Open University Course Team (1989) *Ocean Chemistry and Deep-Sea Sediments*, ch. 2. Oxford: Pergamon.

Redfield AC (1958) The biological control of chemical factors in the environment. *American Scientist* 46: 205–221.

Shaffer G, Bendtsen J and Ulloa O (1999) Fractionation during remineralisation of organic matter in the ocean. *Deep-Sea Research I* 46: 185–204.

Takahashi T, Broecker WS and Langer S (1985) Redfield ratio based on chemical data from isopycnal surfaces. *Journal of Geophysical Research (Oceans)* 90(C4): 6907–6924.

Tyrrell T (1999) The relative influences of nitrogen and phosphorus on oceanic primary production. *Nature* 400: 525–531.

REFRACTORY METALS

K. J. Orians and C. L. Merrin,
The University of British Columbia,
Vancouver, British Columbia, Canada

doi:10.1006/rwos.2001.0285

Introduction

The elements classified as ‘refractory’ here are those that are not readily dissolved in sea water. Their supply to the oceans is low relative to their abundance in the Earth’s crust. In addition, they are rapidly removed from solution by interaction with the surfaces of sinking particles, a process referred to as ‘scavenging.’ This rapid removal means that they are in the oceans for only a short time before being removed to the seafloor. The average time they spend in the oceans, known as the oceanic residence time, ranges from a few tens to a few thousands of years. Both of these factors result in low concentrations in sea water relative to their abundance in the Earth’s crust, a large range of oceanic concentrations, and distributions that typically reflect their sources.

The elements in this category exist as hydroxide species in sea water, mostly as $M(OH)_n^{X-n}$, where M is the metal, X is the oxidation state of the metal, and n is the number of hydroxide ligands in the complex. There is also the possibility that they may exist as organic complexes and/or in association with colloidal phases (particles $\leqslant \mu m$). Organic complexes have been shown to be important for iron, but not much is known about these other forms for many of these elements.

The most abundant of these elements, aluminum and iron (which comprise 8.23%, and 5.63%, respectively, of the Earth’s crust, by weight) are also the most studied. The first reliable reports on dissolved aluminum in the oceans were made in the late 1970s. Since then there have been over 50 articles on the distribution of aluminum in the oceans. Reliable data on iron were not available until the late 1980s but, owing to the importance of iron in regulating primary production in some regions of the ocean, there has been a wealth of studies on this element in the past decade. Most of the other elements discussed here were not studied until the late 1980s or even the 1990s, and for many there are only a couple of articles on their oceanic distributions. There is still much we do not know about their distributions and the processes that control them in the oceans.

History

Advances in our understanding of trace metal distributions in the oceans began with the development of clean sampling methods in the late 1970s and have continued with the ongoing development of highly sensitive analytical methods. Clean sampling and handling methods are critical in the analysis of the more abundant refractory metals, aluminum and iron. Detection of the lower-abundance refractory metals, owing to their exceptionally low concentrations in sea water, has been limited by the sensitivity of available methods. Their analysis has greatly benefited from the increasing sensitivity of modern analytical instruments. The development of highly sensitive mass spectrometers that allow for aqueous sample introduction have revolutionized this field. Inductively coupled plasma mass spectrometers (ICP-MS) using quadrupole mass analyzers, made commercially available in the mid 1980s, and the magnetic and electric sector high-resolution ICP-MS instruments, available since the early 1990s, have allowed the detection of these elements without requirement for excessive sample processing and preconcentration steps.

Distributions

Rapid removal of the scavenged elements results in a low background concentration in the oceans and the potential for a large concentration range, depending on the variations in the magnitude of

Table 1 Summary of the hydroxide speciation, concentrations, and residence times for the refractory elements in the oceans

Element (units)	*Probable main species in oxygenated sea water*	*Concentration*[a]					*Residence time (y)*[b]
		Range (Average)	*Pacific*		*Atlantic*		
			Surface	*Deep*	*Surface*	*Deep*	
Al ($nmol\,kg^{-1}$)	$Al(OH)_3^o$, $Al(OH)_4^-$	0.06–650 (1.5)	4	2	40	20	30–200
Ga ($pmol\,kg^{-1}$)	$Ga(OH)_4^-$	2–60 (17)	10	25	40	25	100–750
In ($pmol\,kg^{-1}$)	$In(OH)_3^o$	0.05–4.8 (0.1)	0.1	0.06	0.6	1.6	(similar to Al)
Sc ($pmol\,kg^{-1}$)	$Sc(OH)_3^o$	7–22 (16)	10	20	15	20	NA
Ti ($pmol\,kg^{-1}$)	$TiO(OH)_2^o$	4–250 (140)	5	200	50	200	100–700
Zr ($pmol\,kg^{-1}$)	$Zr(OH)_5^-$	12–360 (180)	20	270	80	150	800–5600
Hf ($pmol\,kg^{-1}$)	$Hf(OH)_5^-$	0.1–1.5 (0.7)	0.3	0.8	0.4	0.7	650–1300
Nb ($pmol\,kg^{-1}$)	$Nb(OH)_6^-$, $Nb(OH)_5^o$	2.8–4.2 (3.9)	2.8	3.8	NA	NA	5000+
Ta ($pmol\,kg^{-1}$)	$Ta(OH)_5^o$	0.08–0.21 (0.2)	0.09	0.21	NA	NA	5000+
Fe ($nmol\,kg^{-1}$)	Organic Fe, $Fe(OH)_3^o$, $Fe(OH)_2^+$	0.05–0.8 (0.5)	0.05	0.6	0.05	0.5	100–500
Bi ($fmol\,kg^{-1}$)	BiO^+, $Bi(OH)_2^+$, $Bi(OH)_3^o$	25–450 (140)	165	50	400	125	20
Th ($fmol\,kg^{-1}$)	$Th(OH)_4^o$ ($Th(OH)_5^-$?)	50–600 (80)	70	150	500	500	45

NA = data not available.

