Selective Separation of Molybdenum as Volatile Halides from Deep-Sea Ferromanganese Nodules

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Abstract

A simple and rapid method for a selective separation of Mo from deep-sea ferromanganese nodules is described. Sulfation of the ground nodule material with a gas mixture of SO_2 and O_2 at elevated temperatures results in the sublimation of the Mo therein. The sublimates are mainly composed of pure $MoCl_4$ and MoO_2Cl_2 which are readily soluble in water. Addition of alkali metal halides to the nodules prior to sulfation increases the Mo recovery to over 95 % in 30-min sulfation at 400 to 500 °C. The sulfation process, developed primarily for the selective separation of Mn, Cu, Ni, and Co, can be effectively used for Mo separation without complication.

INTRODUCTION

Ferromanganese nodules located at the ocean bottom are considered to be a virtually inexhaustible mineral reservoir containing a large number of economically important metals. Studies have been focused on the recovery of valuable metals and divided mainly into two categories: hydrometallurgical processes which include leaching the nodules with acids, ammonia, or with aqueous solutions containing reducing agents such as SO_2; and pyrometallurgical methods which employ high-temperature smelting and chlorination (1). In these processing schemes the major emphasis thus far has been on the recovery of Mn, Cu, Ni, and Co.

Recently, there has been some interest in the recovery of Mo from deep-sea ferromanganese nodules (*1*). Cronan (*2*) reported a world average Mo concentration of 412 mg/kg ($\sim 0.04\%$ by weight) in ocean ferromanganese deposits, which is relatively low when compared with levels ranging from 0.1 to 0.3 % in land-based ores (*3, 4*). The Mo, although present as a minor component in the nodules, may be economically significant if its recovery can be carried out easily and inexpensively. Little effort, however, has been directed toward Mo recovery from deep-sea nodules. This neglect may be ascribed in part to the low metal concentration in the nodules and in part to the difficulties in separating the metal from the Fe and Mn matrices. In a high-temperature smelting process (*5*), manganese nodules mixed with 5 % coke and 5 % SiO_2 were heated at 1000°C prior to smelting at 1400°C for 1 h, which resulted in about 90 % Mo recovery. Antonine and Van Peteghem (*6*) recently proposed a complex HCl-halidation process to extract metal values including Mo. Wilder and Andrecia (*7*) reported a high-temperature roasting method in which a mixture of ground nodules and carbonaceous materials such as coal and petroleum coke is heated under a N_2 atmosphere at about 800°C. The nodules are then leached with $1\,M$ $(NH_4)_2CO_3$ in 10 % aqueous ammonia solution at a temperature of 80°C, and a Mo recovery of about 80 % obtained. Major techniques for the recovery of Mo from the terrestrial ores are flotation concentration, high-temperature roasting, and halidation (*3, 4*). There are serious drawbacks in these processes. They are energy-intensive, involve complex separation procedures, require time-consuming treatment periods, and hence are costly.

We have developed a novel, simple, and rapid method for the selective separation of Mo from deep-sea ferromanganese nodules. Treatment of the powdered nodule material with a gaseous mixture of SO_2 and O_2 at elevated temperatures results in the formation of a volatile Mo compound which sublimes. Sublimation, therefore, is an effective technique for the separation of low levels of Mo from complex matrices.

EXPERIMENTAL

Specimens of Pacific ferromanganese nodules were supplied by the Hawaii Institute of Geophysics, University of Hawaii, and Atlantic specimens were obtained from the Lamont-Doherty Geological Observatory of Columbia University. The samples were analyzed for Mn, Fe, Cu, Ni, Co, and Mo with a Perkin-Elmer 603 atomic absorption spectrophotometer. Known quantities (0.25 to 0.50 g) of ground nodules were acid-digested in a pressurized Teflon bomb with the technique developed by Bernas (*8*). The resulting homogeneous sample solution was diluted

for the atomic absorption analysis with 0.5 M boric acid. Five replicates of each sample were analyzed. All chemicals, reagents, and gases were of analytical reagent quality. Water was distilled and deionized prior to use.

