Multielement Analysis of Deep-Sea Sediments by Photon Activation

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A nondestructive photon activation with 30 MeV bremsstrahlung has been applied to the multielement determination in the pelagic sediments in a region of the Pacific Ocean. The abundances for 6 major and 10 trace elements were measured in several deep-sea floors and the core samples, discussion being given on the results. Determination of trace elements such as Cr, Co, Ni, and Sr is valuable because of their geochemical significance.

The essential problem involved in the geochemistry of deep-sea sediments is to establish the distribution and original source of a number of their elements. Although research has been performed for this purpose, it seems to be insufficient. It is desirable to develop a method by which it is possible to analyze samples for wide spectra of elements.

The importance of photon activation, mainly with 30 MeV bremsstrahlung, as a nondestructive multielement analytical technique has been stressed for several years. A number of papers have been presented describing methods and application, ranging from the measurements of a number of the elements in round-robin materials[1-3] to the environmental pollution research.[4-7] The availability of a comprehensive body of basic reference data in the form of photonuclear reaction yields,[8-10] sensitivities,[9,10] and gamma rays emitted from numerous products[11] pertaining to 30 MeV bremsstrahlung activation with a linear electron accelerator (Tohoku University) has made the method feasible for further application to a wide variety of materials. This paper deals with the nondestructive determination for several major and trace elements present in oceanographic samples, including several pelagic deep-sea floor sediments and selected core samples of the Pacific Ocean, obtained by the Geophysical and Geological Research Project planned and carried out under the auspices of the Ocean Research Institute, the University of Tokyo (1973). The methodology of photon activation analysis in geochemical application has been reported.[1,2,10] We will descibe some additional comments in individual determinations and discuss the results.

Experimental

Materials.   The study was carried out on the pelagic sediments collected in a region of the Western Equatorial Pacific. The sampling sites, depths and core lengths are given in Table 1. The deep-sea floor sediments which were dredged were dark brown and fairly homogeneous. The core samples consist of piston cores, about 10 m long. The core column was cut into segments each 1 cm thick along its entire length, and selected specimens were subjected to analyses. Age was determined on the basis of calcareous organisms and found to be *ca.* 2 million years at the bottom of the 10-m core.[12] Each sample was dried at 70 °C for 24 h, crushed and mixed in an agate mortar to attain homogeneity. 300 mg of the dried

TABLE 1.   DEEP-SEA SEDIMENTS ANALYZED

Floor samples

Sample	Location	Depth (m)
F-1	North Philippine Basin Lat. 21°55.8′N Long. 133°02.8′E— Lat. 21°51.5′N Long. 133°00.9′E	5618—5622
F-2	North Fiji Basin Lat. 08°00.3′S Long. 172°49.4′E— Lat. 07°58.3′S Long. 172°44.9′E	5350—5375
F-3	Central Basin fault in Philippine Basin Lat. 16°09.1′N Long. 130°33.4′E— Lat. 16°15.0′N Long. 130°36.6′E	6500—6200
F-4	Mariana Basin Lat. 13°44.0′N Long. 151°30.5′E	5600
F-5	Mariana Basin Lat. 11°01.6′N Long. 149°53.6′E	6030
F-6	Mariana Basin Lat. 10°11.7′N Long. 149°16.7′E	6000
F-7	North Fiji Basin Lat. 15°00.0′S Long. 172°22.5′E	4150

Core samples

Sample	Location	Depth (m)	Core length (cm)
C-1	Mariana Basin Lat. 12°37.8′N Long. 151°30.5′E	5920	668
C-2	Melanesia Basin Lat. 02°41.3′N Long. 164°50.2′E	4170	1115
C-3	Melanesia Basin Lat. 01°33.2′S Long. 167°38.6′E	4000	1163

sample was wrapped in a small piece of aluminum foil and then compacted into a disc, diam. 9 mm, height 4 mm. The JB-1 basalt was used as a multielement comparative standard, because of the well-characterized nature of the matrix and the known elemental composition. The abundances of the elements of interest were taken from the data compiled by Ando *et al.*[13] An amount weighing 300 mg was wrapped in a small piece of aluminum foil and made into a diam. 9 mm disc. To assess the magnitude of interference, foils of iron with diam. 9 mm were made from a thin sheet of pure iron, about 10 μm thick, with a chemical purity of 99.99%. A unit of materials to be irradiated consists of a sample disc, two standard discs and four iron foils. They were stacked in a silica tube with the standard discs placed on both sides of the sample and the iron foils between them and at the front and back of the unit for simultaneous irradiation. The

photon flux gradient along the length of this unit was about 10%.