[a] Typical values for the central North Pacific and the central North Atlantic, where 'deep waters' are deeper then 2000 m.

[b] Residence times are estimated from deep water scavenging models for Al, Ga, Ti, Zr, Hf, Fe, and Th (radioactive disequilibria between ^{230}Th and ^{234}U, for Th); river input for Nb and Ta; and the total input to the surface ocean for Bi.

their sources. This is especially true for aluminum, where the concentrations vary by up to 2 orders of magnitude with depth at a given location, by 3 orders of magnitude from one major ocean to another, and by 4 orders of magnitude in extreme environments. This range reflects the large variations in dust sources to the oceans from place to place and rapid removal of aluminum from sea water away from these sources. The range of concentrations for all of the refractory elements, their oceanic average, and some typical concentrations found in surface (<100 m) and deep (>2000 m) waters of the central North Atlantic and North Pacific Oceans are presented in **Table 1**. Although the range of concentrations is largest for aluminum, this difference is most likely exaggerated in the data shown here, as aluminum has been studied in more diverse regions.

Also included in **Table 1** is an estimate of the average oceanic residence times for these elements. A shorter residence time indicates a more rapid removal from the oceans. Another way to estimate the relative reactivity of elements with crustal sources is to compare their sea water concentrations with their abundance in the Earth's crust. This is presented in **Table 2** (with a normalization to

Table 2 The average abundance of the refractory elements in the Earth's crust, and their degree of enrichment, relative to aluminum, in the oceans

Element (M)	*Average crustal abundance*		*Average sea water concentration ($mol\,kg^{-1}$)*	*Sea water / crust ($\times 10^{15}$)*	$(M/Al)_{SW}$	$\frac{(M/Al)_{sw}}{(M/Al)_{crust}}$
	By weight	*mol kg^{-1}*				
Al	8.23%	3.05×10^{6}	1.5×10^{-9}	0.5	1.00	(1.00)
Ga	15 ppm	215	1.7×10^{-11}	80	1.1×10^{-2}	160
In	0.1 ppm	0.87	1.0×10^{-13}	115	6.7×10^{-5}	230
Sc	22 ppm	489	1.6×10^{-11}	33	1.1×10^{-2}	65
Ti	0.57%	1.19×10^{5}	1.4×10^{-10}	1.2	9.3×10^{-2}	2.4
Zr	165 ppm	1810	1.8×10^{-10}	100	1.2×10^{-1}	200
Hf	3 ppm	16.8	7.1×10^{-13}	40	4.7×10^{-4}	90
Nb	20 ppm	215	3.9×10^{-12}	18	2.6×10^{-3}	40
Ta	2 ppm	11	2.0×10^{-13}	18	1.3×10^{-4}	40
Fe	5.63%	1.01×10^{6}	5.4×10^{-10}	0.5	3.6×10^{-1}	1
Bi	0.17 ppm	0.813	1.4×10^{-13}	170	9.3×10^{-5}	340
Th	9.6 ppm	41.4	8.0×10^{-14}	2	5.5×10^{-5}	4

Crustal abundances from Taylor (1964). Seawater concentrations from various references.

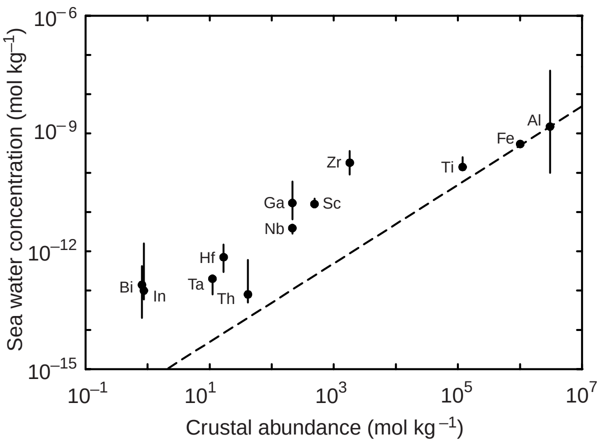

Figure 1 The average and range of concentrations of the elements in the deep ocean from 2000 m to the bottom plotted against their average abundance in the Earth's crust. (Crustal abundances from Taylor (1964) Seawater concentrations from various references.) The dotted line shows a 1:1 slope plotted through the average concentration of aluminum. Elements that plot above this line are enriched in sea water relative to aluminum and their abundance in the crust.

aluminum) and is shown graphically in **Figure 1**. If variations in the composition of continental materials and differences in the solubility of the elements from these materials are not too great, then to a first approximation the removal rate should be inversely related to the degree of enrichment in seawater. Relative to aluminum, iron is the only element considered here that is not enriched in the oceans. Titanium and thorium are very slightly enriched; indium, barium and yttrium are greatly enriched (by 2–3 orders of magnitude), and tantalum, niobium, gallium, scandium, zirconium, and hafnium show intermediate enrichment. The degree of enrichment does not correlate well with estimates of the residence times of these elements. These discrepancies will be discussed in the following sections.

