Multi-element Analysis of Ferromanganese Nodules and Crusts by Inductively Coupled Plasma Mass Spectrometry

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INTRODUCTION

Ferromanganese nodules and crusts occur globally throughout the ocean, and on seamounts and plateaus (1-3). They have been systematically investigated over several decades because of their strategic and critical metals of interest (Bi, Co, Li, Mo, Nb, Ni, Th, W, Zr, and rare earth elements) (3-8) and their potentials for recording paleoceanographic, depositional, and geological environmental changes (8-11). Ferromanganese nodules and crusts typically occur as layered concretions (12), and their individual sub-layers may have distinct chemical compositions formed via different growth processes (8, 13). Therefore, recent studies have focused on the analysis of their individual layers (5, 14, 15), which requires use of only a small amount of sample rather than bulk sampling.

A variety of analytical techniques have been used for the determination of the elemental concentration in ferromanganese nodules and crusts including atomic absorption spectrometry (16-28), neutron activation analysis (22, 29-31), X-ray fluorescence (3, 32-34), and inductively coupled plasma optical emission spectrometry (5, 10, 14, 15, 26, 35, 36). Since the 1990s, inductively coupled plasma mass spectrometry (ICP-MS) has become one of the most powerful techniques used to determine the elemental

ABSTRACT

A method has been developed for the determination of minor, trace, and rare earth elements in ferromanganese nodules and crusts using a novel closed digestion bomb with ICP-MS. This bomb has a double inner arc seal design providing an effective acid circulation, and the upper part of the inner tube plugs tightly into the top of the lower part which prevents any leakage of the acid. The accuracy and precision of the analytical method was tested by analyzing four nodule reference materials. The results agreed to within $\pm 5\%$ for about 34 of 38 elements studied, for which certified or literature values were available. The precision was better than $\pm 5\%$. This method was applied to the analysis and research of ferromanganese nodule and crust samples obtained from the Gagua Ridge and the Northern South China Sea.

composition in ferromanganese nodules and crusts (37-49) due to its high sensitivity, large dynamic linear range and multi-element capabilities, which are superior to most conventional techniques (50-60). Since the technique requires samples in their dissolved form, considerable effort is required to develop simpler and more rapid sample preparation procedures. A number of different digestion procedures for ferromanganese nodules and crusts have been reported in the literature with the majority of them relying on tradi-

tional hot plate digestion and using a combination of various acids, such as HCl-HNO₃ (44), HCl-HNO₃-HF (8, 15, 35, 42, 47, 61-63), HCl-HNO₃-HF-H₂O₂ (38), HNO₃-HF-HClO₄-aqua regia (7, 9, 33, 48), HNO₃-HF-HClO₄ (5), HCl-HNO₃-HF-HClO₄ (32, 41, 44, 65, 66), and HCl-HNO₃-HF-HClO₄-aqua regia (34) in a Teflon[®] vessel, followed by ICP-MS analysis. The use of large volumes of acids or a combination of various acids, or multiple evaporation and dissolution steps, carries the risk of contamination, precipitation losses and spectral interference. Therefore, the analytical requirements for an optimal digestion procedure include accurate and precise data for as many elements as possible, use of small sample size, and provide high sample throughput. A high-pressure digestion technique has been generally applied (38, 42, 67-69). However, acid leakage often occurs during the digestion process, which may leave undissolved residue.

In this study, the traditional high-pressure digestion technique has been improved by using a corrosive-resistant digestion bomb with a double inner arc seal design. The bomb has a tight seal and offers effective circulation of the acid during the digestion process. A small amount of the ferromanganese nodule and crust sample can be digested directly at high temperature and pressure, which speeds up the digestion process and improves the dissolution effect. This sample digestion method is practical and simple, and can deal with 100 sam-

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ples simultaneously. It was successfully applied to the analysis and study of ferromanganese nodule and crust samples obtained from the Gagua Ridge and the Northern South China Sea (8, 63).

