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SEDIMENTS WITH CALIFORNIUM-252

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TRENDS IN ACTIVATION ANALYSIS

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SEDIMENTS WITH CALIFORNIUM-252

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ABSTRACT

A seabed nuclear probe has been developed which permits the measurement of up to 33 elements at the parts per thousand to parts per million levels in continental shelf areas. The probe consists of a neutron irradiation source, californium-252, which neutron activates the elements in the minerals of interest. These resulting radioactive elements emit characteristic gamma radiation which is analyzed in situ in 2- to 10-minute counting intervals with a Ge(Li) detector system. Details of the irradiation source, the Ge(Li) detector, and spectra taken in situ in a marine environment are discussed with respect to the detection of the minerals at concentrations of economic interest.

INTRODUCTION

The exploitation of many seabed minerals has in the past been impeded by our limited knowledge of the locations and extent of seabed mineral deposits. Practical methods of surveying for mineral deposits and assaying their value have not been available. In the past, ocean floor samples have been obtained by coring or other means and then taken to a shore-based laboratory for elemental analyses. More recently, with the development of practical X-ray fluorescence spectrometric analysis, shipboard analyses have begun to be employed. However, because of the low energy of the fluorescent X-rays, it has been necessary to dry and reproducibly mount the samples for analysis. The combination of the time requirements for sampling and subsequent shipboard sample preparation is as yet a substantial deterrent to extensive sea floor mapping by this method.

With the advent of the man-made isotope, californium-252, which decays by spontaneous fission with associated neutron emission, a new and powerful technology became available⁽¹⁾ for ocean floor

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mineral analysis. Californium-252 emits 2.22×10^9 neutrons per second per milligram and has a reasonable physical half-life (2.55 years). It has been studied for its applicability in a variety of neutron irradiation applications, including the analysis of the elemental content of various minerals using both prompt and delayed gamma rays following neutron capture by the elements. (2-6) In recent studies at our laboratory, it has been demonstrated that the elements in various mineral deposits and commercial grade ores, at levels of economic interest, can be readily identified by ^{252}Cf neutron activation analysis procedures. (5) Two possible applications for ^{252}Cf seabed mineral analysis on a survey vessel have been investigated. The first involves the use of a shipboard laboratory in which the ^{252}Cf source and the associated Ge(Li) detector system are employed on dredged or cored specimens to determine the elemental composition. (2) The second method involves the placement of the neutron source and detector system on the ocean floor for the rapid in situ analysis of the surface layer of the ocean floor. In this latter approach which is reported here, a study is being conducted to determine the measurement sensitivity for some 33 elements in matrices of varying density, water content, and elemental composition. The vertical and horizontal neutron fluxes from a ^{252}Cf source were mapped in fresh water and sea water saturated sediments. These neutron flux and shape characteristics (5), together with the determined efficiency for a Ge(Li) diode capable of undersea operation, served as a basis for the design of an undersea nuclear seabed probe which is discussed in this report.

INSTRUMENTATION

The seabed probe system includes a ^{252}Cf neutron source of up to 1 mg intensity, a 15 percent efficiency Ge(Li) diode as the detector, and a nuclear data 4410 analyzer which serves as the central processing unit for data collection and analysis. The system could potentially use a 20-fold smaller ^{252}Cf source in a sub-critical assembly with its neutron multiplication resulting in a 10- to 40-fold increase in effective source size. (7)

The Ge(Li) detector system, designed to operate at depths to 1000 feet, is cooled with a solid cryogen, a freon-propane mixture which permits up to 40 hours of continuous subsurface operation. The multiconductor cable connecting the seabed probe to the surface vehicle is a 19 conductor, shielded cable of "block construction" (Hydro Products) which transmits the detector signal, video signal, control signals and also preamplifier power and AC power for the light and hydraulic pump. A voltage converter is located along with the preamplifier in the Ge(Li) detector pressure housing. This limits the number of DC power lines required between the detector pressure housing and the surface vessel. The Ge(Li) detector through its 1000 feet cable length has a resolution of better than 3.0 KeV at 1.33 MeV where an amplifier which uses pole zero cancellation is employed.