Distributions of scavenged elements in the oceans typically reflect their sources, as they are not in the oceans long enough to be homogenized by thermohaline circulation that mixes the oceans on a timescale of about a thousand years. Many of these elements have a surface source, primarily from continental dust that is partially dissolved in the surface waters. River sources are also possible, although much of the metals entering the ocean by this route is removed in coastal areas. Surface transects for aluminum and gallium (**Figures 2A, B**) show distribution expected with atmospheric dust as the dominant source. The lower values in coastal region result from increased removal in these highly productive waters, and restrict the transport of these elements to the open ocean. In contrast, zirconium and hafnium show a coastal source, possibly from rivers (**Figure 2C**). A bottom source is also evident in the vertical profiles of many refractory elements. The mechanism providing this source is not known, but could be from either dissolution of particles at the sediment surface (a process often referred to as 'remineralization') or a flux from the waters trapped within the sediments (an interstitial or pore water flux). Some of these elements (gallium, iron, and bismuth, for example) also show the effects of internal cycling within the ocean.

Aluminum

Aluminum (Al) is the most abundant metallic element in the Earth's crust. Aluminum is a trivalent metal with a strong tendency to hydrolyse in sea water to form the particle reactive species, $Al(OH)_3$ and $Al(OH)_4^-$. Both of these species are important in sea water, and there is a switch in the speciation within the pH and temperature range of sea water, from mostly $Al(OH)_4^-$ (75%) in surface waters to mostly $Al(OH)_3$ in deeper waters.

Dissolved aluminum has a large dynamic range in the oceans, from less than 0.06 nmol kg^{-1} in the mid-depth waters of the North Pacific to 650 nmol kg^{-1} in the surface microlayer of the Arabian Sea. Vertical distributions (**Figure 3**) typically show a surface maximum, due to eolian dust deposition, a mid-depth minimum, due to scavenging removal, and deep water concentrations that depend largely on the age of these waters. In the absence of recent deep water formation, the concentration is typically low in the bottom waters, with only a small increase (up to 2 nmol kg^{-1}) from sediment sources. The residence time of dissolved aluminum in the deep ocean, estimated using vertical advection diffusion (VAD) scavenging removal models, varies from 30 to 200 years, depending on the flux of particles from the overlying waters. The removal mechanism for dissolved aluminum is primarily via scavenging: a passive adsorption onto the surface of particles. There is some laboratory evidence for active uptake into biological soft tissues and/or silica frustules as well, but passive scavenging controls the distribution of aluminum in the oceans. The residence time in the surface ocean, estimated from soluble dust input, is about 3–4 years.

Surface water dissolved aluminum concentrations range from 0.3 to 10 nmol kg^{-1} in the Pacific Ocean, 0.2 to 85 nmol kg^{-1} in the Atlantic and Mediterranean, and 10 to 300 nmol kg^{-1} in the Arabian Sea. The surface distribution is tightly correlated with the magnitude of the dust fluxes in the region. The solubility of aluminum from eolian