The nodule samples of uniform particle size (100/150 μm in diameter) were treated with a gas mixture of SO_2 and O_2 in a flow-through gas system between 300 and 700°C. A measured amount packed in a Vycor glass tube of 13 mm o.d. was loaded in a high-temperature furnace and dried at 450°C overnight while He gas was passed through. The dehydrated nodules were maintained at preselected temperatures prior to the gas treatment. Sulfur dioxide was mixed with O_2 at a 4:1 volume ratio in a gas mixing chamber, and the mixture introduced into the system at a flow rate of 50 mL/min along with He as the carrier gas until the gas–solid reaction was completed. A volatile product was formed during the reaction, and a crystalline material containing Mo was deposited at the outlet of the sample tube. Molybdenum in the condensates and untreated ferromanganese nodules was identified qualitatively by proton-induced x-ray emission spectrometry (PIXE) with a 2-MeV proton flux, generated by a Van de Graaff accelerator, as an excitation source and an energy dispersive Si(Li) detector. A thick target technique was used to obtain the PIXE spectrum of the untreated nodule samples.

In an identical series of sulfation experiments the nodule material impregnated with 2 to 5% (w/w) of halides such as NaCl, NaBr, and $CaCl_2$ was used to increase the yield of the sublimed material. A Lindberg single-zone tube furnace was mounted on a temperature console with a controlling range that extended up to 1200°C. The temperature control unit equipped with a platinel-II/chromel thermocouple was calibrated against a chromel/alumel couple connected to a digital read-out meter (M-175K, Omega Engineering). Flow rates of gases were measured by Linde-150 meters that had been factory calibrated with the specific gases. Upon completion of the reaction and subsequent flushing of the system with He to eliminate the residual gas mixture, the sample tube was sealed to prevent exposure of the condensates to moist air.

X-ray powder diffraction patterns of the sublimates were obtained with an XRD-5 X-Ray Diffraction Unit from General Electric Co. equipped with a 114.6-mm Debye-Scherrer camera and a copper x-ray tube. The sealed reaction tube was placed in a N_2 atmosphere chamber and disassembled. The sublimates, consisting of deep-green, brown, and yellow material, were removed carefully from the tube for powder target preparation. It was possible to separate the material according to color. A finely powdered form of each portion was packed into a glass capillary, which was then sealed and loaded in the camera. X-ray irradiation of up to about 20 h was usually required to obtain a well-defined diffraction pattern

TABLE 1

Atomic Absorption Analysis of Selected Elements in Pacific and Atlantic Ferromanganese Nodules

Sample	Collection sites (longitude; latitude; depth)	Concentration (% w/w)[a]						
		Mn	Fe	Si	Cu	Ni	Co	Mo
Pacific nodules:								
VALDIVIA	148°30'W; 9°00'N; 5000 m	20.16	6.47	6.06	0.69	1.02	0.11	0.071
MDH-20	178°57'W; 28°49'N; 1090 m	6.27	12.25	12.78	0.03	0.15	0.18	0.029
KK-77	169°06'E; 45°48'N; 4300 m	11.23	10.77	11.14	1.54	0.30	0.16	0.028
Atlantic nodules:								
RC15-D5	55°14'W; 48°28'S; 2400 m	12.97	17.10	11.23	0.07	0.19	0.11	0.070
RC15-D20	61°10'W; 27°42'N; 5390 m	13.70	12.56	6.11	0.12	0.34	0.15	0.032
RC15-D28	61°00'W; 28°02'N; 5550 m	12.93	14.19	7.27	0.12	0.35	0.17	0.032

[a]Each value represents the average of five replicate determinations based on air-dry sample wt.

for each target. The colored deposits were also analyzed for halides; aliquots were dissolved in known quantities of water, and the resulting aqueous solutions were analyzed gravimetrically with 0.1 M AgNO$_3$. Mo concentrations in the sublimates as well as in the gas-treated ferromanganese nodules were measured by atomic absorption spectrophotometry.

RESULTS AND DISCUSSION

Molybdenum is one of the minor elements in deep-sea ferromanganese nodules, yet it may be, like Co, Ni, and Co, an economically valuable metal. In this study we obtained an average Mo concentration of 460 mg/kg (0.046%) from Pacific and Atlantic nodules. The data for Mo from individual nodule specimens are presented in Table 1 which also includes average concentrations for the selected elements. In deep-sea nodules the minor elements are believed to be intimately associated with major mineral phases such as those of Mn and Fe by either adsorption or coprecipitation; the level of Mo varies, but in general it is proportional to the Mn content (9–11).

