, Tb, Ce, Th, Eu, Rb, Hf, Ag, Sn and Ir. Immediately after this run the samples are counted for 80 minutes each with the higher resolution 1cc detector. More reliable Ce and Tb values are obtained, Se is measured, and more precise values of Yb, Hf, Ta and Eu are measured.

Data

The concordance of the Moss Landing Marine Laboratory and Lawrence Berkeley Laboratory sample designations is shown in Table I. The most abundant elements are shown in Table II along with those elements which chemically could be related to them. Rare earths are shown in Table III and the other elements are shown in Table IV. Only those elements which were definitely detected in at least one sample are shown in Table IV plus the element iridium. The Ir limits are given because these might be useful in evaluating the mechanism by which meteoritic Ir ends up in sediments. Abundance limits on elements not detected in any sample are shown in Table VI.

The contribution of elements from seawater has been removed where it is pertinent (in Table II). Contaminants of Sc, Co and Zn have been removed from the 6 plankton samples (because of the impurity levels indicated in the cellulose and Al samples). All data for these last two samples are given in terms of a "normal" pill weight of 100 mg.

As an example of what one might do in the future, 2 plankton samples were measured with our 128cc Li-Ge detector. (See Table V) These have not been calibrated directly against Standards and the abundances are therefore only estimates. Improvements of over an order of magnitude were obtained for some elements. It is possible to count the Standard Pottery samples and the other 4 irradiated plankton samples and obtain calibrated abundances for all of the elements shown in Table V, as well as some others.

Results and Conclusions

The Cl and Na measurements appear to be valid in as much as they have the seawater ratio in 3 of the 6 samples. In P7 the Na value was too small by over 3 standard deviations. This may represent a statistical excursion error in the Na or Cl measurements or fractionation of the Na and Cl. Until other evidence is obtained it will be regarded as a statistical problem. Samples NR and FD have excess Na.

Neutron activation analysis (without chemistry) is an effective measurement technique for all or nearly all of samples studied for determination of Ca, Cl, Na, Br, Ba, Co, Ni, Sb, Se, Sc, U and Zn abundances. Incorporating a 128cc Li-Ge detector into the counting regime gives significantly better precision for many elements and permits measurement of Cr, Fe, Rb, and Ta at the very low abundance levels detected in the plankton. The sensitivities for Sc, Sb, Co and Zn are good enough that corrections are necessary for impurities in the high purity Al wrapping foil.

Substantial improvement in the U and Br precision can be obtained by changing the gamma-ray counting regime slightly. The same changes will also improve the sensitivity for Sm and La. NAA is sporadically effective in measuring the abundances of K, As, many of the rare earths, Mo, Mn, As and Th. It was not effective in measuring Hf, Ir, Cu, In, Ga, Mg, Sn, and Ti.

Accurate values for the abundance of Rb in seawater are needed because the seawater component is comparable to the residual component in some samples. The use of an Al_2O_3 die (rather than tool steel) in

the sample preparation process permits the measurement of Fe, Cr, and Mn, abundances which otherwise would contain uncertainties comparable to the measured values.

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Table I

Sample Concordance

Moss Landing designation	Comment	LBL sample name	LBL pill name
P7	plankton	MLML-14	2002K
P5	plankton	MLML-13	2002J
P3	plankton	MLML-12	2002H
NR	plankton	MLML-11	2002G
C	plankton	MLML-10	2002F
FD	planktonic fish	MLML-9	2002E
-			
.	cellulose	MLML-15	2002M
.	Al wrapping foil	Al	2002L

Table II

Abundances of the most prominent elements and other elements related to them

Sample	Elements									
	Cl (%)	Na (%)	$\left[\begin{array}{c} \text{Seawater} \\ \text{Na} (\%) \\ 0.5564 \\ \times \text{Cl} (\%) \end{array} \right]$	Residual Na (%)	K (%)	Rb (ppm)+Sr	$\left[\begin{array}{c} \text{Seawater} \\ \text{Rb} (\text{ppm}) \\ .062 \\ \times \text{Cl} (\%) \end{array} \right]$	Residual Rb (ppm)+Sr ²	Residual ⁴ Rb	Al (%) (+Si) ³
P7	21.93±.31 ¹	11.52±.10	12.20±.17	<.38	<.8	2.0±.6	1.4	<1.8	<1.2	.105±.031
P5	15.25±.28	8.49±.08	8.48±.16	<.37	<.6	1.9±.5	1.0	<1.9	<1.0	<.39
P3	23.40±.35	13.29±.13	13.02±.19	<.7	<.7	3.8±.6	1.5	2.3±.6	1.5±.6	<.5
NR	2.49±.09	1.600±.012	1.39±.05	.21±.05	<.5	6.1±1.2	.15	6.0±1.2	4.1±.7	.53±.05
C	14.34±.24	8.11±.05	7.98±.13	<.4	<.8	4.9±.7	.9	4.0±.7	-	<.19
FD	3.11±.11	2.032±.015	1.73±.06	.30±.06	1.67±.17	7.5±.7	.19	7.3±.7	7.3±.7	<.05
Cell.	.009±.003	.00330±.00023	.005±.002	<.004	<.021	<.31	.00	<.31	<.31	.0036±.0016
Al	<.007	-	-	-	-	<.39	-	-	-	-

