ELEMENTAL DISTRIBUTION

Overview

Y. Nozaki, University of Tokyo, Tokyo, Japan

Copyright © 2001 Academic Press

doi:10.1006/rwos.2001.0402

Introduction

More than 97% of liquid water on the earth exists in the ocean. The ocean water contains approximately 3.5% by weight of dissolved salt. What is the elemental composition of the salts, how does it vary from place to place and with depth, and why? These are fundamental questions for which chemical oceanographers have sought answers. Despite more than a hundred years of intense investigation by modern chemical oceanography, the answers have not been fully elucidated. Nevertheless, we are now approaching complete understanding of the chemical composition of sea water and its variability in the ocean.

Historical Review

By the late nineteenth century it was well-established that the major components of sea water are extremely constant in their relative abundance, and comprise some ten constituents including Cl^-, Na^+, Mg^{2+}, SO_4^{2-} (*see* **Conservative Elements**). The analytical results reported by W. Dittmar in 1884 for waters collected during the British RMS Challenger Expedition (1872–1876) from the world's oceans were almost the same as today's values. The constancy of major chemical composition has led oceanographers to define 'salinity' as a fundamental property together with temperature to calculate the density of sea water. It was routine for classic physical oceanographers to titrate sea water for chloride (plus bromide) ion with silver nitrate standard solution, until the mid 1960s when salinity could be determined more practically by measurement of conductivity.

On the other hand, for minor elements, there has been little information gained since the establishment of major chemical composition of sea water. Measurements of trace constituents in sea water are difficult because of their very low abundance. There was a clear tendency for the reported concentrations of many trace elements to become lower and lower as time elapsed. This trend was, of course, not real but an artifact. It is a famous story that, to aid Germany's national deficit after World War I, the Nobel Prize winning chemist F. Haber attempted to recover gold from sea water which according to the current literature occurred at about 5 mg m^{-3}. He completely failed however, but, after long and rigorous examination, he found that the concentration was $\sim$1000 times less than that expected. Incidentally, Haber's value of gold concentration was two orders of magnitude higher compared to later reports (**Table 1**). Another good example may be found in the measurements of lead in sea water by Patterson and his associates (*see* **Anthropogenic Trace Elements in the Ocean**). The vertical profile of Pb in the North Pacific obtained by Schaule and Patterson in 1981 had concentrations about two orders of magnitude lower than those reported earlier ($\sim$1970) by the same workers although their 1981 values are believed to be accurate and real (**Table 1**).

Technical Challenge

It is now known that the most obvious reason for these trends is the continuous improvement in removing sources of contamination during sampling, handling, storage, and analysis. Significant efforts and advances in such field and laboratory techniques had been made until the GEOSECS (Geochemical Ocean Section Study) program started at around 1970. For example, polyvinyl chloride Niskin-bottle multisampling system together with CTD (conductivity–temperature–depth) sensors has routinely been employed in the hydrocasts, replacing the serial Nansen (metallic) bottle sampling method most widely used prior to that time. Yet, this was not enough for many trace metals except for barium, and an intercalibration exercise made in the early stage of the program did not produce any congruent results between laboratories. It was a significant and wise decision of the GEOSECS leaders that they focused on radionuclides and stable isotopes, which are almost free from contamination, and did not get involved in trace element geochemistry. Obviously, without having the real concentration data, any arguments that might be built upon them would be meaningless.

Obtaining clean (uncontaminated) water samples from various depths of the ocean is of prime importance in the study of trace metals. In this