During the course of sulfation with a SO$_2$–O$_2$ gas mixture in the 300 to 700°C range, we observed that the Mo compound sublimes from the nodules. When the nodules are treated at 350°C or higher, deep-green, brown, and yellow bands form at the outlet of the reaction tube. These bands remain unchanged until the tube is opened to the atmosphere or moisture is introduced; thereupon the colored condensates immediately turn blue and remain as a viscous material that dissolves readily in water. In an oxidizing environment the initial colored deposits change slowly to a white solid. A qualitative identification of Mo in the blue residue was made by the PIXE technique. Figure 1 represents a PIXE spectrum of the blue residue obtained during the sulfation at 400°C of a specimen (MDH-20) from the Pacific Ocean. The Mo K_α and K_β peaks shown in the energy range between 17 and 20 keV are of remarkably high intensity and no other spectral lines of significance can be detected in the whole energy range, which shows that the sublimate is a Mo compound of high purity. For comparison, the PIXE spectrum of untreated manganese nodules of the same origin obtained under identical conditions is presented in Fig. 2, and shows the low intensity of Mo lines. The Mo concentration in the sample was found to be 287 mg/kg by AA analysis.

The extent to which Mo can be separated by sublimation from the solid nodules seems to depend upon the conditions used. When the nodules were treated with SO$_2$ in the absence of O$_2$, the colored condensates were hardly noticeable in the sample tubes. In contrast, when