¹Errors are 1 sigma counting errors²⁸⁶Rb is also produced by the reaction ⁸⁶Sr(n,p) ⁸⁶Rb as well as the reaction ⁸⁵Rb (n,γ) ⁸⁶Rb.³²⁸Al is also produced by the ²⁸Si(n,p) ²⁸Al reaction as well as the ²⁷Al(n,γ) ²⁸Al reaction. 100% SiO₂ appears as 0.51% Al.⁴This calculation assumes all ⁸⁶Rb found in sample C is due to the ⁸⁶Sr(n,p)⁸⁶ reaction.

Table II (cont.)

Abundances of most prominent elements and other elements related to them

Sample	Elements										
	Br(ppm)	Seawater Br(ppm) 34.2 × Cl(%)	Residual Br(ppm)	Ca(%)	Seawater Ca(%) .021 × Cl(%)	Residual Ca(%)	Sr(%)	Ba(ppm)	Cs(ppm)	Seawater Cs(ppm) 1.5×10^{-4} × Cl(%)	Residual Cs(ppm)
P7	1500±300	750	750±300	5.5±1.0	.46	5.0±1.0	3.00±.07	45±7	.032±.015	.003	<.06
P5	2400±500	520	1880±500	4.1±1.6	.32	3.8±1.6	2.16±.06	28±7	<.07	.002	<.07
P3	1800±360	800	1000±360	4.0±2.0	.49	3.5±2.0	1.180±.034	35±6	<.06	.003	<.06
NR	1250±250	85	1165±250	7.9±.8	.05	7.8±.8	2.84±.07	183±11	.114±.039	.000	.114±.039
C	2000±400	490	1510±400	6.4±1.2	.30	6.1±1.2	6.05±.14	114±9	<.04	.002	<.04
FD	180±35	107	73±35	2.4±.7	.07	2.3±.7	.046±.011	<12	.056±.016	.000	.056±.016
Ce11.	1.15±.23	.31±.10	.84±.25	<.06	.000	<.06	<.002	<1.2	<.015	.000	<.015
A1	.22±.12	-	-	-	-	-	-	<2.5	<.013	-	-

Table III

Abundances of rare earths (expressed in ppm)

Sample	Elements				
	Ce	Sm	Eu	Tb	Yb
.					
P7	<.4	<.09	<.014	<.07	<.16
P5	<.5	<.09	<.013	<.04	<.09
P3	<.5	<.10	<.023	<.04	<.11
NR	3.6 \pm .6*	.327 \pm .011	.052 \pm .015	.057 \pm .012	.140 \pm .032
C	<1.2	<.10	<.017	<.07	<.10
FD	<.9	<.05	<.014	<.06	<.12
-					
Cell.	<.031	<.0007	<.008	<.019	<.013
Al	<.05	<.0004	<.010	<.009	<.006

*Errors are 1 sigma counting error

Table IV
Abundances of other trace elements (expressed in ppm)⁽¹⁾

Sample	Elements								
	Ag ⁽²⁾	As	Cr	Co	Fe	Hf	Ir	Mn	Mo
P7	<.16	<16	<1.9	.472±.026	<84	<.07	<.0018	<7	<7
P5	<.16	<10	<.9	.328±.023	<73	<.06	<.0017	<9	<4
P3	.20±.08	<11	1.3±.5	.382±.024	52±23	<.07	<.0013	<10	<4
NR	<.7	8.3±3.3	11.0±.6	1.75±.05	3579±63	.25±.05	<.004	47.4±1.6	47.5±3.2
C	<.33	<16	<1.9	.965±.035	68±24	<.12	<.0017	<65	<4
FD	<.27	<6	<1.2	.111±.018	<74	<.07	<.0035	3.9±1.4	<2
Cell.	<.05	<.8	.16±.04	.025±.006	<15	<.009	<.0003	<.31	<.21
A1	<.06	<.31	<.08	.041±.007	<1.5	<.012	<.0003	-	<.13

Table IV (con't)