Table 1 Estimated mean oceanic concentrations of the elements

Atomic number	*Element*	*Species*	*Type of distribution*[a]	*Oceanic mean concentration* (ng kg^{-1})
1	Hydrogen	H_2O	—	—
2	Helium	Dissolved gas	c	7.6
3	Lithium	Li^+	c	180×10^3
4	Beryllium	$BeOH^+$	s + n	0.21
5	Boron	$B(OH)_3$	c	4.5×10^6
6	Carbon	Inorganic ΣCO_2	n	27.0×10^6
7	Nitrogen	Dissolved N_2	c	8.3×10^6
		NO_3^-	n	0.42×10^6
8	Oxygen	Dissolved O_2	inverse n	2.8×10^6
9	Fluorine	F^-	c	1.3×10^6
10	Neon	Dissolved gas	c	160
11	Sodium	Na^+	c	10.78×10^9
12	Magnesium	Mg^{2+}	c	1.28×10^9
13	Aluminum	$Al(OH)_3^0$	s	30
14	Silicon	$H_4SiO_4^0$	n	2.8×10^6
15	Phosphorus	$NaHPO_4^-$	n	62×10^3
16	Sulfur	SO_4^{2-}	c	898×10^6
17	Chlorine	Cl^-	c	19.35×10^9
18	Argon	Dissolved gas	c	0.62×10^6
19	Potassium	K^+	c	399×10^6
20	Calcium	Ca^{2+}	almost c	412×10^6
21	Scandium	$Sc(OH)_3^0$	(s + n)	0.7
22	Titanium	$Ti(OH)_4^0$	s + n	6.5
23	Vanadium	$NaHVO_4^-$	almost c	2.0×10^3
24	Chromium	CrO_4^{2-}(VI)	r + n	210
		$Cr(OH)_3^0$ (III)	r + s	2
25	Manganese	Mn^{2+}	s	20
26	Iron	$Fe(OH)_3^0$	s + n	30
27	Cobalt	$Co(OH)_2^0$?	s	1.2
28	Nickel	Ni^{2+}	n	480
29	Copper	$CuCO_3^0$	s + n	150
30	Zinc	Zn^{2+}	n	350
31	Callium	$Ga(OH)_4^-$	s + n	1.2
32	Germanium	$H_4GeO_4^0$	n	5.5
33	Arsenic	$HAsO_4^{2-}$(V)	r + n	1.2×10^3
		$As(OH)_3^0$(III)	r + s	5.2
34	Selenium	SeO_4^{2-}(VI)	r + n	100
		SeO_3^{2-}(IV)	r + n	55
35	Bromine	Br^-	c	67×10^6
36	Krypton	Dissolved gas	c	310
37	Rubidium	Rb^+	c	0.12×10^6
38	Strontium	Sr^{2+}	almost c	7.8×10^6
39	Yttrium	YCO_3^+	n	17
40	Zirconium	$Zr(OH)_5^-$	s + n	15
41	Niobium	$Nb(OH)_6^-$	almost c	0.37
42	Molybdenum	MoO_4^{2-}	c	10×10^3
43	Technetium	TcO_4^-	—	—
44	Ruthenium	RuO_4^-	?	< 0.005
45	Rhodium	$Rh(OH)_3^0$?	n	0.08
46	Palladium	$PdCl_4^{2-}$?	n	0.06
47	Silver	$AgCl_2^-$	n	2
48	Cadmium	$CdCl_2^0$	n	70
49	Indium	$In(OH)_3^0$	s	0.01
50	Tin	$SnO(OH)_3^-$	s	0.5
51	Antimony	$Sb(OH)_6^-$	s?	200
52	Tellurium	$Te(OH)_6^0$	r + s	0.05
		$TeO(OH)_3^-$	r + s	0.02
53	Iodine	IO_3^-	almost c	58×10^3
		I^-	(r + s)	4.4

Table 1 *Continued*

Atomic number	*Element*	*Species*	*Type of distribution*[a]	*Oceanic mean concentration* (ng kg^{-1})
54	Xenon	Dissolved gas	c	66
55	Cesium	Cs$^+$	c	306
56	Barium	Ba^{2+}	n	15×10^3
57	Lanthanum	LaCO$_3^+$	n	5.6
58	Cerium	Ce(OH)$_4^0$	s	0.7
59	Praseodymium	PrCO$_3^+$	n	0.7
60	Neodymium	NdCO$_3^+$	n	3.3
61	Promethium	—	—	—
62	Samarium	SmCO$_3^+$	n	0.57
63	Europium	EuCO$_3^+$	n	0.17
64	Gadolinium	GdCO$_3^+$	n	0.9
65	Terbium	TbCO$_3^+$	n	0.17
66	Dysprosium	DyCO$_3^+$	n	1.1
67	Holmium	HoCO$_3^+$	n	0.36
68	Erbium	ErCO$_3^+$	n	1.2
69	Thulium	TmCO$_3^+$	n	0.2
70	Ytterbium	YbCO$_3^+$	n	1.2
71	Lutetium	LuCO$_3^+$	n	0.23
72	Hafnium	Hf(OH)$_5^-$	s + n	0.07
73	Tantalum	Ta(OH)$_5^0$	s + n	0.03
74	Tungsten	WO$_4^{2-}$	c	10
75	Rhenium	ReO$_4^-$	c	7.8
76	Osmium	OsO$_4^0$	almost c	0.009
77	Iridium	Ir(OH)$_3^0$	s?	0.00013
78	Platinum	PtCl$_4^{2-}$	c	0.05
79	Gold	AuOH(H$_2$O)^0	c	0.02
80	Mercury	HgCl$_4^{2-}$	(s + n)	0.14
81	Thallium	Tl$^+$	c	13
82	Lead	PbCO$_3^0$	anth. + s	2.7
83	Bismuth	Bi(OH)$_3^0$	s	0.03
84	Polonium	PoO(OH)$_3^-$	s	—
85	Astatine	—	—	—
86	Radon	Dissolved gas	c	—
87	Francium	Fr$^+$	—	—
88	Radium	Ra^{2+}	n	0.00013
89	Actinium	AcCO$_3^+$	n	—
90	Thorium	Th(OH)$_4^0$	s	0.02
91	Protactinium	PaO$_2$(OH)^0	s	—
92	Uranium	UO$_2$(CO$_3$)$_3^{4-}$	c	3.2×10^3
93	Neptunium	NpO$_2^+$	—	—
94	Plutonium	PuO$_2$(CO$_3$)(OH)$^-$	(r + s)	—
95	Americium	AmCO$_3^+$	(s + n)	—