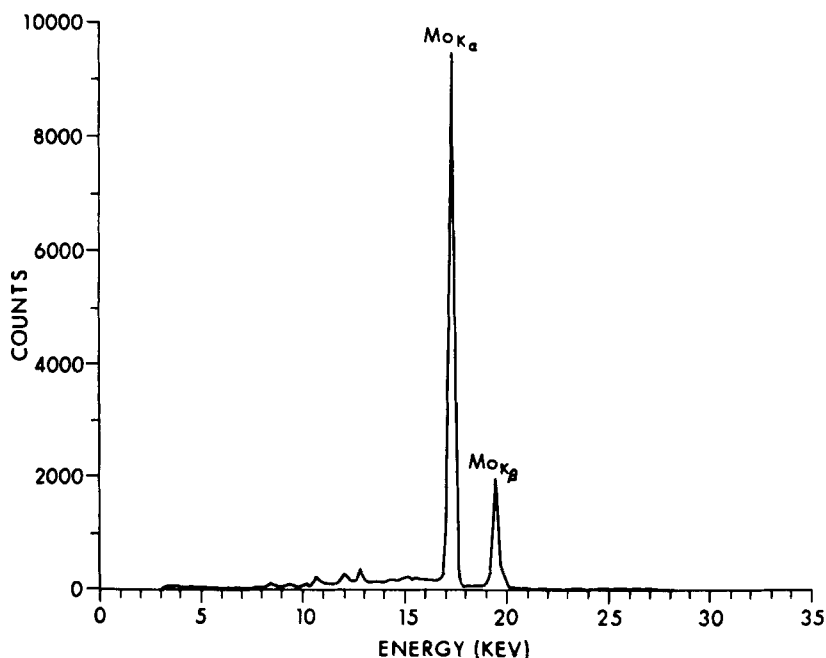
the nodules were treated with a SO_2–O_2 mixture, sublimation occurred. A yield of approximately 70% of Mo was observed in a 2-h sulfation at 400 to 450°C, which is also the temperature range that is required for the maximum sulfation of the nodule sample. The high-temperature sulfation process, developed initially for a selective separation of Mn, Cu, Ni, and Co from the deep-sea nodules (12), can thus be effectively employed for Mo separation with little additional effort. The separation of other metals from the sulfated nodules from which Mo has been extracted can be readily carried out by a simple leaching procedure. The Mo sublimation appears to be enhanced somewhat as the gas–solid contact time increases. Figure 3 presents experimental results for the recovery of Mo from three specimens of ferromanganese nodules in the 400 to 600°C sulfation, and shows that approximately 75% of the metal is recovered when the reaction time is increased to 5 h. The yields were calculated by determining the Mo concentration before and after the sublimation by the atomic absorption spectrophotometric analysis.
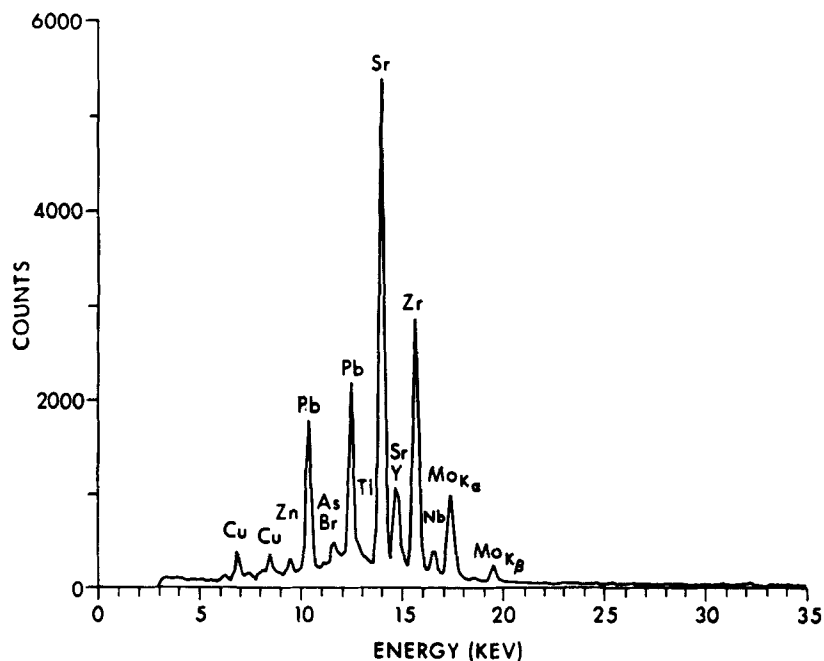
FIG. 2. PIXE spectrum of untreated MDH-20 ferromanganese nodules. The samples were prepared by the thick target technique. The spectrum was obtained under the instrumental condition described in Fig. 1.
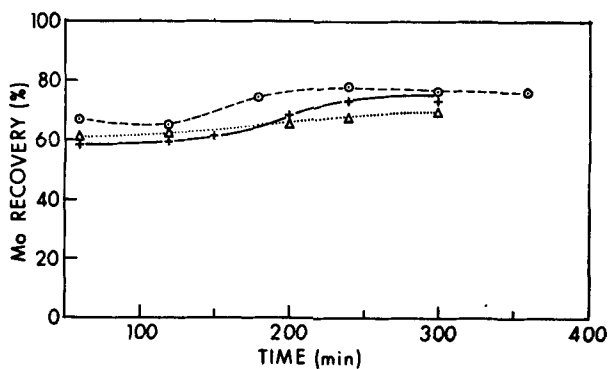

