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Simultaneous Multielement Determination of Trace Metals in Seawater by Inductively Coupled Plasma Atomic Emission Spectrometry Using Chelating Resin Column Preconcentration

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Preconcentration of trace metals in seawater using a Chelex-100 resin column was investigated for simultaneous determination by inductively coupled plasma atomic emission spectrometry (ICP-AES). The optimum preconcentration conditions were examined in detail. With 100 ml of 1 M ammonium acetate buffer solution (1 M=1 mol dm^{-3}), the matrix elements in seawater could be removed sufficiently without loss of analytes. The concentration factor of 200 times could be achieved by dissolving the dried HNO_3 eluent of the column. The blanks of the method were negligibly small for most elements investigated. The detection limits were in the range of several ng/l to 100 ng/l for Al, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Ti, V, and Zn. The present technique was applied to the determination of trace metals in coastal and ocean seawater.

In recent years various methods for the determination of trace elements in seawater have been developed. Since the concentration levels of trace elements in seawater are very low, sensitive analytical techniques such as spectrophotometry,[1] atomic absorption spectrometry,[2–4] anodic stripping voltammetry,[5] isotope dilution mass spectrometry,[6] neutron activation analysis,[7] and X-ray fluorescence spectrometry[8] have been applied to seawater analysis.

Inductively coupled plasma atomic emission spectrometry (ICP-AES) which has the capability of simultaneous multielement detection has been often employed for determination of trace metals in seawater samples.[9–14] Adequate preconcentration techniques are, however, required prior to ICP-AES measurement because of insufficient sensitivity for the trace metal level in seawater and serious interferences caused by salts at high concentration. Therefore, preconcentration techniques such as solvent extraction,[9,10] coprecipitation,[11,12] and chelating exchange,[13,14] have been employed for seawater analysis with ICP-AES.

It has been shown that Chelex-100 chelating resin is an efficient exchanger of many trace metals and provides low analytical blank.[15] Further, as it is a strong chelator, it can remove metal ions from natural chelators existing in seawater.[15–17] Therefore, Chelex-100 resin may be useful for preconcentration of analytes prior to the ICP-AES measurement. Even so, it should be noted that Chelex-100 chelating resin often collects a part of Mg and Ca as well as trace metals in seawater.[18]

Berman *et al.* tried preconcentration of trace metals from seawater by Chelex-100 chelating resin followed by ICP-AES measurement.[13] They avoided the physical interference caused by salts using an ultrasonic nebulizer. Ammonium acetate buffer solution was known to remove the Mg and Ca cations from the resin,[19] but it also has the disadvantage to elute partly some of analytes such as Mn, Fe, and Cu.[20] Although an ICP-AES spectrometer equipped with a conventional cross flow nebulizer is widely prevailed, the preconcentration method using the Chelex-100 resin column and ICP-AES with a conventional cross flow nebulizer has not been reported. The Chelex-100 resin preconcentration procedure which allows minimum loss of analytes and efficient removal of matrix salts should be established in order to utilize ICP-AES effectively as a monitoring method of trace metals in seawater.

In this study, Chelex-100 resin column treatment is evaluated for preconcentration followed by ICP-AES measurement. Recoveries of trace metals and concentration of matrix elements in concentrated analysis solution are examined in detail for optimization of preconcentration conditions in ICP-AES analysis.

Experimental

Apparatus. An ICP instrument (Model Plasma Atomcomp Mk II from Jarrell-Ash Co., USA) was used with a conventional crossflow type nebulizer. The instrumental components and operating conditions for ICP-AES are summarized in Table 1. The emission lines used are shown in Table 2 along with the detection limit of each element. A pH meter (Model F-7, Horiba Seisakusho Ltd.) was used for the pH measurement. A class-100 clean booth (Model KCR-2D) was made by San-ei Seisakusho, and all column performance and preconcentration procedures were carried out in there.