[a] c, conservative; n, nutrient-like; s, scavenged; r, redox sensitive; anth., anthropogenic.

regard, various types of sampling bottles have been developed both domestically and commercially. They include the Cal-Tech Patterson sampler, modified Go-Flo bottles, and lever-action or X-type Niskin bottles. None of them are easy to keep clean and handle properly, and experience is needed in their operation depending on the type of bottle. Hydrowire is also important, since normal steel wire has rust and grease that can easily contaminate the water. To avoid this, some workers use plastic Kevler line and others use stainless-steel wire or a titanium armored cable.

With the rapid growth of semiconductor industries from the early 1970s, clean laboratory techniques also become more popular in the field of marine chemistry and helped considerably to reduce contamination from reagents, containers, and dust in the room atmosphere. Real oceanic concentrations of trace metals are so low that conventional analytical techniques prior to 1970 were not normally sensitive enough to detect them except in polluted or some coastal waters. Thus, significant efforts were also devoted to developing more sensitive and reliable methods using atomic absorption spectrophotometry, chemiluminesence detection, isotope dilution mass spectrometry, etc. As a result, in the late 1970s, data of some transition metals, like Cd, Cu, and Ni were obtained by the Massachusetts Institute of Technology group and soon after confirmed by others using different or modified methods. Their oceanic profiles were quite consistent with known biogeochemical cycling and scavenging processes in the ocean. Thus, these features have often been referred as 'oceanographically or geochemically consistent' distribution by subsequent workers. Since then, growing numbers of publications describing the oceanic distributions of trace elements in sea water based on modern technologies have appeared year by year.

Oceanic Profiles

It is now possible to compile, with reasonable confidence, the vertical profiles in the form of Periodic chart (**Figure 1**), where the data from the North Pacific have been chosen since physical processes that affect the distribution are relatively simple and well documented. **Figure 1** is an updated version of the original, including new data for Nb, Ta, Hf, Os, Ag, and rare earth elements. Now, there remains only one element, Ru on which no real data have been reported (*see* **Platinum Group Elements and their Isotopes in the Ocean**). However, confirmation is needed for many elements, including Sn, Hg, Rh, Pd, Au, Ir, Pt, etc., since they are based on a single study or on controversial results by different workers. Nevertheless, it is clear that the long-standing dream to establish the chemical composition of sea water is about to become a reality.

Trace elements follow one or more of the categories which are described below.

Conservative type Some of the trace elements such as U, W, and Re form stable ionic species, $UO_2(CO_3)_2^{2-}$, WO_4^{2-}, and ReO_4^- in sea water. Hence, their oceanic behavior is conservative (follow salinity) and their mean residence times in the ocean are generally long (e.g., $>10^5$ years). There is no significant variation in their concentration between different oceanic basins.

Recycled type (nutrient-like) Many others, e.g., Ni, Cd, Zn, Ge, and Ba, show a gradual increase in their concentration from the surface to deep water, much like nutrients (nitrate, phosphate, and silicate or alkalinity), suggesting their involvement in the biogeochemical cycle of biological uptake in the surface water and regeneration in deep waters. As a result of global ocean circulation, the deep-water concentrations of this type are higher in the Pacific than in the Atlantic.