The central processing unit controls all data collection, display functions and data processing. Two magnetic tape cassettes are used to store spectra for historical record and possible later investigation with a sophisticated laboratory computer. A paper tape system provides backup storage in the event the two cassette transports malfunction. Using this programmed system for pulse

height analysis allows quantitative analysis to be automated so that the system can be utilized by a technician unskilled in nuclear gamma-ray analysis. The set of basic software programs allows the analysis of S, Ca, Cl, Mo, Mg, Al, F, K, Na, In, Ga, Nd, Ni, Co, Cu, Ba, Sn, V, I, Eu, Ti, Nb, W, Sb, Dy, Ag, Os, Br, Rh, Pt, La, Ir and As in the seabed where their concentrations are adequate.

As is shown in Figure 1, the detector-irradiator unit of the seabed probe assembly is a triangular-shaped structure (includes angle at axis of 57°) with 2 meters long legs (distance from axle to detector-irradiator). The outside dimensions of both the irradiator and detector housing are 24 cm diameter by 40 cm long. The irradiator contains the ^{252}Cf source near the bottom and is filled with paraffin which serves as a moderator. This assembly is shifted between irradiation and detection positions by a hydraulically driven rotary actuator. Power is supplied by an electrically driven hydraulic pump located in a pressure housing on the probe. The reversible pump controls the positioning of the irradiator and detector. In the detection mode of operation, the irradiator assembly is moved beyond its normal 57° angle by a hydraulically driven rod energized from the same hydraulic pump. Separation at its extreme extension is 3 meters away from the detector. The detector-irradiator assembly is protected from an irregular sea floor by a lucite trough extending 7.5 cm below the bottom of the framework. A television monitor and a light assembly are mounted on the probe structure in a manner such that the site can be observed by the operator. The video camera has a capability for remote focusing from 7.5 cm to infinity with a field of view 1 by 1.3 meters at the 2 meter focusing distance which is employed. A 4000 candlepower thallium iodide light assembly furnishes the illumination at depth.

OPERATIONAL CRITERIA

The thermal neutron flux that develops in a substrate below the ^{252}Cf source has been characterized for several types of natural materials. In the irradiation position, a 1 mg ^{252}Cf source gives a maximum flux in the substrate of $1.5 \times 10^6 \text{ on}^1(\text{th}) \cdot \text{cm}^{-2} \cdot \text{sec}^{-1}$ with a fast to thermal ratio of 0.11. This flux is obtainable in the underlying sea floor at the distance of closest approach which is 7.2 cm. The average flux is about $0.75 \times 10^6 \text{ on}^1(\text{th}) \cdot \text{cm}^{-2} \cdot \text{sec}^{-1}$ through a 20 cm hemisphere and $0.5 \times 10^6 \text{ on}^1(\text{th}) \cdot \text{cm}^{-2} \cdot \text{sec}^{-1}$ through a 35 cm diameter hemisphere. Of course, this does not totally describe the efficiency for detection of an element since the gamma rays of interest vary in energy from a few hundred to a few thousand KeV and thus have a definite range through the sediment layers. Irradiation of the ocean floor with a ^{252}Cf source in seawater results in a 30% lowering of the neutron flux over that observed in fresh water. Studies of the possible effect of various overlying sediment layers on the detection efficiency of the minerals of interest were conducted. Californium-252 was used to irradiate simulated mineral specimens. These specimens were prepared by placing known amounts of various elements in dunite and then covering them with a 2.5 cm layer of dunite-water-indium, water, dunite, dunite-cadmium, dunite-iron, dunite-iron-water, dunite-iron-water-cadmium, and dunite-iron-water-indium. As is shown in Figure 2, the absorption of neutrons by the addition of 1% cadmium to the 2.5 cm surface layer above the specimen being analyzed reduced the

resulting detection efficiency about fourfold in minerals of 1.8 gm/cc density. If the element of interest were in a matrix of 4.0 gm/cc, the detection efficiency would be reduced an additional two-fold. Methods for determining the density using photons scattered by the sediments have been developed by other investigators⁽⁸⁾, and are being considered for utilization on the seabed probe. The density determination will allow data correction for density variations.