EXPERIMENTAL

Instrumentation

An ELAN® DRCII™ ICP-MS (PerkinElmer, Inc., Shelton, CT, USA) was used for sample analysis at the Institute of Oceanology, Chinese Academy of Sciences. The instrumental parameters used for the determination of minor, trace, and rare earth elements are listed in Table I. The detected isotopes were as follows: ^7Li , ^{45}Sc , ^{51}V , ^{52}Cr , ^{59}Co , ^{60}Ni , ^{65}Cu , ^{66}Zn , ^{85}Rb , ^{86}Sr , ^{89}Y , ^{90}Zr , ^{93}Nb , ^{98}Mo , ^{114}Cd , ^{133}Cs , ^{135}Ba , ^{178}Hf , ^{181}Ta , ^{182}W , ^{208}Pb , ^{209}Bi , ^{232}Th , ^{238}U and ^{139}La , ^{140}Ce , ^{141}Pr , ^{146}Nd , ^{147}Sm , ^{151}Eu , ^{160}Gd , ^{159}Tb , ^{163}Dy , ^{165}Ho , ^{166}Er , ^{169}Tm , ^{172}Yb and ^{175}Lu . ^{187}Re was used as an internal standard. The background counts for the 2% HNO_3 solutions were normally <2 cps.

TABLE I
Instrumental Operating
Parameters Used for
ICP-MS Analysis

Parameters	Value
RF power	1250 W
Plasma gas	15 L min ⁻¹
Aux gas	1.20 L min ⁻¹
Nebulizer gas	0.80 L min ⁻¹
Sweeps	10
Readings	1
Replicates	3
Scan mode	Peak hopping
Channel	
dwell time per sweep	100 ms
Sampling cone (Pt)	1.10 mm
Skimmer cone (Pt)	0.90 mm
$^{156}\text{CeO}/^{140}\text{Ce}$ ratio	2.87%
$\text{Ba}^{++}/\text{Ba}^{+}$ ratio	1.13%

Reagents and Standards

A 10 mg L⁻¹ multi-element mixed standard solution and 10 mg L⁻¹ REE standard solution (PerkinElmer, Inc.) were used and diluted with 2% HNO_3 to 1, 5, 10, and 100 ng mL⁻¹, respectively. A 1000 mg L⁻¹ Re standard solution (Environmental Express, USA) was diluted to 10 µg L⁻¹ with 2% HNO_3 and used as an internal standard. The reagents used were ultrapure HNO_3 (J. T. Baker, USA), and electronic industry-grade HF and HCl. Distilled water (18.2 MΩ·cm grade) was obtained using an ULTRA IONIC ultrapure water system (ELGA, UK). Four certified manganese nodule reference samples (GBW07295, GBW07296, NOD-A-1, and NOD-P-1) were obtained from the National Research Center for Geoanalysis, Chinese Academy of Geological Sciences, and the United States Geological Survey (USGS).

Laboratory Ware

A screw-top PTFE-lined, corrosive-resistant digestion bomb with a volume of ~15 mL was used for this study (Figure 1). The upper part of the inner tube plugs into the top of the lower part, and the axial cross-section of the inner tube is oval. The inner tube was pre-cleaned with 10% HNO_3 and heated to boiling for about 12 hours at 120 °C on

an electro-thermal plate, then rinsed with DI water.

Sample Preparation

A 40 mg powdered sub-sample was weighed into the PTFE bombs and HF (0.5 mL), HNO_3 (0.5 mL), and HCl (1.5 mL) were added. The sealed bombs were then placed in an electric oven at 180 °C for 12 hours. After cooling, the bombs were heated on a hot plate to evaporate to dryness, after which HNO_3 (1 mL) and water (1 mL) were added. The bombs were re-sealed and placed in an electric oven at 150 °C for about 12 hours to dissolve the residue. After cooling, the sample was diluted by a factor of ~1000 using 2% HNO_3 prior to measuring the elemental composition by ICP-MS.

RESULTS AND DISCUSSION

Method Efficiency

The advantage of the corrosive-resistant digestion bomb is its double inner arc seal design, which allows the evaporating acid from the top of the inner tank to the bottom without clinging onto the tank wall, thus providing an effective circulation. The upper and lower parts of the inner tank couple tightly, and the double inner arc seal design ensures a tight seal as

Fig. 1. Sketch of the corrosive-resistant digestion bomb (cited from reference 70).

the pressure increases. This prevents any acid from leaking and avoids incomplete digestion. In comparison to previously reported methods where the ferromanganese nodule and crust samples are pretreated (Table II), the present method requires a small amount of sample (50 mg). This will be of particular value when studying elemental distribution in the layers of the nodules and crusts, thus provide information on the growth process and the change in environmental conditions in the sampling region. The advantages of the present method include shorter digestion time than previously reported methods requiring 100 mg samples (9, 64, 47), reduced number of evaporation (only once), and consumes a small amount of acids (0.5 mL of HF, 0.5 mL of HNO₃ and 1.5 mL of HCl to digest a 40 mg sample completely) in comparison to the method which conducts an evaporation (45, 65), avoids risk of contamination during repeated evaporations (7, 9, 38, 42, 44, 47, 64) and is carried by use of large volumes of acids.