Irradiation.   Bremsstrahlung irradiation was carried out with a linear electron accelerator. Typically, a 70 μA beam of 30-MeV electrons was made to impinge on a 2 mm thick platinum converter. Details involving irradiation assembly and converter-sample configuration have been reported.[8-10] After irradiation for 4—5 h, the wrapping foil was rejected and the content of each sample was again wrapped in fresh aluminum foil for gamma-counting.

Counting and Abundance Determination. The counting equipment consists of a 68 cm³ Ge(Li) detector, Canberra Model 7200-7600-1423. Its output was coupled to a 4096-channel pulse height analyzer (Toshiba Electric Co., Ltd.). Details involving counting, characterization of gamma rays and quantitative treatment of the spectrum data were essentially the same as reported.[10] A mean specific activity for any specified gamma ray in terms of the peak areas from the standard discs on both sides was used for calculating the abundance of the element in question. Because of the adverse nuclear properties, aluminum was determined separately by means of spectrophotometric measurement followed by solvent extraction with 8-hydroxyquinoline.[14]

Results and Discussion

As in the multielement analysis of standard rocks,[1,2] 6 major and 10 trace elements were subjected to determination. Pertinent nuclear data for the reaction products are given in Table 2 together with the optimal time intervals for measurement after irradiation and practical detection limits. The practical detection limits were estimated from the spectral data of the JB-1 rocks. They are the amounts of the elements giving a full-energy peak area corresponding to three times the standard deviation of the area under the peak of interest,

with 5 h irradiation time with a 70 μA beam of 30 MeV electrons, counting at optimal time intervals given in Table 2. We see that major elements (Ca—Ti) in crustal materials can not be highly activated. This turns out to be advantageous over competing methods when simultaneous multielement determination is the goal. In thermal neutron activation analysis, the full capability of the method might be restricted by high levels of interference, such as that from ²⁴Na. Such difficulty is not inherent in the present method. Nondestructive analysis of several specific elements such as Nb, Y, and Zr, not readily determined by thermal neutron activation analysis, is significant in geochemical substances. Comments are given on the individual determinations in the following.

The results for calcium are the average values obtained for each of the 374 and 617 keV peaks of ⁴³K, and the 1298 keV peak of ⁴⁷Ca. When the values obtained from these three different peaks were averaged, the relative deviations from the means were within ±2% for all of the samples studied. The samples were relatively high in titanium. For titanium, therefore, the 1121 keV peak of 83.9 d ⁴⁶Sc was given prior consideration, because of the favorable peak-to-background ratios obtained at longer decay times. For the sake of confirmation, the gamma rays from ⁴⁷Sc and ⁴⁸Sc were used.

The inter-element interference problems can be found in Table 3 in which major competing reactions yielding nuclides identical to those used for abundance determinations are given. In some cases, neutron-induced reactions other than the photonuclear processes are the major sources of interferences. Degrees of their contribution were determined from relative probability of forming pertinent nuclide through different reaction