SEABED PROBE UTILIZATION

In order to determine the detection sensitivity of the in situ seabed probe for elements in the minerals of interest, samples containing known quantities of minerals or specific elements were placed in a simulated sea floor assembly^(2,5) or on the tideland ocean bottom. These specimens were neutron irradiated and the resultant gamma-rays analyzed. The detection sensitivity for these elements, as calculated for a 1 mg ^{252}Cf source is summarized in Table I. These values are for a two minute irradiation, followed by a one-minute decay and a two-minute analysis with the 15% efficiency Ge(Li) gamma-ray spectrometer. These experiments have shown that the majority of the induced radioactivity as seen by the nuclear probe assembly is contained in a 15 cm radius hemisphere of the ocean floor. For example, 90 percent of the 1.811 MeV gamma rays as well as 95 percent of the 0.848 MeV gamma rays from ^{56}Mn are emitted from this volume.

The gamma-ray spectra of representative ocean sediments are shown in Figures 3 and 4 to illustrate the quality and type of information developed by the in situ seabed probe. The photopeaks are due to gamma rays emitted from the radionuclides formed by activation of the parent elements. The energies of the gamma rays are given in thousands of electron volts (keV). The photopeak areas are proportional to the concentrations of the elements in the seabed and thus with the appropriate correction factors allow a digital printout of the seabed elemental concentrations.

DISCUSSIONS

Currently, major interest centers on the economic potential of manganese oxide nodules and metal bearing muds. It has been estimated that 1.7 trillion tons of nodules exist on the seabed containing 400 billion tons of manganese, 16.4 billion tons of nickel, 8.8 billion tons of copper and 9.8 billion tons of cobalt.⁽⁹⁾ Most of the elements in manganese nodules are easily measurable by the in situ neutron activation analysis technique. The elements Mg, Al, Co, Cu, Sr and Ba have detection sensitivities of 0.1% using a 1 mg ^{252}Cf source, a 15% efficiency diode, a 2-minute irradiation and a 2-minute analysis, yet the actual concentrations in nodules are 2- to 30-fold greater. Manganese, normally about 25%, can be detected at 0.01%. Although nickel cannot be analyzed directly, the ratios of the minor elements as well as the copper concentration provide information as to the nickel content of the nodules. Ocean sediments that contain Na, Fe, La, Sm, Br, Co, Sc, Cr, Eu, Hg, Th, Tb, Ta, Cs, Sn, Sb and Zn do not mask detection of some of the more important elements such as Mn, Co and Cu in the nodule deposits. Although seawater contains about 3.6% NaCl, there were no significant interferences from neutron induced ^{24}Na and ^{38}Cl in the seawater or the sediment interstitial waters (see Figure 3).

Simulated seabed minerals were prepared by solidifying the sample with cement for underwater calibrations. Figure 4 shows the spectra of one of these concrete specimens containing 400 ppm silver. The silver can be measured at this concentration to an accuracy of $\pm 10\%$. The other major induced radionuclides in the matrix, ^{56}Mn , ^{52}V and ^{28}Al , provide a ready means for the measurement of their parent stable isotopes.

The probe also has a very important potential for measuring an added tracer in studies of continental shelf sand or sediment drift. Sea sands were studied for their elemental content to determine which elements might interfere with the in situ activation analysis of inert tracers which might be added to study sand movement in a littoral system or through a continental shelf region. The rare earths La, Eu, Sm and Ba were detected with long irradiations, while ^{165}Dy (74 sec) from natural Dy could not be detected in the sand during the short irradiation and counting procedures which would be practical for the ocean floor tracer studies. Thus, Dy could be added to sand as a rare earth ore such as gadolinite and the seabed probe used to activate and follow its movement in tideland or deeper ocean areas. If 180 kgs of Dy were distributed over a square kilometer of ocean floor to a depth of 1 cm, it could be measured at 2 kg/km^2 , 3-fold concentration above the normal Dy content.

As is shown in Table II, many minerals have already been found on the seabed, and some are currently being exploited or technology for their exploration developed. As indicated in the table, most of the minerals have the necessary characteristics to allow their detection and mapping with the seabed nuclear probe. In general, the concentrations of elements which must be present before economic mining is practical are well in excess of their detection range with the nuclear probe system.

While there are a variety of parameters affecting the accuracy of in situ analysis, they can be adequately accounted for through use of the appropriate factors discussed in this paper. Compared with any other in situ method, this approach of sea floor neutron activation with a ^{252}Cf source, followed by in situ analysis of the resulting photon radiation apparently provides a superior approach for establishing the elemental content of ocean floors, the floors of lakes and, perhaps, terrestrial areas and planetary surfaces.