The microwave-assisted digestion method (62) has the advantages of shorter digestion time and the ability to measure more than 40 elements simultaneously; however, it requires careful ventilation in a fume hood and extensive washing procedures. In contrast, this novel digestion bomb is safer and more reliable, and the digestion vessels require only a simple washing procedure. The smaller volume of the PTFE tank and the oval axial cross-section design prevent the evaporating acid to cling onto the tank wall which happened while using the larger vessels (9, 42, 64). In addition, the use of an analogue detection mode increases the detection range of element concentrations, allowing 38 elements in the ferromanganese nodule samples to be measured at the same time without need for dilution by different

factors (62). In addition, up to 100 samples can be prepared simultaneously.

Interference and Correction

The ferromanganese nodules and crusts mainly consist of iron (Fe) (~6-7%) and manganese (Mn) (~26-30%) (14). Thus, interference from Fe and Mn should be considered. Iron has four stable isotopes at the nominal masses of 54, 56, 57, and 58, with a representative isotopic composition of 5.8, 91.72, 2.2, and 0.28%, respectively; manganese only occurs as ⁵⁵Mn. Most spectral interferences arise from iron, manganese, oxygen, and argon polyatomics. The mass spectra observed for the 100 mg L⁻¹ iron and manganese standard solutions indicated significant interference for ⁷⁰Zn (interference by ⁵⁴Fe¹⁶O), ⁷⁰Ge (interference by ⁵⁴Fe¹⁶O), ⁷²Ge (interference by ⁵⁴Fe¹⁸O and ⁵⁶Fe¹⁶O), ⁷³Ge (interference by ⁵⁷Fe¹⁶O), ⁷⁴Ge (interference by ⁵⁸Fe¹⁶O), ⁷¹Ga (interference by ⁵⁵Mn¹⁶O), ⁹²Zr (interference by ⁵⁴Fe³⁸Ar), ⁹⁴Zr (interference by ⁵⁴Fe⁴⁰Ar), ⁹⁶Zr (interference by ⁵⁶Fe⁴⁰Ar and ⁵⁸Fe³⁸Ar), ⁹²Mo (interference by ⁵⁴Fe³⁸Ar), ⁹⁴Mo (interference by ⁵⁴Fe⁴⁰Ar), ⁹⁵Mo (interference by ⁵⁵Mn⁴⁰Ar), ⁹⁶Mo (interference by ⁵⁶Fe⁴⁰Ar and ⁵⁸Fe³⁸Ar), ⁹⁷Mo (interference by ⁵⁷Fe⁴⁰Ar), and ⁹⁸Mo (interference by ⁵⁸Fe⁴⁰Ar).

The interference coefficient correction method does not reduce or eliminate the interferences; therefore, the concentration of Ga and Ge in the ferromanganese nodule and crust sample cannot be determined accurately using the proposed method. In addition, ⁶⁶Zn and ⁹⁰Zr were selected for analysis, thus, avoiding the poly-atomic interferences. The correction formula $^{98}\text{Mo}_{\text{true}} = ^{98}\text{Mo}_{\text{analyzed}} - 0.00618^{54}\text{Fe}$ was used to correct the interference. During the analysis of the ferromanganese nodule and crust samples, the interference by Ba-oxides on the REEs was significant, i.e., of

¹³⁶Ba¹⁶O on ¹⁵²Sm, ¹³⁵Ba¹⁶O on ¹⁵¹Eu, and ¹³⁷Ba¹⁶O on ¹⁵³Eu. ¹⁴⁷Sm was selected for analysis, thus, avoiding the interference by ¹³⁶Ba¹⁶O. The BaO⁺/Ba⁺ ratio (1.873%), obtained by the determination of a 10 mg L⁻¹ Ba standard solution, and the correction formula $^{151}\text{Eu}_{\text{true}} = ^{151}\text{Eu}_{\text{analyzed}} - 0.001873 \times ^{135}\text{Ba}$ was used to correct the interference by the Ba-oxides on Eu.