FIG. 3. Recovery of Mo from ferromanganese nodules as a function of the treatment time. The nodule samples were treated with a SO_2-O_2 gas mixture at 400–425 °C for the specified time, after which the temperature was increased to 615 °C and maintained for 30 min in all cases. The samples used are KK-77 (⊙), RC15-D5 (+), and VALDIVIA (△).

To further increase the efficiency of the Mo recovery, tests were made on the basis of an assumption that sublimation of the metal would depend mainly on the availability of halide ions in the nodule material. Powdered nodules were mixed uniformly with measured quantities of alkali metal halides, followed by sulfation as described above. Figure 4 shows the results of the Mo recovery from Atlantic ferromanganese nodules impregnated with 5% w/w NaCl during sulfation that lasted for only half an hour. As can be seen in the figure, the recovery yield was in excess of 95% in the temperature range employed. Addition of halides can therefore not only increase the recovery yield, but can also decrease the reaction time considerably. This method also works well for other Mo-bearing minerals such as molybdenite (MoS_2) and ammonium molybdate. The unexpected trend in the Mo recovery shown in Fig. 3 may reflect the nonuniform distribution and limited availability of halide for reaction in the nodule matrices.

In dehydrated manganese nodules the Mo may be present as its trioxide, MoO_3, since synthetic nodule samples spiked with pure MoO_3 exhibit the same behavior as the natural nodules. The pure oxide sublimes at 1155°C, although some of its halides and oxyhalides are fairly volatile and sublime at much lower temperatures (*13*). The following sequence of events is suggested to account for the phenomena observed in this study. First, it is essential that the major matrices be disrupted in order to free the metals that are intimately associated with them. This disruption is accomplished
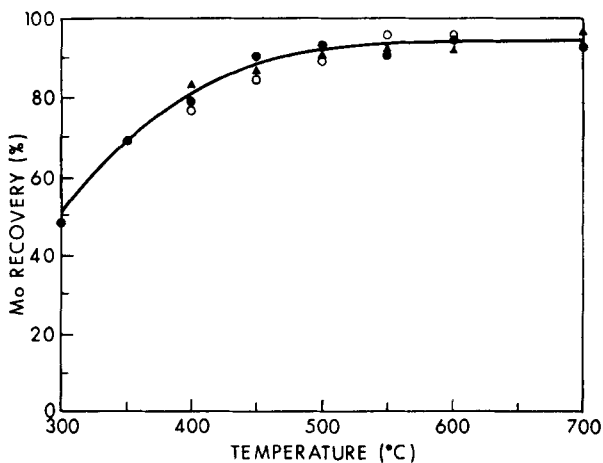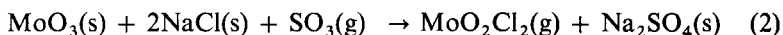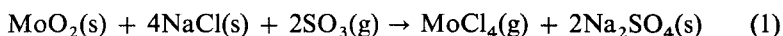

FIG. 4. Recovery of Mo from ferromanganese nodules spiked with 5% of NaCl as a function of temperature. The nodule samples treated with a gas mixture of SO_2 and O_2 for 30 min are RC15-D5 (●), RC15-D20 (▲), and RC15-D28 (○).

by reaction of the metal oxides such as those of Mn and Fe with the SO_2, and SO_3 present in the gas mixture. The addition of O_2 is important primarily for maximizing the matrix disruption or sulfation (12). The next step involves a reduction of the MoO_3 to MoO_2 by SO_2. Once MoO_2 is formed it may react with the halides available in the solid matrices and produce volatile halides of the metal, and the remaining MoO_3 may also be directly transformed into its oxyhalide in the following solid phase reactions:

$$MoO_2(s) + 4NaCl(s) + 2SO_3(g) \rightarrow MoCl_4(g) + 2Na_2SO_4(s) \qquad (1)$$

$$MoO_3(s) + 2NaCl(s) + SO_3(g) \rightarrow MoO_2Cl_2(g) + Na_2SO_4(s) \qquad (2)$$

These Mo-bearing volatiles will sublime and be deposited in a cooler part of the reaction tube. When hydrolyzed, these Mo compounds produce a series of oxyhydroxides in which the average oxidation state of Mo is between 5 and 6 (14). The Mo oxyhydroxides are often given the generic name "molybdenum blue" because of their blue color. The observed conversion, upon exposure to moisture, of the colored condensates into viscous blue material (15) may thus be due to the formation of Mo oxyhydroxides.

Crystalline compounds in the deposits were identified by x-ray powder diffraction. The proportions of the colored sublimates seem to vary depending upon the amount of halides available in ferromanganese nodules, but the nodules mixed with 2 to 5% NaCl always produce more than 70% deep-green, about 25% brown, and the rest yellow material. The observed d-spacings and relative percentage intensities for the identified phases were measured with Cu K_{α_1, α_2} ($\lambda_{\alpha_1, \alpha_2}$ = 1.5418 Å) radiation and the results are presented in Table 2. Both the deep-green and brown powder samples gave identical diffraction patterns which have been identified in repeated examinations as the diffraction pattern obtained with molybdenum tetrachloride, $MoCl_4$. Because of the inherent purity of the material obtained, no further purification was required for target preparation. The powder targets were prepared in an anhydrous N_2 gas environment because the crystalline material was highly deliquescent when exposed to moist air. The x-ray pattern obtained is in excellent agreement with that previously reported by Couch and Brenner (16), considering that these workers used Cu K_{α_1} (λ_{α_1} = 1.5405 Å) for the calculation of d-spacings. The yellow condensate, only 5% or less of the total deposits produced, has been identified as molybdenum dioxydichloride, MoO_2Cl_2; the diffraction pattern changes when the material is allowed to stand in contact with moisture. The structure of $MoO_2Cl_2 \cdot H_2O$ was determined by Schröder and Christensen (17) using a single crystal diffraction technique, and the reported pattern of the compound is in close agreement