Chemicals. All chemicals used were of analytical reagent grade or of better grade. The standard solutions for Al, Cd, Co, Cr^{3+}, Cu, Fe, Mg, Ni, Pb, Ti, and Zn were prepared from pure metals, and those for As, Cr^{6+}, Mo, V, Y, Na, K, and Ca from corresponding salts or oxides. HCl, HNO_3, acetic acid, and ammonium solution were of extra pure grade purchased from Wako Chemical Co., Ltd. HCl

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Table 1. Instrumental components and operating conditions

ICP spectrometer	Jarrell-Ash Plasma Atomcomp Mk II
RF frequency	27.12 MHz
RF Power	1.1 kW
Coolant gas	Argon 15 l/min
Auxiliary gas	Argon 0.5 l/min
Carrier gas	Argon 1.0 l/min
Observation height	17 mm above work coil
Nebulizer	Cross-flow type
Polychromator	Paschen-Runge type (75 cm focal length)
Grating	2400 grooves/mm
Reciprocal linear dispersion	0.54 nm/mm at 270 nm
Entrance slitwidth	25 μm
Exit slitwidth	50 μm

Table 2. Analytical wavelengths and detection limits

Element	Wavelength[a] nm	Detection limit μg/l
Al	I 308.2	10
As	I 193.6	40
Cd	I 228.8[b]	3
Co	II 228.6	4
Cr	II 205.5[b]	8
Cu	I 324.7	2
Fe	II 238.2	3
Mn	II 257.6	0.6
Mo	II 202.0	5
Ni	II 231.6[b]	10
Pb	II 220.3	20
Ti	II 334.9	1
V	II 292.4	8
Zn	I 213.8[b]	1

a) I and II indicate atomic and ionic lines, respectively. b) The 2nd order lines were used.

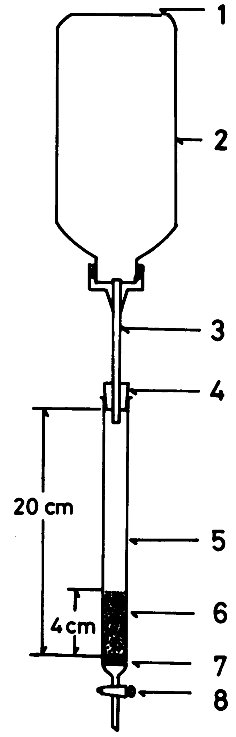

Fig. 1. Apparatus for preconcentration of trace elements in seawater.
1: Pin hole (0.5 mmϕ), 2: Polyethylene bottle (1 l), 3: Polyethylene tube, 4: Silicone rubber stopper, 5: Glass column (14 mm I.D.), 6: Chelex-100 resin (200—400 mesh), 7: porous glass (pore size=35 μm), 8: Teflon stopcock.

and HNO_3 used for resin purification and column conditioning were prepared by sub-boiling the acids of extra pure grade. Pure water for ordinary use was deionized/distilled water, and it was further purified by sub-boiling distillation when necessary. Ammonium acetate was prepared by mixing ammonium solution and acetic acid, and was purified by passing 2 times through the Chelex-100 column. Chelex-100 resin (200—400 mesh) was purchased from Bio Rad Laboratories, U.S.A. Before packing the resin in the column, the resin was kept for cleaning in 5 M HCl five times for 5 d, and then with pure water, 2 M HNO_3, and finally pure water. The HCl solution used for the resin cleaning was changed with new one everyday. The artificial seawater used for the recovery test was prepared after the prescription reported by Kester *et al.*[21] It contained 13 constituents whose concentrations are higher than 1 mg/l, and its salinity was adjusted at 35‰.

Column Preparation. The column system used is shown schematically in Fig. 1. The inner diameter of the column was 14 mm. A polyethylene bottle for the sample reservoir was connected with the column through the polyethylene tube. To avoid contamination the column system was designed as a closed one from the atmosphere, just being open to the air *via* a pin hole in the sample reservoir and a column outlet. Sample flow rate was controlled by the stopcock. All parts of the column were well precleaned with 1:1 HNO_3 and pure water. The Chelex-100 resin (dry weight 2.5 g) was packed in the column. The packed column was preconditioned with 10 ml of 2 M ammonium solution, 30 ml of sub-boiled pure water, and 20 ml of 1 M ammonium acetate buffer solution (pH 6) prior to each use. The length of the preconditioned resin in the column was about 40 mm.