Calibration Curves and Limits of Detection

Prior to determining the elemental composition, the ICP-MS instrument was optimized using a tuning solution containing 1 ng mL⁻¹ Be, Co, In, Mg, Ce, Pb, and U, and 10 ng mL⁻¹ Ba, then calibrated using four synthetic element standard solutions of 1, 5, 10, and 100 ng mL⁻¹ in 2% HNO₃. A Re internal standard (10 ng mL⁻¹) was added online using a polypropylene T-connector to assess the signal drift of the instrument. It is possible to acquire analytical signals using both ion counting and analogue detection modes with automatic switching between modes at an ion current of ~3 Mcps. This allows increased dynamic range of the instrument to about nine orders of magnitude and thus, the contents of the minor and trace elements in the ferromanganese nodule and crust samples can be obtained simultaneously. The method's detection limits were defined as three times the standard deviation for 10 preparation blanks assuming a dilution factor of 1000 (Table III). The limits of detection (3σ) ranged from the sub-ng g⁻¹ level up to a few μg g⁻¹. The precision was better than ±5%.

Analysis of Reference Materials and Application of the Method

In order to validate the applicability and suitability of this method, four certified manganese nodule reference samples (GBW07295, GBW07296, NOD-A-1 and NOD-P-1)

TABLE II
Methods of Digestion Prior to ICP-MS Analysis

No. of Elements- by ICP-MS	Sample Mass (mg)	Reagent (mL)						Sample Preparation	Digestion Time	Reference
		HCl	HNO ₃	HF	HCl ₄	H ₂ O ₂	aqua regia			
34	100	10	10	10	2	5		Kept overnight for digestion → heated for about 1 h → evaporated to near dryness → repeat addition of acids and evaporation again → dissolved the residue → removed excess of peroxide by gentle boiling → cooled and made up to 100 mL volume	Overnight + 1 h + evaporation twice	(64)
16	50	1	>3	2		0.5		Digested in a pressure digestion system for 8 h at 180°C → evaporated to dryness → dissolved and fumed off again → dissolved the residue in the pressure digestion system for another 8 h at 18 °C → cooled and made up to 100 mL volume	16 h + evaporation twice	(38)
More than 40 elements with accuracy within ±10%	50	0.5	1.5	0.1				Heated at 325 W power for 30 min → cooled to room temperature → transferred to a test tube → rinsed the microwave vessel and combined the rinse with the digestion solution → made up to 10 mL → diluted according to the determination requirement	30 min	(62)
31	100		>5	√	√		4	Digested in 12 or 25 mL Teflon PFA screw-cap beakers → heated for 3-5 days at 16°C → progressively evaporated at 130°C for 12 h, 160°C for 6 h, and 190°C until dryness → dissolved the residue for 12 h at 160°C → evaporated again → dissolved the residue and diluted to 1:1000 by mass	3-5 days	(9)
23	50	9	1	1				Digested in a 30 mL PTFE pressure vessels for 12 h at 180°C → evaporated to incipient dryness at 120°C and repeated 3 times → dissolved residue and diluted to 1:1000 by mass	12 h + evaporation three times	(42)
10	20	20	5					Digested in a Teflon vial → evaporated to dryness at 80 °C → dissolved and then evaporated to dryness at 80 °C and this operation was repeated once → dissolved residue by 10 mL HCl	Digestion + evaporation three times	(44)
40	50	1	8	2	0.8			Digested overnight at 130 °C → cooled and progressively evaporated at 110°C for 12 h, 160°C for 3 h, and 190 °C until dryness dissolved the residue and then diluted	Overnight + evaporation once	(45)
29	100	>4	√	√				Digested in a Teflon bottle for 24 h at 120°C → extracted by centrifuge and digested for 48 h at 120°C → evaporated and remixed with the previously digested phase → evaporated again → dissolved the residue and made up to 10 mL	72 h + evaporation twice	(47)

√ = Acid was used, but there was no volume value in the reference.