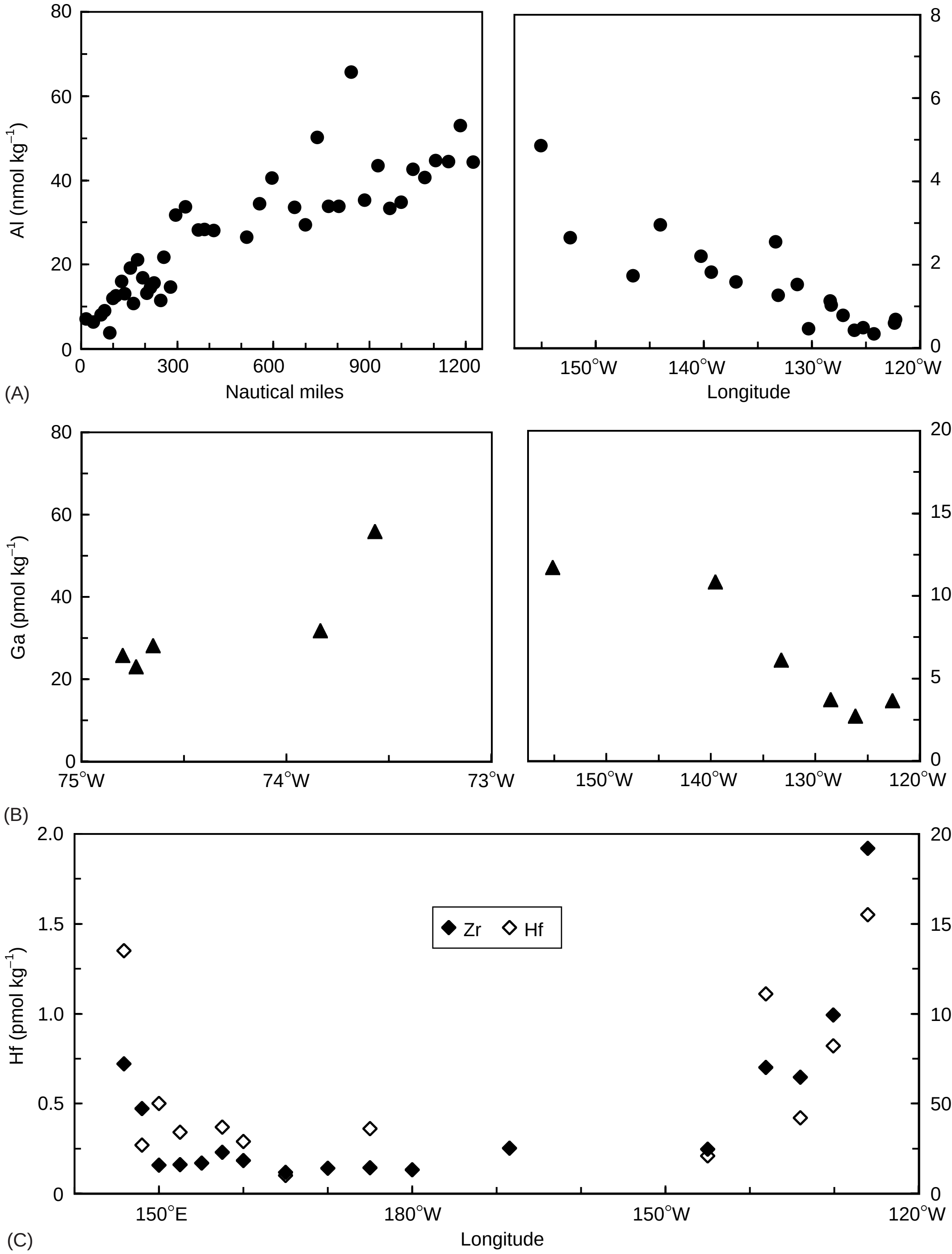

Figure 2 The surface distribution of (A) aluminum, (B) gallium, and (C) zirconium and hafnium from coastal to open ocean regions in the North Pacific and western North Atlantic. Note the scale changes between oceans. In all panels, the coastal locations are plotted at the outside edges, with more oceanic locations in towards the middle. The data for Al and Ga in the eastern North Pacific are from 28°N 155°W to 36°N 123°W (Orians and Bruland, 1986, 1988b). For the Atlantic, the Ga data are from 37°N 75°W to 36°N 73°W (Orians and Bruland, 1988b), and the Al data are from Rhode Island, across the Gulf Stream, into the Sargasso Sea, then down toward the Caribbean (Measures *et al*, 1984, stations #0-1206). For Zr and Hf the western North Pacific data are from 38°N 146°E to 16°N 169°W, and in the eastern North Pacific from 50°N 145°W to 49°N 126°W (McKelvey and Orians, 1993; McKelvey, 1994).

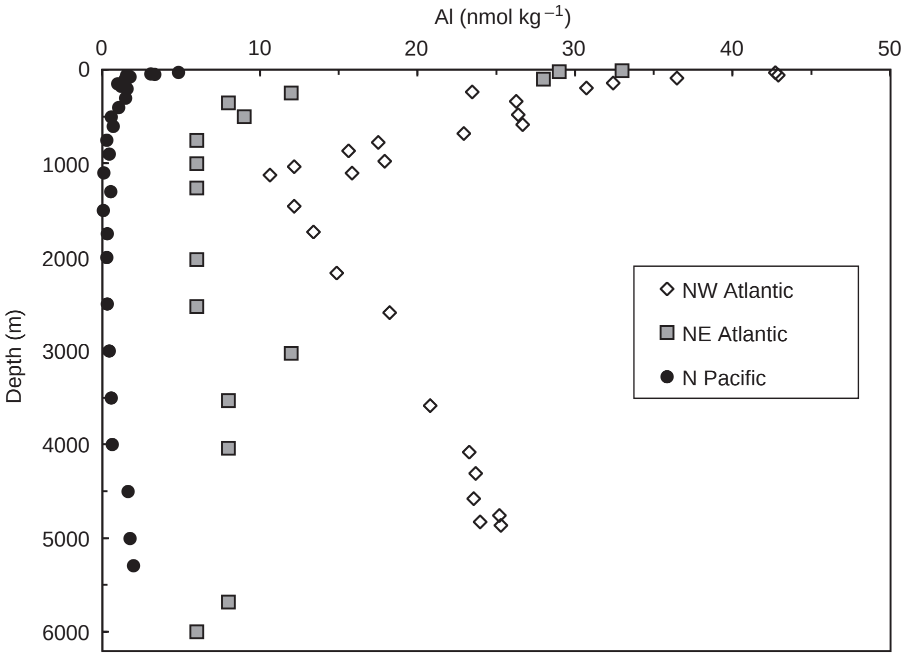

Figure 3 Depth profiles of dissolved aluminum in the central North Pacific (28°N 155°W; Orians and Bruland, 1986), in the eastern North Atlantic (31°W, 26°N; Hydes, 1983), and in the western North Atlantic (near Bermuda, EN120 Station 3; Measures *et al.*, 1986).

particles is about 5–10%. Fluvial input of aluminum, while significant, is rapidly removed in the estuaries and highly productive coastal regions (**Figure 2A**). Owing to the low background concentrations of aluminum in the oceans, and the large concentration of aluminum in crustal materials, aluminum is an excellent tracer of dust input to the oceans and of advective transport of water masses.

Deep water dissolved aluminum concentrations range from 0.5 to 2.0 nmol kg^{-1} in the Pacific Ocean, 8–30 in the Atlantic, and 135–170 in the Mediterranean. The western North Atlantic and the Mediterranean deep waters are high in dissolved aluminum from their recent contact with the surface (deep waters are 'young'). The western North Atlantic dissolved aluminum concentrations are 8–40 times higher than those in the North Pacific at similar depths – the largest interocean fractionation yet observed for any element (**Figure 3**). As the deep waters travel from the western North Atlantic to the eastern North Atlantic or on to the North Pacific, dissolved aluminum is continually removed from the water. Thus the lowest concentrations are found in the oldest waters of the North Pacific.