	Ni	Sb	Se ⁽²⁾	Sc	Ta	Th	U	Zn ⁽²⁾
P7	6.4 \pm 1.0	.138 \pm .026	2.22 \pm .38	.0273 \pm .0029	<.020	<.08	1.35 \pm .27	20.4 \pm 1.2
P5	4.0 \pm .9	.102 \pm .023	3.14 \pm .36	.0108 \pm .0029	<.04	<.05	1.4 \pm .4	47.2 \pm 1.7
P3	8.0 \pm .9	.124 \pm .024	2.35 \pm .38	.0070 \pm .0029	<.018	<.04	1.4 \pm .4	20.7 \pm 1.2
NR	21.6 \pm 2.6	.186 \pm .035	1.46 \pm .28	1.431 \pm .014	.029 \pm .015	.217 \pm .031	.96 \pm .05	60.2 \pm 2.3
C	13.2 \pm 1.2	.182 \pm .029	3.4 \pm .4	.0141 \pm .0030	<.019	<.11	.72 \pm .18	44.3 \pm 1.6
FD	<3.2	<.029	5.7 \pm .5	.0060 \pm .0031	<.024	<.05	<.2	55.7 \pm 2.0
Cell.	<.6	<.02	<.14	.0110 \pm .0009	.0036 \pm .0005	<.008	<.014	1.79 \pm .34
Al	<.36	<.02	<.11	.0102 \pm .0009	.0010 \pm .0004	<.005	<.008	.64 \pm .27

(1) Errors are 1 values of the sigma counting uncertainties. Limits are 2 sigmas values.

(2) Flux monitors were used in the abundance calibrations. There may be systematic errors of 10-20%, besides the counting errors.

Table v

Estimates⁽⁴⁾ of abundances in plankton determined with a 128 cc Ge-Li detector
(expressed in parts-per-million)

Sample	γ ray detector volume	Elements												
		Co ⁽⁵⁾	Cr	Cs	Fe	Hf	Ir	Ni	Rb(+Sr) ⁽⁷⁾	Sb ⁽⁶⁾	Ta ⁽⁶⁾	Th	Ag	Sr
P7	128cc ⁽¹⁾	.446±.006	1.06±.17	.0066±.0008	29.2±1.5	<.010	<.00028	5.84±.11	3.30±.21	.173 ±.004	.0055 ±.0005	<.021	.04±.004	-
	7cc ⁽²⁾	.472±.026	<1.9	.032 ±.018	<84	<.07	<.0018	6.4 ±1.0	2.0 ±.6	.138 ±.026	<.020	<.08	<.16	-
FD	128cc ⁽³⁾	.127±.007	.17±.04	.0503±.0011	34.6 ±.9	<.0032	<.00009	1.60±.07	6.97±.18	.0154±.0012	.00135±.00018	<.008		576± 14
	7cc ⁽²⁾	.111±.018	<1.2	.056 ±.016	<74	<.07	<.0035	<3.2	7.5 ±.7	<.029	<.024	<.05		460±110

- (1) 464 minute gamma-ray count about 70 days after the end of the long irradiation.
- (2) 60 minute gamma-ray count about 24 days after the end of the long irradiation.
- (3) 754 minute gamma-ray count about 71 days after the end of the long irradiation.
- (4) Only estimates were obtained for the measurements made with the 128 cc detector as flux monitors were used for all elements. Uncertainties (due to calibration) of ~10% are possible. The listed errors are 1σ values of the counting error and would be the precision if a multielement standard were used.
- (5) Abundances have been modified to reflect an estimated .03-.04 ppm Co contribution from the Al wrapping foil.
- (6) Estimated contaminants from the Al wrapping foil of ~.001±.004 ppm for Ta and ~.01 ppm for Sb have not been removed. Accurate abundances of these elements can be obtained by removing the Al foil from each of the pills and measuring its gamma-ray spectrum.
- (7) The ⁸⁶Rb radiation is also produced by the reaction ⁸⁶Sr (n,p) ⁸⁶Rb. The Sr contribution has not been removed. Sea water and Sr probably account for all the ⁸⁶Rb detected in P7 and very little of that detected in FD.

Table VI

Abundance Limits on elements that were not detected in any sample

Sample	Cu(ppm)	Dy(ppm)	In(ppm)	La(ppm)	Lu(ppm)	Mg(%)	Sn(ppm)	Ti(%)
P7	<70	<.8	<.5	<5	<.022	<3.4	<44	<.10
P5	<95	<1.2	<1.0	<5	<.019	<6	<40	<.22
P3	<105	<1.0	<.9	<3.6	<.033	<5	<36	<.36
NR	<69	<.5	<.33	<3.0	<.04	<2.7	<67	<.11
C	<73	<.6	<.4	<7	<.037	<3.9	<58	<.17
FD	<40	<.26	<.28	<1.8	<.019	<1.8	<64	<.07
Cell.	<3.6	<.05	<.011	<.25	<.0022	<.08	<3.6	<.010
Al	-	-	-	<.08	<.0018	-	<4	-

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