(cont'd)

TABLE II (cont'd)
Methods of Digestion Prior to ICP-MS Analysis

No. of Elements- by ICP-MS	Sample Mass (mg)	Reagent (mL)						Sample Preparation	Digestion Time	Reference
		HCl	HNO ₃	HF	HCl ₄	H ₂ O ₂	aqua regia			
39	20	3	4	6.3	2.7			Digested in a Teflon beaker → heated until it became a paste → added HCl and evaporated to dryness → dissolved the residue and warmed for 5-10 min → diluted to 100 mL	Digestion + evaporation once	(65)
19	50	1	6	4	0.8		2	Digested in a 12 mL Teflon PFA vial for 2 h at 130 °C → progressively evaporated at 110°C for 12 h, 160°C for 6 h, and 190°C until dryness → dissolved the residue for 12 h at 90°C → evaporated again at 110°C → dissolved the residue and diluted to 1:4000 gravimetrically	2 h + evaporation twice	(7)
38	40	1.5	0.5	0.5				Digested in a PTFE bomb for 12 h at 180°C → evaporated to dryness → dissolved the residue in a PTFE bomb 150 °C for 12 h → cooled and diluted to 1:1000 by mass	24 h + evaporation once	This study

TABLE III
Detection Limits (µg g⁻¹)

Element	DL	Element	DL
Li	0.019	Pr	0.003
Sc	0.003	Nd	0.011
V	0.086	Sm	0.005
Cr	0.013	Eu	0.001
Co	0.124	Gd	0.004
Ni	0.878	Tb	0.0009
Cu	1.131	Dy	0.002
Zn	0.522	Ho	0.0009
Rb	0.007	Er	0.002
Sr	0.070	Tm	0.0009
Y	0.007	Yb	0.003
Zr	0.037	Lu	0.0009
Nb	0.007	Hf	0.001
Mo	0.061	Ta	0.001
Cd	0.006	W	0.010
Cs	0.0002	Pb	0.044
Ba	0.263	Bi	0.001
La	0.009	Th	0.005
Ce	0.025	U	0.001

DL = Detection Limit.

were analyzed repeatedly, and the results are listed in Table IV. For NOD-A-1 and NOD-P-1, 18 out of 38 element concentrations were certified values, whereas other data were referenced from previously reported studies (62). Our data compare well with the values for the reference materials of GBW07295, GBW07296, NOD-A-1, and NOD-P-1, and showed that the agreement was better than 5% for 34 elements. This sample preparation method using a novel digestion bomb prior to ICP-MS analysis improves the determination of minor, trace and rare earth elements in ferromanganese nodules and crusts, and was applied to the analysis of the ferromanganese nodule and crust samples obtained from the Gagua Ridge and the Northern South China Sea (8, 63).

CONCLUSION

The proposed method provides quantitative information on 38 elements in ferromanganese nodules and crusts with an accuracy better than ±5% for the majority of the

elements studied. This method has the advantages of requiring a small amount of sample and acid as well as less evaporation, with a precision better than ±5%. This method was successfully applied to the analysis of ferromanganese nodule and crust samples obtained from the Gagua Ridge and Northern South China Sea.

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TABLE IV
Results for GBW07295, GBW07296, NOD-A-1, and NOD-P-1, and
Comparison With Certified and Published Data (concentrations in $\mu\text{g g}^{-1}$)