Gallium

Gallium (Ga) is a trivalent metal that exists as the strongly hydrolyzed $Ga(OH)_4^-$ ion and to a much lesser extent as $Ga(OH)_3$ ($< 2\%$) in sea water. Dissolved gallium ranges from 2 to 60 pmol l^{-1}, with the lowest values in the surface waters of the high-latitude North Pacific, and the highest values in the surface waters of the North Atlantic. Vertical distributions of dissolved gallium are complex. In the Pacific there is a surface minimum, a shallow subsurface increase then a mid-depth decrease, and concentrations increasing with depth below 1000 m to a maximum in the bottom waters (**Figure 4A**). Variable surface sources and advection of the mid-depth water masses complicate the distribution in the Atlantic Ocean. Profiles typically show concentrations increasing with depth without a sub-surface feature; at some stations there is also a surface maximum. The residence time of dissolved Ga in the deep ocean, estimated using VAD scavenging removal models, varies from 100 to 750 years.

Surface distributions (**Figure 2B**) show that eolian input is the dominant source of dissolved gallium to the surface ocean. The subsurface maximum seen in the Pacific is not an advective feature, but rather the result of internal cycles. The similarity in the ionic radii of gallium and iron, a known nutrient element, is thought to explain the subsurface maximum for gallium, which may be taken up along with iron in the surface waters and regenerated at the nutricline, with subsequent removal via scavenging in the deeper waters. There is a strong bottom source for gallium. The North Atlantic dissolved gallium con-

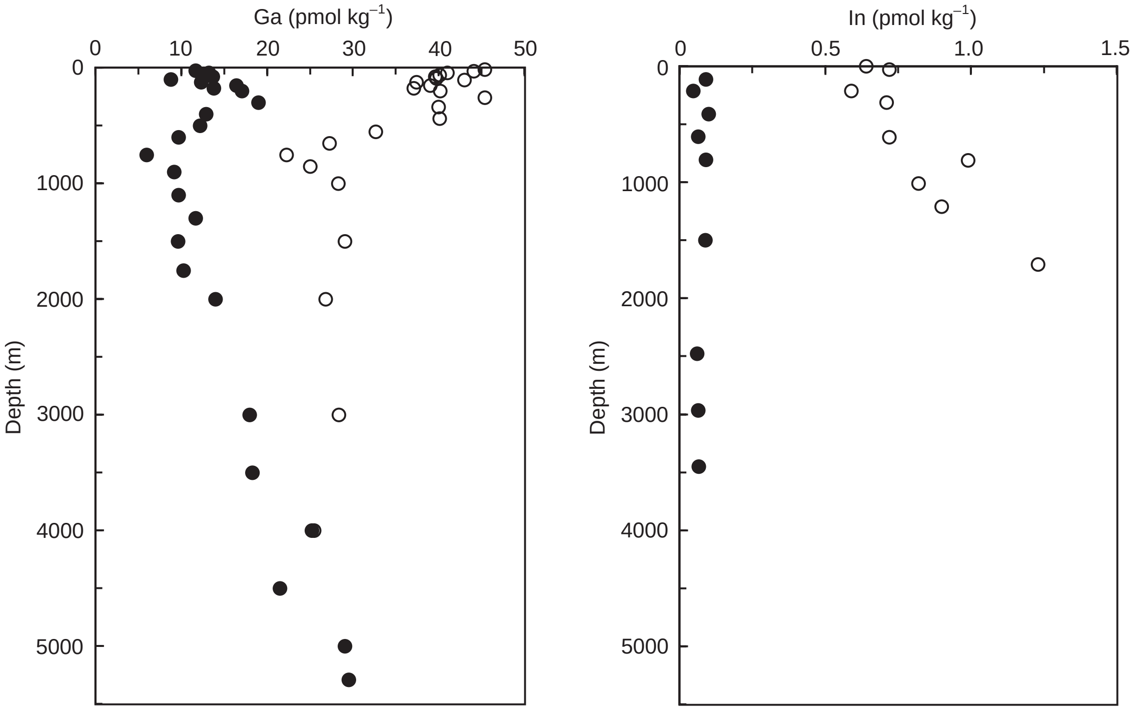

Figure 4 Depth profiles of (A) dissolved gallium in the central North Pacific (solid symbols; 28°N 155°W; Orians and Bruland, 1988) and in the western North Atlantic (open symbols; 32°N 64°W; Shiller, 1998), and (B) dissolved indium in the western North Pacific (solid symbols 34°N 142°E; Amakawa *et al.*, 1996) and in the eastern North Atlantic (open symbols; 26° N, 37°W; Alibo *et al.*, 1999).

centrations are 2–6 times higher than those in the North Pacific at similar depths, showing a net scavenging with age in the deep waters. The residence times estimated for dissolved gallium are 3–5 times higher than those for aluminum at the same locations. A combination of the longer residence time and the likelihood that gallium is more soluble than aluminum from crustal materials, owing to its larger ionic radius, is thought to produce the observed Ga/Al enrichment in sea water of roughly two orders of magnitude (**Table 2**, **Figure 1**).

Indium

Indium (In) is a trivalent metal that exists as $In(OH)_3$ in sea water, with a minor contribution from $In(OH)_4^-$ (6%). Dissolved indium ranges from 0.05 to 4.7 pmol kg^{-1}, with the lowest values in the North Pacific and the highest values in the Mediterranean. Vertical profiles of dissolved indium in the Pacific show low concentrations (0.06–0.10 pmol kg^{-1}) that are relatively invariant with depth, with a slight suggestion of a surface maximum. In the Atlantic the concentrations increase gradually with depth from 0.6 to 1.7 pmol kg^{-1}, and in the Mediterranean the concentration is about 4 pmol kg^{-1} and relatively invariant with depth. North Atlantic dissolved indium concentrations are 10–20 times higher than those in the North Pacific, showing a large degree of scavenging removal as deep waters age. The residence time of dissolved indium in the ocean is presumed to be similar to that of aluminum, owing to the similarity in their interocean fractionations and in their chemical speciation. The observed In/Al enrichment in sea water, as shown in **Table 2**, is not understood. It has been argued to be due to enrichment in the sources for indium, but it should be noted that increased dissolution of indium from dust can only account for a 10–20-fold enrichment, unless the solubility of aluminum from these sources (5–10%) has been grossly overestimated (there cannot be more than 100% dissolution!). The interocean differences in surface concentrations suggest that atmospheric sources are likely to dominate, as seen for gallium and aluminum.