TABLE 2.   PERTINENT NUCLEAR DATA AND DETECTABILITY OF THE PRODUCTS

Element	Process	Product nuclide	Half-life	γ-Ray used for determination (keV)	Other γ-rays observed	Suitable decay time for measurement	Detection limit (μg)
Ca	(γ,p)	⁴³K	22.4 h	374	219, 394, 593,	1—2 d	123
				617	990, 1021,	1—2 d	200
					1524 (⁴²K)		
	(γ,n)	⁴⁷Ca	4.53 d	1298	160 (⁴⁷Sc), 488, 808	10—15 d	470
Fe	(γ,p)	⁵⁶Mn	2.576 h	847	1811, 2110	2—5 h	400
Mg	(γ,p)	²⁴Na	15.0 h	1368	1732 (DE),	1—2 d	37
					2243 (SE), 2754		
Mn	(γ,n)	⁵⁴Mn	303 d	835		>10 d	5.2
Na	(γ,n)	²²Na	2.60 y	1275	1786 (sum)	>10 d	82
Ti	(γ,p)	⁴⁶Sc	83.9 d	1121	889, 160 (⁴⁷Sc),	>10 d	32
					893, 1040, 1314 (⁴⁸Sc)		
Ba	(γ,n)+(γ,γ')	¹³⁵ᵐBa	28.7 h	268		1—2 d	37
Ce	(γ,n)	¹³⁹Ce	140 d	166	145 (¹⁴¹Ce)	30—40 d	1.0
Co	(γ,n)	⁵⁸Co	71.3 d	811		30—40 d	2.1
Cr	(γ,n)	⁵¹Cr	27.8 d	319		10—15 d	13
Nb	(γ,n)	⁹²ᵐNb	10.16 d	934		10—15 d	0.5
Ni	(γ,n)	⁵⁷Ni	36.0 h	1378	1757, 1918	1—2 d	19
Rb	(γ,n)	⁸⁴Rb	33.0 d	881	1076, 1897	10—15 d	2.6
Sr	(γ,n)	⁸⁷ᵐSr	2.83 h	388		2—5 h	3.9
Y	(γ,n)	⁸⁸Y	108 d	1836	898	>10 d	1.0
Zr	(γ,n)	⁸⁹Zr	78.4 h	910		2—3 d	1.1

TABLE 3.   MAJOR INTERFERENCES IN MULTIELEMENT PHOTON ACTIVATION ANALYSIS

Element to be detected	Competing reaction	Effect of interference	Interfering contribution (%)		
			JB-1	Sediment	Earth's crust
Ca	$^{45}Sc(\gamma, 2p)^{43}K$	$Sc/Ca=7.2\times10^1$	6.0×10^{-4}	neg.	7.3×10^{-4}
	$^{49}Ti(\gamma, 2p)^{47}Ca$	$(Ti/Ca=4\times10^1)$	(0.3)	neg.	(0.3)
Fe	$^{55}Mn(n,\gamma)^{56}Mn$	$Mn/Fe=2.8$	0.66	1.6—8.3	0.60
Mg	$^{27}Al(n,\alpha)^{24}Na$	$Al/Mg=206$	0.79	0.7—1.7	2.0
	$^{23}Na(n,\gamma)^{24}Na$	$Na/Mg=225$	0.20	0.4—1.4	0.53
Mn	$^{56}Fe(\gamma,pn)^{54}Mn$	$Fe/Mn=1.2\times10^2$	31	3—17	33
Na	$^{24}Mg(\gamma,pn)^{22}Na$	$Mg/Na=7.7\times10^1$	2.8	0.4—1.5	1.1
	$^{27}Al(\gamma,\alpha n)^{22}Na$	$Al/Na=1.3\times10^3$	0.28	0.06—0.2	0.26
Ti	$^{51}V(\gamma,\alpha n)^{46}Sc$	$V/Ti=5.7\times10^2$	4.6×10^{-3}	neg.	0.004
Ba	$^{140}Ce(\gamma,\alpha n)^{135m}Ba$	$(Ce/Ba=9\times10^2)$	(<0.02)	neg.	(<0.02)
Ce	$^{141}Pr(\gamma,pn)^{139}Ce$	$(Pr/Ce=2\times10^3)$	—	neg.	(0.007)
Co	$^{60}Ni(\gamma,pn)^{58}Co$	$Ni/Co=7.2\times10^1$	4.6	1.3—8.4	4.0
Cr	$^{56}Fe(\gamma,\alpha n)^{51}Cr$	$Fe/Cr=1.6\times10^4$	0.96	2.2—10.2	3.4
Nb	$^{94}Mo(\gamma,pn)^{92m}Nb$	$Mo/Nb=1.7\times10^3$	0.07	neg.	4.4×10^{-3}
Ni	None				
Rb	$^{86}Sr(\gamma,pn)^{84}Rb$	$Sr/Rb=1.1\times10^4$	0.10	0.005—0.9	0.038
Sr	$^{89}Y(\gamma,pn)^{87m}Sr$	$Y/Sr=5.9\times10^2$	0.01	0.002—0.08	0.015
Y	$^{90}Zr(\gamma,pn)^{88}Y$	$Zr/Y=4.3\times10^2$	1.4	0.2—1.2	1.2
Zr	$^{94}Mo(\gamma,\alpha n)^{89}Zr$	$Mo/Zr=2.3\times10^4$	7×10^{-4}	neg.	4×10^{-5}