Element	GBW07295(n=10)			GBW07296(n=10)			NOD-A-1(n=10)			NOD-P-1(n=10)		
	Certified	Mean	RSD%	Certified	Mean	RSD%	Certified	Mean	RSD%	Certified	Mean	RSD%
Li	78±5	79.3	4.2	205±17	201	1.9	76.1±0.8*	72.0	1.5	140±1*	141	3.4
Sc	13±1	13.2	3.5	9.4±1.0	9.30	2.1	12.4±0.3*	12.2	1.3	9.70±0.10*	9.32	0.6
V	456±49	453	4.9	442±51	454	1.1	770±6	779	0.9	570±10	577	0.9
Cr	17±3	17.1	4.2	18±4	16.1	4.5	20.9±0.7	20.4	2.5	13.3±0.01*	14.9	4.3
Co	2900±200	3013	4.6	1700±100	1766	1.3	3110±11	3327	0.8	2240±11	2387	1.2
Ni	10200±800	10752	4.2	15500±700	15760	1.5	6360±24	6536	0.8	13400±64	13369	1.0
Cu	6900±400	7191	4.0	13600±500	14390	1.5	1100±10	1143	1.3	11500±49	11731	0.9
Zn	918±66	907	4.0	1600±100	1506	2.2	590±5	584	1.2	1600±6	1630	1.0
Rb	16±2	16.7	4.4	17±3	17.2	1.2	10.6±0.1*	10.4	1.4	23.7±0.7*	24.9	2.2
Sr	869±74	854	2.3	561±62	550	1.8	1750±14	1737	1.2	680±3	689	1.9
Y	133±6	140	1.6	84±3	90.2	1.6	120±1*	117	1.1	90.0±0.6*	92.2	1.7
Zr	618±58	616	4.4	256±31	253	1.7	310±3*	310	0.9	280±1*	285	1.4
Nb	48±8	49.8	3.4	21±3	20.1	1.1	43.1±1.1*	43.9	0.9	21.3±0.1*	21.9	1.6
Mo	473±33	467	4.6	622±37	607	1.6	448±9	457	2.4	760±4	739	4.2
Cd	10±2	10.1	1.5	23±3	22.2	1.2	7.50±0.16*	7.87	1.1	22.6±0.3*	23.3	2.1
Cs	0.84±0.08	0.84	1.6	1.2±0.3	1.23	1.5	0.61±0.01*	0.60	1.8	1.80±0.01*	1.83	2.0
Ba	1800±100	1781	1.9	2400±200	2368	1.4	1670±31	1665	0.7	3350±28	3436	2.1
La	184±22	181	1.4	96±10	96.0	1.7	120	119	0.8	104	110	1.5
Ce	620±60	626	1.2	249±21	256	2.0	730	721	1.5	290	293	1.6
Pr	49±5	47.0	1.8	29±2	30.0	1.7	25.0±0.01*	24.8	1.1	31.0±0.2*	33.4	1.6
Nd	198±22	199	1.8	121±15	122	1.5	94	93.9	1.4	120	120	1.7
Sm	46±5	47.9	2.1	31±2	31.9	1.3	21	21.3	1.1	30	30.8	1.4
Eu	11±1	11.2	1.7	7.6±0.7	7.33	3.0	5	5.18	1.7	7.5	7.83	2.5
Gd	48±7	47.0	2.1	28±4	29.1	2.0	26	25.6	1.4	28	29.8	1.4
Tb	7.6±0.8	7.38	2.8	4.6±0.5	4.66	1.3	4.00±0.07*	4.04	1.0	4.90±0.02*	4.92	1.9
Dy	42±3	38.5	2.2	27±3	25.3	1.0	23	22.1	1.2	27	26.2	1.8
Ho	8.2±0.6	7.80	2.2	5.1±0.3	5.03	1.3	5.00±0.01*	5.00	1.1	5.00±0.01*	5.19	1.4
Er	21±2	20.0	2.4	13±1	12.7	1.2	12	12.7	1.2	12	12.2	1.5
Tm	3.1±0.4	3.16	2.6	1.9±0.1	1.97	1.5	2.00±0.06*	2.06	1.0	1.90±0.02*	1.93	2.3
Yb	20±2	19.1	2.6	12±1	12.1	1.5	14	13.6	0.9	13	12.5	2.0
Lu	2.9±0.4	2.89	2.1	1.8±0.2	1.82	1.7	2.2	2.11	1.6	1.8	1.82	1.5
Hf	10±2	9.93	2.3	3.9±0.5	3.83	2.1	5.80±0.66*	5.68	1.9	4.20±0.02*	4.11	1.9
Ta		0.51	4.8		0.29	2.2	0.76±0.03*	0.78	2.1	0.33±0.01*	0.34	1.7
W	67±5	65.5	1.7	61±5	62.9	1.3	87.0±0.8*	87.8	0.8	57.8±1.1*	56.7	0.7
Pb	709±44	677	1.1	328±33	319	1.2	846	876	1.1	560±6	573	1.7
Bi	15±1	14.9	1.4	5±1	5.09	1.7	10.2±0.1*	10.0	1.2	5.80±0.40*	5.72	3.2
Th	26±4	22.8	1.2	15±2	14.3	1.8	25.1±0.6*	23.0	1.5	16.7±0.2*	15.8	1.8
U	6.2±1.0	6.04	1.5	3.8±0.7	3.70	1.8	7.00±0.08*	7.22	1.5	4.00±0.04*	3.94	2.5

* Data from Reference (62).

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