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TABLE I. SENSITIVITY FOR THE MEASUREMENT OF
ELEMENTS IN SEABED⁽¹⁾

<u>Element</u>	<u>Detectable Concentration</u>	<u>Element</u>	<u>Detectable Concentration</u>
Aluminum	0.1-1%	Magnesium	0.1-1%
Antimony	1-10%	Manganese	0.01-0.1%
Barium	0.1-1%	Mercury	1-10%
Cadmium	1-10%	Molybdenum	0.01-0.1%
Chromium	4-40%*	Nickel	1-10%
Cobalt	0.1-1%	Niobium	1-10%
Copper	0.1-1%	Scandium	1-10 ppm
Dysprosium	10-100 ppm	Selenium	1-10 ppm
Fluorine	0.01-0.1%	Silver	10-100 ppm
Gold	10-100 ppm*	Strontium	0.1-1%
Hafnium	1-10 ppm	Tin	3%
Indium	1-10 ppm	Titanium	10-100 ppm
Iron	50-100%*	Tungsten	0.1-1%
Lanthanum	0.01-0.1%	Vanadium	10-100 ppm

(1) Based on 2 minute irradiation with 1 mg of Cf-252 and 2 minute count with a 15% efficiency Ge(Li) detector.

* Sensitivity increases almost linearly with irradiation and counting time.

TABLE II - HARD MINERALS FOUND IN THE SEABED

Mineral	Composition	Neutron Activated Element	Detectable Concentration	Nominal Concentration Present
*Aragonite, Lime Sand	CaCO_3	----	----	80% CaCO_3
*Barite	BaSO_4	Ba	0.1-1%	60-95%
Bauxite	$\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$	Al	0.1-1%	21-30%
*Cassiterite	SnO_2	Sn	3%	0.01-1.5%
Chromite	$\text{FeO} \cdot \text{Cr}_2\text{O}_3$	Cr	4-40%	
Diamonds	C	----		
Glauconite	Fe,K Hydrous Silicate			1% Fe
Gold	Au	Au	10-100 ppm 0.3-3 tr oz/ton	0.2-1 oz/ton (lode)
Ilmenite Iron Sand	FeTiO_3	Fe Ti	10-100 ppm	1% min. mineable
Leucoxene (titanite)	CaTiSiO_5	Ti	10-100 ppm	1% min. mineable
Magnetite Iron Sand	Fe_3O_4			3%
*Manganese Nodules	(Mn, Cu, Ni, Co)	Mn Cu Co Ni	0.01-1% 0.1-1% 0.1-1% 1-10%	10-25% Mn 0.2-0.75% Cu 0.2-1.1% Co 0.15-1.1% Ni
Monazite	(Ce, La) PO_4	La Th	1-10 ppm	0.05-1%
*Metal Bearing Mud	(Zn, Cu, Pb)	Zn Cu	0.1-1%	5% Zn 5% Cu
Phosphorite Nodules	29% P_2O_5	U	----	
Rutile Sand	TiO_2	Ti	10-100 ppm	5% Ti, 0.1% TiO_2
Scheelite	CaWO_4	W (a)	0.1-1%	0.24-1.3% W
Sulfur	S	Se	1-10 ppm	
Wolframite	(Fe, Mn) WO_4	W Mn	0.1-1% 0.01-1%	0.24-1.3% W
Zircon Sand	ZrSiO_4	Hf	1-10 ppm	10-40 ppm Hf

(a) Molybdenum is usually present (up to 8%) in Scheelite (Dana) and possibly could be detected.

* Seabed minerals currently being exploited or being actively developed.

FIGURE 1. IN SITU OCEAN FLOOR MINERAL ANALYZER SYSTEM

FIGURE 2.

RELATIVE GAMMA-RAY DETECTION EFFICIENCY OF A SIMULATED OCEAN MINERAL OF 1.8 gm/cc DENSITY COVERED BY LAYERS OF VARYING DENSITY AND NEUTRON ABSORPTION CHARACTERISTICS

GAMMA RAY SPECTRA OF NEUTRON ACTIVATED SEDIMENT

GAMMA RAY SPECTRA OF NEUTRON ACTIVATED SEDIMENT, CONTAINING 400 ppm SILVER