Scandium

Scandium (Sc) exists in the +3 oxidation state as $Sc(OH)_3$ in sea water. Dissolved scandium has a nutrient-type vertical profile (**Figure 5A**), with low concentrations at the surface and enrichment at depth, yet no significant interocean fractionation is observed. Scandium was detected by neutron activation analysis in the early 1970s and there have

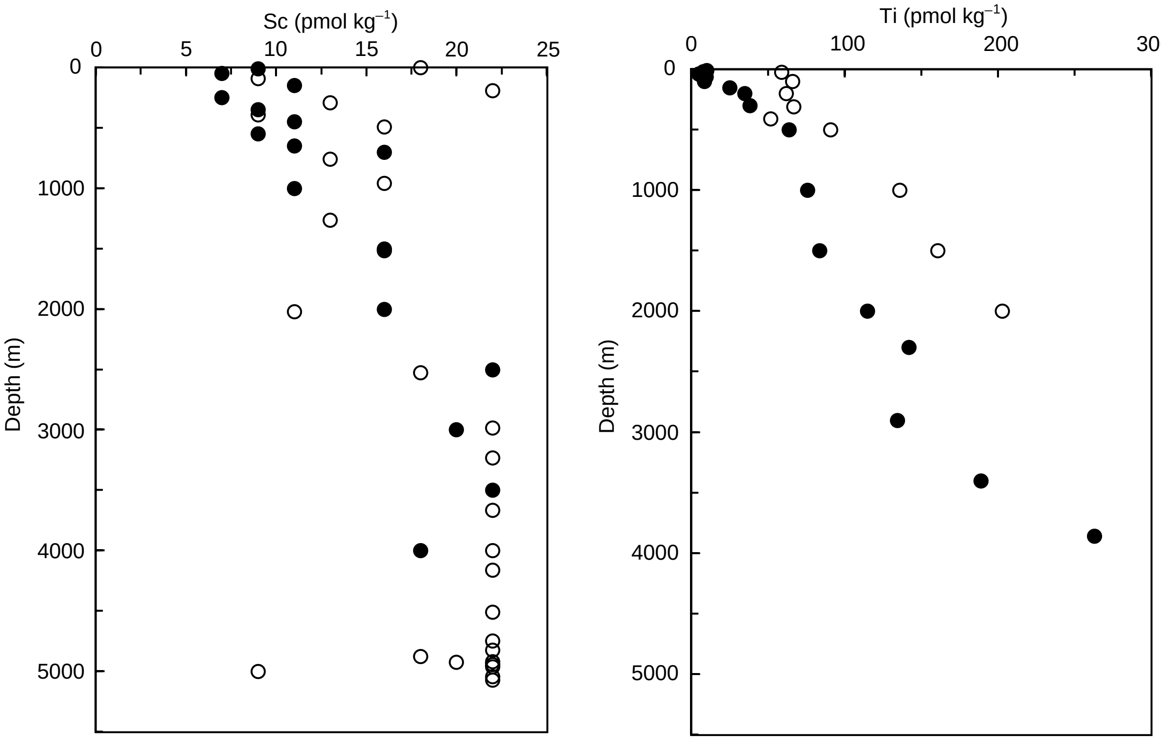

Figure 5 Depth profiles of (A) dissolved scandium in the central North Pacific (solid symbols; 28°N 122°W; Spencer *et al.*, 1970) and in the western North Atlantic (open symbols; 36°N 68°W; Brewer *et al.*, 1972), and (B) dissolved titanium in the North Pacific (solid symbols; 50°N 145°W; Orians *et al.*, 1990) and the western North Atlantic (32°N 64°W; Orians *et al.*, 1990).

not been any recent reports on scandium in the oceans. In the north-east Pacific, dissolved scandium is 7–11 pmol kg^{-1} in the surface water and 18–22 pmol kg^{-1} in deep waters. The Sargasso Sea has slightly higher scandium concentrations: 9–18 pmol kg^{-1} in the surface water and roughly 22 pmol kg^{-1} in the deep water. The residence time for scandium has not been determined.

Titanium

Titanium (Ti) exists in the +3 oxidation state as the neutral oxyhydroxide, $TiO(OH)_2$, in sea water. Dissolved titanium ranges from 4 to 300 pmol l^{-1}, with the lowest values in the surface waters of the North Pacific and the highest values in the deep waters. Vertical profiles of dissolved titanium in the Pacific show a minimum in the surface waters, with gradually increasing concentrations with depth to a maximum at the bottom. Dissolved titanium concentrations in surface waters range from 4 to 8 pmol l^{-1} in the North Pacific, from 50 to 100 pmol l^{-1} in the Atlantic, and from 100 to 150 pmol l^{-1} in the Mediterranean. Deep water data are scant in other regions, but the North Atlantic dissolved titanium concentrations may be slightly higher (up to 50%) than those in the North Pacific at comparable depths. The residence time of dissolved titanium in the high-latitude North Pacific is estimated to be 100–200 years, by VAD scavenging models. This is a region of high particle fluxes, where other elements are known to have a shorter than usual residence times. A comparison of titanium with aluminum and gallium at the same location shows that the residence time for titanium is about three times as long as for aluminum and 50% longer than for gallium. A global average is therefore expected to be higher – perhaps 500–700 years. The very small observed Ti/Al enrichment in sea water (**Table 2**) suggests that the residence time for titanium cannot be much longer than that for aluminum and that titanium is probably less soluble from continental materials. The interocean differences in surface concentrations suggest that atmospheric sources are likely to be important, as seen for aluminum and other metals in this group, but rivers have also been shown to be a significant source of titanium to the oceans, even after estuarine removal.