Preconcentration Procedure. One liter of a seawater sample was filtered with Nuclepore filter (pore size 0.4 μm) and the pH of the solution was adjusted to pH 5.5—6 with 10 ml of 1 M ammonium acetate solution. The seawater sample was then taken into the sample reservoir and eluted at a flow rate of 2 ml/min through the preconditioned column. For removal of matrix salts the column was treated with 100 ml of 1 M ammonium acetate buffer (pH 6) and 50 ml of sub-boiled pure water after each seawater elution. Trace metals collected on the resin were then eluted with 25 ml of 2 M HNO_3 solution into a PTFE beaker. The eluent in the beaker was heated to dryness on a hot plate, and then the residue was dissolved with 5 ml of 0.2 M HNO_3. Thus a 200-fold concentrated solution (hereafter called "analysis solution") was prepared for ICP-AES measurement. In case of the recovery test, the eluent was filled up to 50 ml with pure water.

Results and Discussion

pH Dependence of Calcium and Magnesium Concentrations in the Analysis Solution. In ICP-AES measurement, high concentrations of matrix elements in the analysis solution are sometimes prone to spectral and physical interferences.[22,23] Since parts of Ca and Mg in seawater were collected on the Chelex-100 resin,[18] the effects of Ca and Mg on the emission intensities of analytes were investigated by aspirating the test solutions which contained Ca and Mg at various concentrations. The emission intensities observed for the test solutions included both spectral and physical interferences. The emission intensities due to spectral interference were first corrected by using the correction coefficients for spectral interference,[11,12] which were estimated by introducing pure Ca or Mg solution (lower than 200 mg/l) into the ICP. Then physical interference was estimated. When the total concentration of the two elements was 1600 mg/l, the intensities were reduced by 10%. When their total concentration was smaller than 200 mg/l, the intensity changes due to the influences of nebulization process were negligibly small. Therefore, it was desirable that the total concentration of matrix elements was less than 200 mg/l.

The concentrations of Ca and Mg collected on 1 g resin are shown as a function of pH in Fig. 2. These values were obtained with artificial seawater which contained matrix elements at the same concentration levels as natural seawater, *i.e.*, 1350 mg of Mg/l and 400 mg of Ca/l. The concentrations of Ca and Mg on the resin increased at higher pH. The results agreed well with those reported previously.[24] When 2.5 g resin was used and the 200-times preconcentration was made even at pH 3, the concentrations of Mg and Ca in the final analysis solution were 2500 mg/l and 1200 mg/l, respectively. Matrix elements at such high concentration levels may seriously influence the analytical results in ICP-AES due to their spectral and physical interferences. Therefore, a proper procedure to remove matrix elements on the resin was necessary prior to elution of analyte elements.

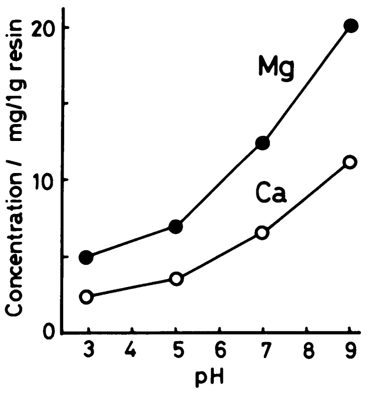

Fig. 2. pH Dependence of concentrations of Ca and Mg in 1 g resin after column preconcentration. The original concentrations of Ca and Mg were 400 mg/l and 1350 mg/l, respectively, which were the same as those in seawater.

Removal of Matrix Elements with Ammonium Acetate Buffer Solution. Kingston *et al.* reported that Mg and Ca retained on the resin could be removed by ammonium acetate solution.[19] However, excess amounts of ammonium acetate solution may cause loss of analytes.[20] In Table 3, the effect of ammonium acetate solution (pH 6) on removal of matrix elements are summarized. The values in the table are the concentrations in 50 ml of the eluent, when 1 l of artificial seawater was treated with the chelating resin column. As can be seen in Table 3, the concentrations of matrix elements were lowered remarkably when the volume of the buffer solution for washing was increased. In the analysis of natural seawater, the volume of the final analysis solution was 5 ml. Thus the concentration values should be multiplied by ten. Therefore, at least 100 ml of 1 M ammonium acetate buffer solution (pH 6) is required in treatment of natural seawater samples. Fortunately, the recoveries of all the elements were not affected by using the ammonium acetate buffer solution up to 100 ml. Thus 100 ml of the ammonium acetate solution was used for removal of matrix elements in natural seawater samples.