paths. The effects of interferences were expressed as a ratio of the weights of the elements to produce same amounts of nuclide under consideration. To evaluate the effects, the yield data for the reactions of various types obtained on irradiating a series of individual elements under comparable conditions to those used for samples[9] were used. The values in parentheses are not experimentally obtained, but estimated from the yield data as a function of atomic number.[9] Interfering contributions thus evaluated are for several matrices. Values for the sediments are interfering contributions for the samples used in this work. In order to provide information on geochemical application of this method, corrections necessary for the average composition of the earth's crust were also calculated in Table 3. For this purpose, the abundance data compiled by Turekian and Wedepohl[15] were used.

A severe interference problem is the $^{56}Fe(\gamma,pn)^{54}Mn$ contribution to the total ^{54}Mn activity in the manganese determination. Corrections required for the samples were made by using the production rate ratio, $^{54}Mn/$ ^{56}Mn, found in the irradiated iron foils.[1,2] However, it was found that the ratio varies depending on the converter-material configuration in an irradiation system. An increase of 3% of the ratio obtained in the front foil was found in the back foil in the material unit. In such cases where the interfering contributions turn out to be very large, careful corrections should be made by using monitor foils irradiated under identical conditions to those used for samples. The $^{27}Al(n,\alpha)^{24}Na$ contribution to the total ^{24}Na activity was estimated from the aluminum values determined spectrophotometrically. Corrections required for the samples studied were less than 2%. Thus this source of interference may not be serious.

All elemental abundances are given in Tables 4 and 5. Reproducibility and reliability of the method have been demonstrated by analyzing a series of standard

rocks of various types.[1,2] The abundance values obtained were reproducible: The average relative deviations for all the elements determined, based on the duplicate samples, were within 4%. Agreement of the results with published data was excellent. Although no replicate analyses were made on each of the samples, we estimate that the overall uncertainties associated with individual determinations for all of the elements studied are within ±10%.

The sodium values will be high to some extent because of sea water which was trapped within the accumulating sediments. The floor samples F-6 and F-7 are very high in calcium. The marked difference coincides with a

TABLE 4.   ELEMETAL ABUNDANCES OF DEEP-SEA FLOOR SEDIMENTS

Sample	Major element (%)						
	Ca	Fe	Mg	Mn	Na	Ti	Al
F-1	1.04	4.97	1.74	0.98	3.27	0.34	6.30
F-2	1.80	7.12	2.14	1.35	4.96	0.46	5.47
F-3	1.03	7.26	2.04	1.85	3.01	0.50	7.16
F-4	1.17	5.89	1.92	0.55	3.02	0.52	6.86
F-5	1.25	5.60	2.02	0.56	3.74	0.53	6.29
F-6	21.2	3.56	2.18	0.31	1.89	0.42	3.20
F-7	27.6	3.53	1.04	0.36	2.26	0.17	1.83

Sample	Trace element (ppm)									
	Ba	Ce	Co	Cr	Nb	Ni	Rb	Sr	Y	Zr
F-1	425	79	56	60	6.4	85	273	182	31	166
F-2	626	64	88	39	5.2	188	58	243	78	125
F-3	223	99	146	86	8.9	178	180	198	44	143
F-4	410	102	106	87	9.2	176	359	178	76	175
F-5	376	90	91	73	8.0	166	245	185	72	167
F-6	220	40	47	75	5.4	121	114	699	49	108
F-7	314	17	18	29	1.5	17	58	1218	28	29