Zirconium and Hafnium

Zirconium (Zr) and hafnium (Hf) exist in the +4 oxidation state as $Zr(OH)_5^-$ and $Hf(OH)_5^-$ (with less than 2% in the neutral forms, $Zr(OH)_4$ or $Hf(OH)_4$). Owing to the lanthanide contraction, these two elements are very similar in their size and

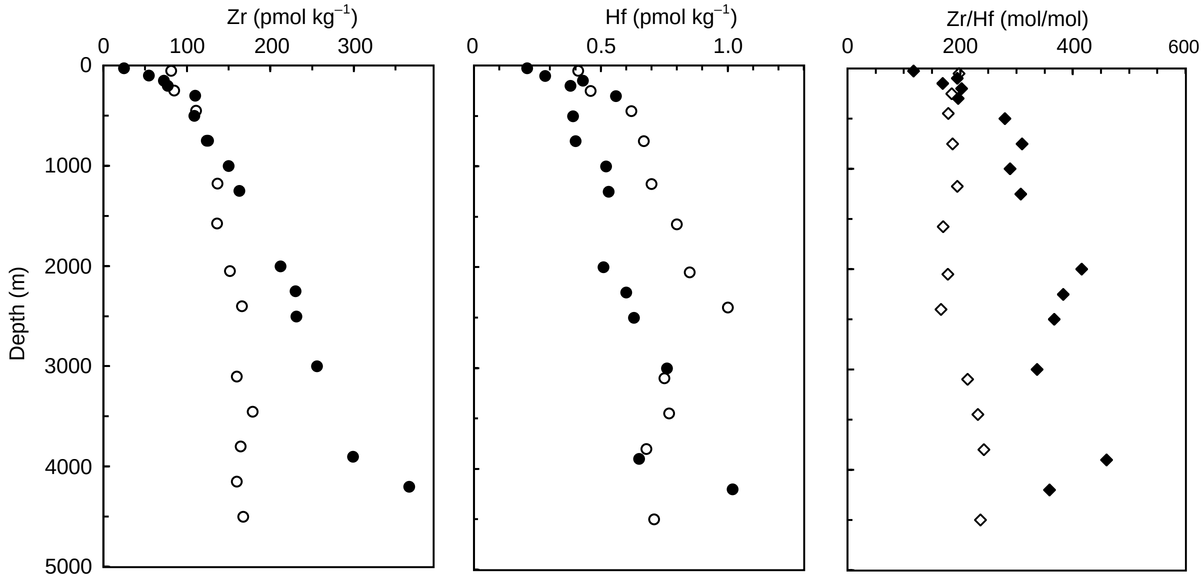

Figure 6 Depth profiles of (A) zirconium, (B) hafnium, and (C) the Zr/Hf atom ratio, in the North Pacific (solid symbols; 50°N 145°W; McKelvey and Orians, 1998) and in the North Atlantic (open symbols; 48°N 15°W; Godfrey *et al.*, 1996).

chemical properties. In most geological samples, their ratio remains nearly constant. In sea water, however, the ratio varies considerably. Both elements show a surface minimum, with concentrations gradually increasing to a maximum at the bottom (**Figure 6A, B**). The source to the bottom is similar to that seen for gallium and titanium. Surface distributions (**Figure 2C**) indicate that fluvial and/or reducing shelf sediments may be a significant source for zirconium and hafnium.

The concentration range for zirconium with depth is much larger than that for hafnium. This leads to a Zr/Hf atom ratio that increases from a near-crustal value (75–100) in the surface waters of the Pacific (even in the elevated costal waters shown in **Figure 2C**) to ~ 350 in the deep waters (**Figure 6C**). In the high-latitude North Atlantic, the ratio is higher in the surface (180–200), but not as high in the deep waters (~ 240, and quite variable from place to place). It appears that the Zr/Hf enrichment increases with the age of the water. Residence times estimated from river input suggest that zirconium has a longer residence time than hafnium (5600 versus 1300 y); estimates using VAD scavenging removal models, while shorter, lead to the same conclusion (see **Table 1**). The difference in residence time, however, is not sufficient to explain the Zr/Hf enrichment found in deep waters. It is suspected that there must be a zirconium enrichment in the source to these bottom waters as well, although the details of this source are not known. Zirconium and hafnium are both enriched in sea water relative to aluminum, which is likely due to a combination of their longer residence times and the greater supply of these elements to the bottom and in coastal regions.

There appears to be little interocean fractionation for zirconium and hafnium; surface waters are higher in the Atlantic for both, and the deep waters are higher in the Pacific for zirconium (no change for hafnium). Atlantic data are limited to high latitudes, however, and may not be representative of the central gyre. The higher concentrations in the deep North Pacific imply a net input of dissolved zirconium to the deep waters as they age, consistent with the shape of the profile.