Scavenged type Trace metals such as Al, Co, Ce, and Bi, show surface enrichment and depletion in deep waters, in contrast to the opposite trend in nutrient types. These elements are highly particle-reactive and are rapidly removed from the water column by sinking particulate matter and/or by scavenging at the sediment–water interface. Their mean oceanic residence times are short ($<10^2$–10^3 years). Interoceanic variations in their concentration can be large (e.g., Atlantic/Pacific concentration ratio $= \sim 40$ for Al) depending on kinetic balance between supply and removal for the specific basins.

Redox-controlled type Elements such as Cr, As, Se, and Te exist in sea water at more than one oxidation state. Their oceanic behavior is strongly dependent on the chemical form. Their reduced states are thermodynamically unstable in normal oxygenated waters but are probably formed through biological mediation. Reduced species can also be formed in anoxic basins, the Black Sea, Cariaco Trench, some fiords, and in organic-rich sediments.

Anthropogenic and transient type Finally, Pb and Pu are good examples of elements whose oceanic distributions are globally influenced by human activities (*see* **Anthropogenic Trace Elements in the Ocean**). Their oceanic distributions are changing with time. Although some others, such as Hg, Sn, Cd, and Ag, are deduced to be similarly influenced, their transient nature has not yet been proven through direct observation.

Particle Association and Speciation

One of the important features of **Figure 1** is that the concentration, even for trace elements, varies fairly smoothly and continuously with depth. This casts doubt on some erratic and highly discontinuous values unless there are obvious reasons for them, such as hydrothermal influence or difference in the water masses. The data shown in **Figure 1** are largely based on filtered samples and therefore, can be referred as 'dissolved concentration.' For conservative elements, it does not matter whether the water sample is filtered or not, since there is virtually no difference in the analytical results. For most nutrient-type elements, particle association in the open ocean is generally small ($< \sim 5\%$) and therefore, the gross features of unfiltered samples remains the same as dissolved samples. However, filtration becomes important for coastal waters, and certainly