pH Dependence of Recoveries of Analytes. In Fig. 3, pH dependences of recoveries of Cu and Mn are shown. Since Cu has the largest stability constant and Mn has the smallest one with Chelex-100 resin, these two elements among fifteen elements were chosen as representative examples. In Fig. 3 the values indicated by black and white circles show the

TABLE 3. CONCENTRATIONS (mg/l) OF MATRIX ELEMENTS IN THE 50 ml ELUENT AFTER WASHING WITH VARIOUS VOLUMES OF AMMONIUM ACETATE BUFFER

Element	Volume of buffer[a)] (ml)				
	0	50	100	200	300
Ca	337	18.6	3.1	0.9	0.6
Mg	500	11.1	4.5	2.0	1.2
Na	137	10.1	5.2	2.7	1.6
K	6	0.3	0.2	0.1	0.06

a) 1 M CH_3COOH/CH_3COONH_4 (pH 6) was used.

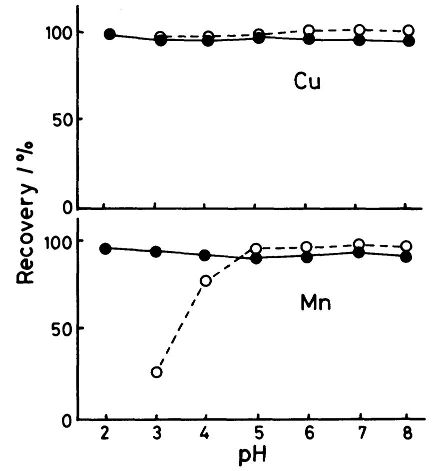

Fig. 3. pH Dependence of recoveries for Cu and Mn. Black circles (●) indicate the values for pure water sample without washing with buffer solution.
White circles (○) indicate the values for artificial seawater after washing with 100 ml of 1 M ammonium acetate buffer solution.
The original concentrations of Cu and Mn were 100 μg/l.

TABLE 4. RECOVERIES OF METAL ELEMENTS ADDED TO SEAWATER OBTAINED BY CHELEX-100 PRECONCENTRATION AND ICP-AES METHOD

Element	Added	A[a]		B[b]
		Recovery	C.v. ($n=3$)	Recovery
	μg	%	%	%
Al	100.2	97.6	4.0	92.7
As	100.7	7.3	6.8	—[c]
Cd	113.9	94.7	1.3	96.4
Co	100.5	95.9	2.1	95.0
Cr^{3+}	106.6	67.9	7.9	62.6
Cr^{6+}	103.5	32.7	—[d]	—[c]
Cu	102.9	100.2	0.7	97.1
Fe	99.0	98.1	2.7	93.0
Mn	101.4	98.7	2.2	96.8
Mo	92.8	90.5	—[d]	—[c]
Ni	102.5	96.5	1.3	97.1
Pb	96.8	92.6	0.8	97.9
Ti	100.0	96.8	1.3	92.4
V	100.1	95.4	1.8	—[c]
Zn	102.7	95.8	1.0	96.7

a) The 1 l seawater sample was concentrated to 50 ml without evaporation. b) The 1 l seawater sample was concentrated to 5 ml with evaporating the eluent to dryness. c) Not observed. d) Not estimated.

TABLE 5. BLANK AND ANALYTICAL DETECTION LIMITS

Element	Blank[a] μg/l	Analytical detection limit[a] μg/l
Al	0.8	0.05
Cd	<0.02	0.02
Co	<0.02	0.02
Cr	<0.04	0.04
Cu	<0.01	0.01
Fe	0.08	0.02
Mn	0.004	0.003
Mo	0.02	0.02
Ni	<0.05	0.05
Pb	<0.1	0.1
Ti	<0.005	0.005
V	<0.04	0.04
Zn	0.08	0.005

a) Estimated for analysis solution with 200 fold concentration.

experimental results for acidified water and artificial seawater used as the samples, respectively. Both solutions contained all the analytes at a concentration of 0.1 mg/l. In the case of artificial seawater the resin was treated with ammonium acetate buffer in order to remove the matrix elements. The pH dependences of recoveries for Al, Cd, Co, Fe, Mo, Ni, Pb, Ti, V, and Zn in acidified water was similar to those for Cu and Mn, *i.e.*, constant recoveries more than 90% in the pH range of 2—8. The pH dependences of the recoveries for As and Cr, however, were greatly different from those for the other elements, being less than 90% at any pH.