TABLE 5. ELEMENTAL ABUNDANCES OF CORE SAMPLES

Sample	Depth in core (cm)	Major element (%)						Trace element (ppm)									
		Ca	Fe	Mg	Mn	Na	Ti	Ba	Ce	Co	Cr	Nb	Ni	Rb	Sr	Y	Zr
C-1	Top of core	0.87	7.15	2.08	1.54	3.04	0.58	332	109	115	84	6.4	181	208	197	80	195
	Bottom of core (668)	0.86	7.03	2.15	1.91	3.37	0.61	479	87	129	70	8.4	306	125	210	101	193
C-2	9—10	34.3	0.92	0.44	0.06_3	1.19	0.09_6	347	7.6	12	26	1.2	31	14	884	18	21
	205—206	35.4	1.04	0.40	0.14	1.08	0.12	225	7.3	11	22	0.8	41	11	1000	17	20
	405—406	33.2	1.20	0.50	0.07_1	1.19	0.12	623	11	8.5	26	1.1	27	16	1600	23	29
	605—606	21.8	2.43	0.84	0.10	1.60	0.20	611	23	24	50	2.2	64	26	1880	42	56
	805—806	27.4	1.84	0.72	0.08_9	1.57	0.15	547	16	19	29	1.8	46	22	1490	35	41
	1005—1006	26.3	1.35	0.50	0.08_0	1.42	0.12	432	12	8.8	20	1.2	25	17	1340	29	31
	1105—1106	29.4	1.59	0.60	0.15	1.60	0.12	501	8.5	22	27	1.4	45	20	1390	34	38
C-3	105—106	35.3	0.77	0.35	0.16	1.17	0.04_1	328	4.4	7.4	11	0.7	49	6	1380	18	14
	205—206	29.8	1.08	0.38	0.07_8	1.12	0.08_5	330	7.6	7.4	14	0.4	17	8	1580	22	20
	305—306	33.4	1.22	0.50	0.13	1.32	0.10	751	8.8	12	19	0.4	39	12	1520	31	27
	405—406	33.0	0.82	0.34	0.06_1	0.98	0.06_5	371	6.7	6.8	9.1	0.6	18	8	2040	20	17
	605—606	34.2	1.12	0.44	0.06_9	1.12	0.10	399	7.8	7.5	17	0.8	23	9	1970	24	22
	805—806	34.1	0.90	0.41	0.07_0	1.17	0.08_1	419	7.1	9.1	11	0.8	18	6	1560	27	19
	905—906	34.1	0.87	0.38	0.08_5	1.08	0.05_7	505	7.1	11	9.5	0.2	19	5	1470	25	16
	1055—1056	32.0	1.24	0.46	0.12	1.27	0.06_9	739	8.3	13	21	0.7	33	10	1310	31	20
	Bottom of core (1163)	31.8	1.02	0.45	0.09_9	1.26	0.13	712	7.8	14	8.0	0.9	29	11	1380	20	23

considerable amount of calcareous shell materials found in them (Table 4).[12] These two samples were the carbonate type sediments and could be distinguished visually from the other clay type sediments. The carbonate compensation depth occurs at 3500 m in the Pacific Ocean.[16] Since the samples were collected at depths below it, the high contents of calcium can not be attributed to descent from the overlying water. Major parts of calcium in these samples may thus be due to calcareous organisms originating in the seamount which is located near the sampling sites. The deep-sea sediment of the carbonate type has only a relatively low content of most of trace elements, while the clays are generally rich in trace elements as compared to the carbonates.[16] The results in Table 4 show a typical pattern of this sort in the elemental composition. Strontium is an exception to this category. A similar exception has also been reported.[15] Samples F-3, F-4, and F-5 seem to be high in some trace elements such as Co, Cr, and Ni.

Of the core samples tested, C-1 sample contained less calcium at both the top and bottom of the core column. The elemental composition of this core can be related to the clay type sediments. In contrast, the other two core samples are highly calcareous and are characterized by their low contents of other major and trace elements except strontium. Each core sample is homogeneous in the elemental composition along the core column. No direct evidence of the early diagenesis or post-depositional migration of the elements has been obtained.

In conclusion, photon activation analysis with 30 MeV bremsstrahlung provides useful information on the elemental distribution in deep-sea sediments. The technique is nondestructive and can provide reliable abundance data for at least 6 major and 10 trace elements of geochemical significance.

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