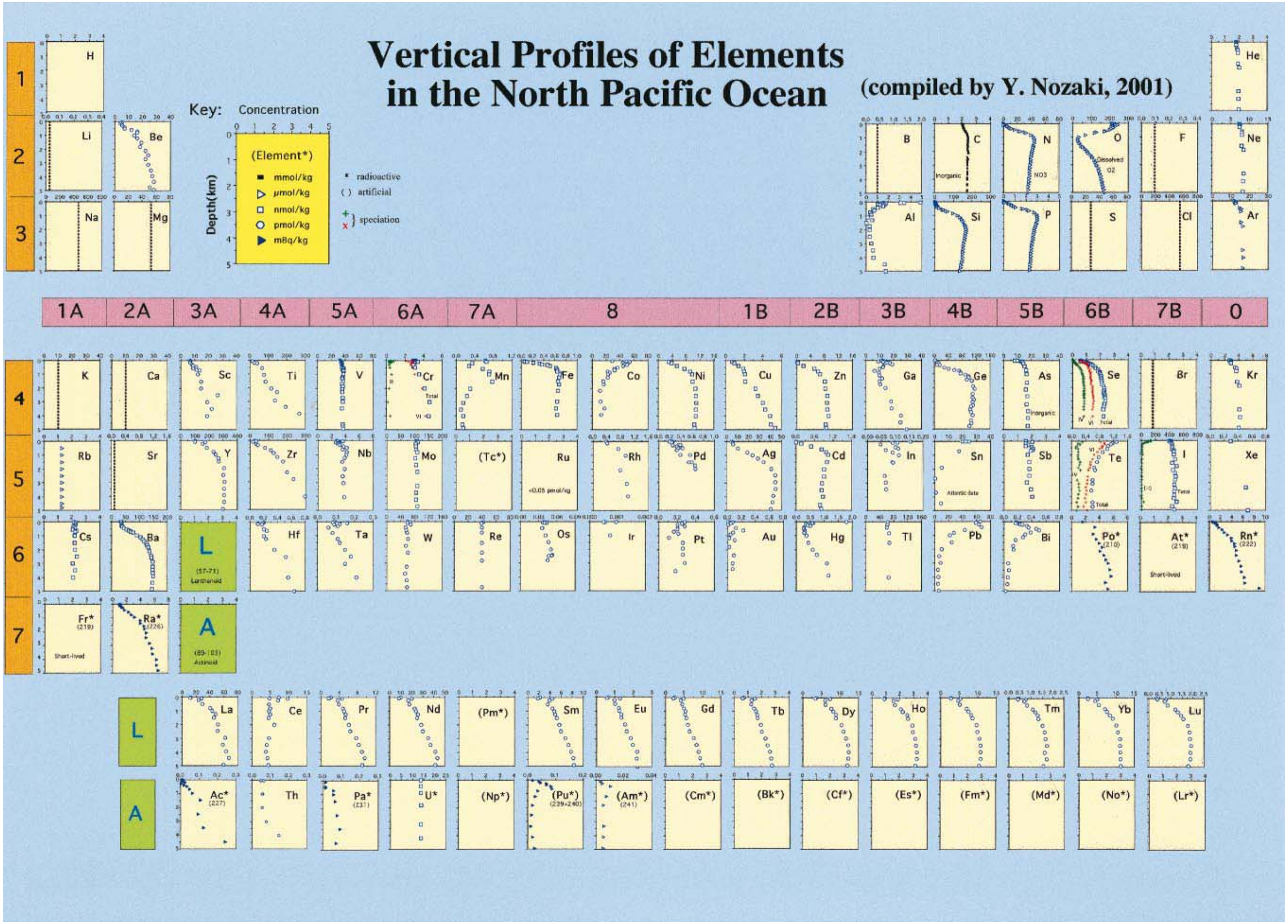

Figure 1 Vertical profiles of elements in the North Pacific Ocean.

for scavenged-type elements in any place, since particle association could easily exceed dissolved concentration. Various types of membrane filters with different pore sizes, generally in the range ~1–0.04 μm, have been used, and, therefore, the so-called 'dissolved' concentration includes different amounts of colloidal form.

Furthermore, ionic species of many trace elements form complexes with ligands in sea water. **Table 1** lists the most probable inorganic species as deduced from thermodynamics. Recently, complexation of heavy metals (e.g., Fe, Zn, Cu, and Co) with organic ligands which occur at nanomolar concentration levels in the surface water has been investigated (*see* **Transition Metals and Heavy Metal Speciation**). These organic complexes are particularly important for understanding the roles of trace elements in plankton biology and metabolism. However, the technologies to detect and separate these metal–organic complexes are not yet available.

Summary

The chemical constituents of sea water show a very wide range in their concentration of more than 15 orders of magnitude, from chlorine ($\sim 0.5\,\mathrm{mol\,kg^{-1}}$) to the least abundant platinum group elements (e.g., $\mathrm{Ir} < \sim 1\ \mathrm{fmol\,kg^{-1}}$). The measurement of trace elements in sea water is extremely difficult for a long time and was not achieved properly for most elements due to large contamination problems in various stages of sampling and analysis. It was only during the last quarter of the twentieth century that those problems were eventually overcome by current efforts of chemical oceanographers. Since then, more and more reliable data have accumulated and now the oceanic distribution is known for almost all the elements. Some of the trace metals, such as Al, and rare earth elements (*see* **Rare Earth Elements and their Isotopes in the Ocean**) serve as useful tracers of water masses in describing hydrographic structures and patterns of ocean circulation. Others, such as Fe, Si, and perhaps Zn, have an essential role in phytoplankton growth and hence affect the global carbon cycle through the 'biological pump.' Resemblance in the oceanic distribution between Cd and phosphorus, and between Ba and alkalinity, provides a basis by which those heavy metals can serve as useful proxies in reconstructing the paleo-oceanographic environment from deep-sea sediment strata.

See also

Anthropogenic Trace Elements in the Ocean. Conservative Elements. Refractory Metals. Transition Metals and Heavy Metal Speciation.

Further Reading

Nozaki Y (1997) A fresh look at element distribution in the North Pacific Ocean. *EOS Transactions*, *AGU* 78: 221.

Li YH (1991) Distribution patterns of elements in the ocean: a synthesis. *Geochimica et Cosmochimica Acta* 55: 3223–3240.

ENSO

See **EL NIÑO SOUTHERN OSCILLATION (ENSO); EL NIÑO SOUTHERN OSCILLATION (ENSO) MODELS**

EQUATORIAL CURRENTS

See **ATLANTIC OCEAN EQUATORIAL CURRENTS; INDIAN OCEAN EQUATORIAL CURRENTS; PACIFIC OCEAN EQUATORIAL CURRENTS**

ESTUARIES

See **ESTUARINE CIRCULATION; GAS EXCHANGE IN ESTUARIES**