On the other hand, Mn in artificial seawater showed poor recovery at pH lower than 5 (see Fig. 3). The same deterioration in recovery from artificial seawater was also observed for Cd. Other elements such as Al, Co, Fe, Mo, Ni, Pb, Ti, V, and Zn showed constant recoveries similar to Cu (see Fig. 3). As mentioned previously, the concentrations of Ca and Mg in the analysis solution increased with pH, and so treatment with a large volume of ammonium acetate solution was needed for the removal of salts in the higher pH region. Thus pH 5.5—6 was chosen for preconcentration of the natural sample, which allowed efficient preconcentration of 12 elements including Mn and Cd on the chelating resin.

Recovery, Blank, and Detection Limits. The recovery and standard deviation obtained by the present method are summarized in Table 4. As can be seen in the table, the reproducibility in preconcentration is good for almost all elements except As and Cr. The poor reproducibilities of As and Cr may be caused by their poor recoveries in the column concentration, while other elements were quantitatively collected on the Chelex-100 resin with recoveries greater than 90%.

When natural seawater sample was analysed, the HNO_3 eluent from the column was heated to dryness. The recovery values including the drying process were examined by using artificial seawater which contained the analytes at the same levels as those in Table 4. The results are shown in the last column of Table 4. It can be seen that the recoveries of the analytes did not significantly deteriorate through drying.

Blank and detection limits in the present method were summarized in Table 5. The blank values were obtained by performing the same preconcentration procedure using 100 ml of sub-boiled pure water and were converted to the concentration corresponding to 1 l of an original sample. The analytical detection limits were calculated by dividing the detection limits (Table 2) for analytes by the concentration factor (200). As for Cd, Co, Cr, Cu, Ni, Pb, Ti, and V, the blank values were lower than the analytical detection limits. This may have resulted from the use of the well-closed column system, purification of chemicals, and a class-100 clean air system. The blank values for Al, Fe, and Zn were larger than the analytical detection limits. For these elements corrections of the blank values were carried out in the actual seawater analysis.

Application to Natural Seawaters. In Table 6 the analytical results for natural seawaters which were sampled on the cruises of the Tansei-Maru research vessel (the Ocean Research Institute, University of Tokyo) and the Toyoshio-Maru research vessel (Faculty of Applied Biological Science, Hiroshima University) are summarized. The analytical results for most elements except Mo in the ocean seawater sample were lower than those in the coastal seawater samples. The concentration levels in the ocean seawater were similar to those reported by Turekian *et al.*[25] The concentrations of Al, Fe, and Ti in the Seto Inland Sea water were much larger than those in the Tokyo Bay water.

TABLE 6. ANALYTICAL RESULTS FOR TRACE METALS IN NATURAL SEAWATERS[a]

Element	Concentration/μg/l		
	North Pacific Ocean	Inland Sea of Japan	Tokyo Bay[b]
Al	2.6	93.9	11.0 (14.1)
Cd	<0.02	0.04	0.06
Co	<0.02	0.15	0.30
Cu	0.07	1.08	1.01
Fe	0.28	67.1	9.46 (11.8)
Mn	0.04	5.73	5.69 (6.2)
Mo	10.6	9.32	9.38
Ni	0.25	0.45	40.8 (41.0)
Pb	0.2	5.0	1.1
Ti	0.01	2.48	0.23 (0.60)
V	2.98	3.32	3.26
Zn	0.52	4.79	4.33 (5.3)

a) The seawater samples were stored after acidifying at pH 2 with HNO_3. b) The values in parenthesis were obtained by ICP-AES using gallium coprecipitation (Ref. 11).

The analytical results for several elements in seawater from the Tokyo Bay were compared with those obtained by the gallium coprecipitation method.[11] The concentrations of Al, Ni, Fe, Mn, and Zn obtained by the two analytical methods were consistent with each other. This indicates that the present method is accurate enough to apply to the multielement determination of trace metals in seawater.