TABLE 2

X-Ray Powder Diffraction Data[a] on Various Molybdenum Compounds in the Sublimation Condensates Produced through Treatment of Ferromanganese Nodules with a SO_2–O_2 Mixture at 450°C

$MoCl_4$[b]		MoO_2Cl_2[c]		$MoO_2Cl_2 \cdot H_2O$[d]	
$(I/I_o)_{ob}$	d (Å)	$(I/I_o)_{ob}$	d (Å)	$(I/I_o)_{ob}$	d (Å)
4	6.478	80	7.010	5	6.176
100	5.841	5	4.169	100	5.542
5	5.272	100	3.789	30	4.603
3	3.011	10	3.437	40	3.606
20	2.913	3	2.966	50	3.476
80	2.696	20	2.775	50	3.416
4	2.574	5	2.576	35	2.801
60	2.101	60	2.291	5	2.497
50	1.754	55	2.249	20	2.412
20	1.681	20	1.964	40	2.297
40	1.636	5	1.894	20	2.244
15	1.471	50	1.753	15	1.993
20	1.456	4	1.711	10	1.959
10	1.345	4	1.642	50	1.909
10	1.197	10	1.487	20	1.847
5	1.114	3	1.385	3	1.826
		8	1.307	8	1.775
		3	1.257	8	1.735
		3	1.221	10	1.705
		7	1.184	5	1.663
		3	1.168	5	1.624
				5	1.601
				5	1.564
				20	1.503
				15	1.491
				3	1.476
				5	1.437
				4	1.410
				8	1.383
				8	1.370
				8	1.259

[a]Values are the average of three determinations. The relative intensities in percent and d-spacings were measured with Cu $K\alpha_{1,\alpha_2}$ ($\lambda\alpha_{1,\alpha_2}$ = 1.5418 Å) as the radiation source.
[b]Identified from both deep-green and brown sublimates.
[c]Identified from yellow sublimate.
[d]Yellow sublimate exposed to moist air.

with that obtained from the powder target of the moisturized yellow condensate.

The production of $MoCl_4$ and MoO_2Cl_2 as the sublimation condensates was also confirmed by gravimetry and atomic absorption spectrophotometry. Chemical analysis shows that the molecular ratios Cl:Mo are 4.01:1 for the former and 2.04:1 for the latter from four replicate determinations. In another series of experiments, powdered MoO_3 mixed with varying quantities of NaCl (2 to 50%) was reacted with a mixture of gaseous SO_2 and O_2 under the same conditions as described above. Sublimation occurred immediately upon introduction of the gas mixture into the reaction tube, and the reaction was completed within 10 min. We observed that the condensate from these tests consisted of MoO_2Cl_2 with trace amounts of $MoCl_4$ irrespective of the ratio in which the MoO_3 and NaCl was mixed. This result differs from that obtained in the gas–solid reaction with ferromanganese nodules spiked with NaCl. It appears that, in the latter case, there is a redox reaction that takes place between the SO_2 gas and Mo compound during the time required to disrupt the nodule matrices. The solid phase reaction will then occur with a reduced form (MoO_2) of the molybdenum oxide, and hence Reaction (1) will be predominant. In the former case, however, the sublimation occurs without a time lag since the MoO_3 phase is in direct contact with the chloride ions, and Reaction (2) will be predominant because there is insufficient time for the reduction of MoO_3.

The Mo-halides produced from the nodule material are readily soluble in water; this should simplify any subsequent treatment that is required for the recovery of Mo metal. The sublimation does not interfere with or complicate the sulfation process for the selective extraction of Cu, Ni, Co, and Mn from the marine nodules. In fact, the Mo sublimation can be effectively coupled with sulfation by the addition of only a single step: sulfation of the nodules at 400 to 500°C with the SO_2–O_2 mixture for 30 min wherein Mo is separated by distillation. The other metals can then be removed by leaching the sulfated nodules with water, and can eventually be recovered by electrodeposition. The recovery process for Mo described here is simple and economical when compared with HCl-halidation and high-temperature roasting and smelting processes (5–7).

Acknowledgments

use of his XRD-5 X-Ray Diffraction Unit. This is journal contribution UNIHI-SEAGRANT-JC-81-06.

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