Conclusion

The present Chelex-100 resin column method is convenient and effective for multielement preconcentration of trace metals in seawater. Ammonium acetate buffer solution reduced the concentration of remaining salts on the resin low enough so as to obtain a large concentration factor of 200 for the ICP-AES determination. Therefore, the present method can be successfully applied to determine trace metals such as Al, Cd, Co, Cu, Fe, Mn, Mo, Ni, Pb, Ti, V, Y, and Zn in coastal and open seawater. However, it does take about 9 h for one sample treatment by the column method, which may not be useful in routine analysis of seawater. A more efficient treatment system using the chelating resin, for example, a flow or batch preconcentration system is therefore required in such ICP-AES analysis.

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References

1) K. Yoshimura, S. Nigo, and T. Tarutani, *Talanta*, **27**, 693 (1980).

2) L.-G. Danielsson, B. Magnusson, S. Westerlund, and K. Zhang, *Anal. Chim. Acta*, **144**, 183 (1982).

3) R. E. Sturgeon, S. S. Berman, A. Desaulniers, and D. S. Russell, *Talanta*, **27**, 85 (1980).

4) K. Fujiwara, S. Toda, and K. Fuwa, *Bull. Chem. Soc. Jpn.*, **54**, 3209 (1981).

5) C. Brihaye, G. Gillain, and G. Duyckaerts, *Anal. Chim. Acta*, **148**, 51 (1983).

6) A. P. Mykytiuk, D. S. Russell, and R. E. Sturgeon, *Anal. Chem.*, **52**, 1281 (1980).

7) K. Jørstad and B. Salbu, *Anal. Chem.*, **52**, 672 (1980).

8) F. Clanet, R. Deloncle, and G. Popoff, *Water Res.*, **15**, 591 (1981).

9) A. Miyazaki, A. Kimura, K. Bansho, and Y. Umezaki, *Anal. Chim. Acta*, **144**, 213 (1982).

10) C. W. McLeod, A. Otsuki, K. Okamoto, H. Haraguchi, and K. Fuwa, *Analyst (London)*, **106**, 419 (1981).

11) T. Akagi, K. Fuwa, and H. Haraguchi, *Anal. Chim. Acta*, in press.

12) T. Akagi, M. Matsui, Y. Nojiri, and H. Haraguchi, *Appl. Spectrosc.*, **39**, 662 (1985).

13) S. S. Berman, J. W. McLaren, and S. N. Willie, *Anal. Chem.*, **52**, 488 (1980).

14) H. Watanabe, K. Goto, S. Taguchi, J. W. McLaren, S. S. Berman, and D. S. Russell, *Anal. Chem.*, **53**, 738 (1981).

15) E. W. Davey and A. E. Soper, "Analytical Method in Oceanography," ed by T. R. P. Gibbs, Jr., Adv. Chem. Ser., American Chem. Soc., Washington, D. C. (1975), p. 147.

16) T. M. Florence and G. E. Batley, *Talanta*, **23**, 179 (1976).

17) T. M. Florence and G. E. Batley, *Talanta*, **24**, 151 (1977).

18) J. P. Riley and D. Taylor, *Anal. Chim. Acta*, **40**, 479 (1968).

19) H. M. Kingston, I. L. Barnes, T. J. Brady, T. C. Rains, and M. A. Champ, *Anal. Chem.*, **50**, 2064 (1978).

20) R. E. Sturgeon, S. S. Berman, J. A. H. Desaulniers, A. P. Mytytiuk, J. W. McLaren, and D. S. Russell, *Anal. Chem.*, **52**, 1585 (1980).

21) D. R. Kester, I. W. Duedall, D. N. Connors, and R. M. Pytkowicz, *Limnol. Oceanogr.*, **12**, 176 (1967).

22) S. Greenfield, H. McD.-McGeachin, and P. B. Smith, *Anal. Chim. Aca*, **84**, 67 (1976).

23) A. Sugimae, *Bunseki Kagaku*, **28**, 555 (1979).

24) K. Kawabuchi, M. Kanke, T. Muraoka, and M. Yamauchi, *Bunseki Kagaku*, **25**, 213 (1976).

25) M. S. Q.-Hunt and K. K. Turekian, *EOS*, **64**, 130 (1983).