Niobium and Tantalum

Reports on the marine chemistry of niobium (Nb) and tantalum (Ta) are limited to one study in the Pacific Ocean. Niobium and tantalum are pentavalent metals that are predicted to exist in sea water either as hydroxides ($Nb(OH)_5$, $Nb(OH)_6^-$, $Ta(OH)_5$ and $Ta(OH)_6^-$) or possibly as oxyacids, similar to molybdenum and tungsten. Their distributions are not conservative like those of molybdenum and tungsten, but they may not be as particle-reactive as the other hydroxide-dominated species discussed. Dissolved niobium is low in the surface (3.0 pmol kg^{-1}) and increases to a nearly constant level from 400 m to the bottom (3.8 pmol kg^{-1}). Dissolved tantalum is low in the surface (0.08 pmol kg^{-1}) and gradually increases with depth to a maximum at the bottom (0.2–0.3 pmol kg^{-1})

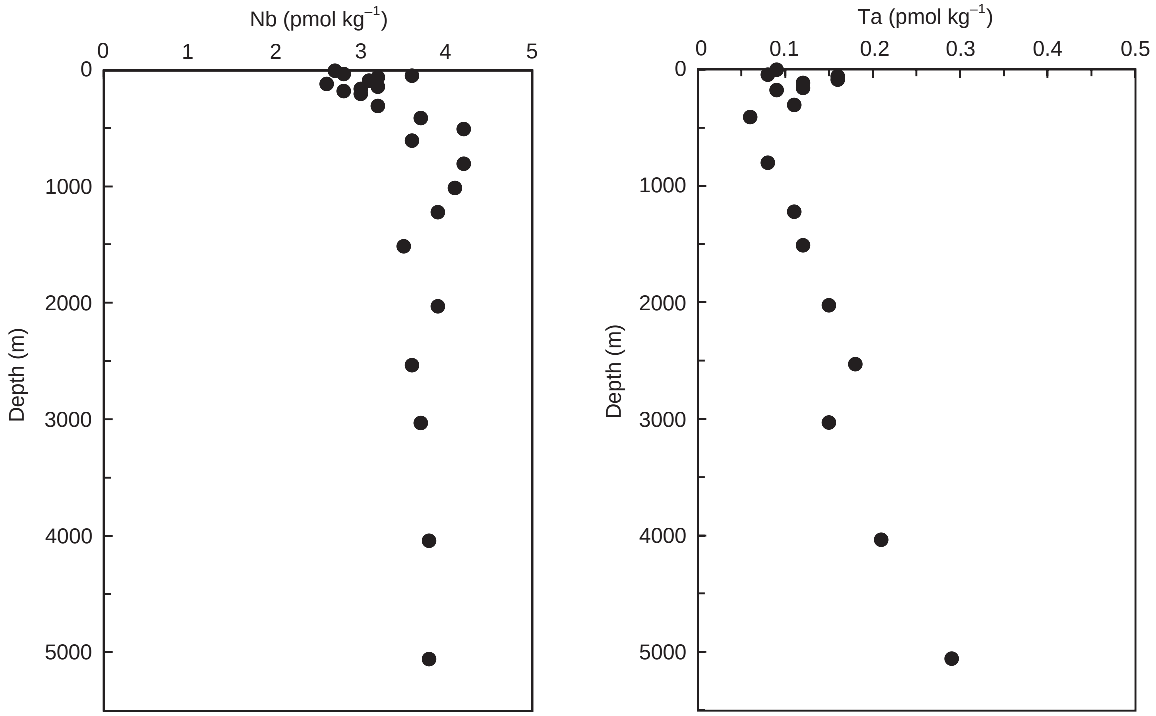

Figure 7 Depth profiles of (A) niobium and (B) tantalum in the western North Pacific (45°N 165°E; Sohrin *et al.*, 1998).

(**Figure 7**). Residence times very crudely estimated from their predicted river sources range from 5000 to 60 000 years for both elements. The upper end of this range seems quite unlikely, given their distributions and relatively small enrichment in sea water relative to aluminum (**Table 2**). Residence times calculated from river sources are often overestimates for scavenged elements that are removed in estuaries and coastal environments, but niobium and tantalum may indeed be less reactive than the other refractory elements if they exist as oxyacids rather than hydroxides.

Iron

Iron (Fe) is the second most abundant metal in the Earth's crust. It is a group 8 element and its stable oxidation state in oxygenated seawater is Fe(III). Dissolved Fe(III) has a strong tendency to hydrolyze to form $Fe(OH)_3$ and $Fe(OH)_2{}^+$ in sea water. Iron is very insoluble with respect to precipitation of hydrous iron oxides and is expected to exist at extremely low concentrations in oxygenated seawater ($< 200\,\mathrm{pmol\,kg^{-1}}$). Organic ligands that bind iron strongly, however, are found in both the Atlantic and Pacific Oceans at concentrations near $0.60\,\mathrm{nmol\,kg^{-1}}$. These ligands may prevent loss of iron and allow higher concentrations of iron than would be expected from inorganic solubility alone. Under anaerobic conditions, Fe(II) is the thermodynamically favored species. It exists primarily as the free ion with a minor contribution from the $FeCl^+$ complex. Oxidation kinetics for Fe(II) are rapid above pH 6 and, as a result, Fe(II) is rapidly oxidized to Fe(III) in oxygenated sea water.

Dissolved iron has a nutrient-type vertical profile, and is known to be a required element for phytoplankton growth. Surface water concentrations of dissolved iron in the Pacific, Atlantic, and Southern Oceans are typically $< 0.2\,\mathrm{nmol\,kg^{-1}}$ (average 0.07). A maximum is observed at around 500–700 m (a bit deeper than the maximum for nutrients, nitrate, or phosphate) with relatively uniform concentrations in deep waters. The average concentration below 500 m is $0.6\,\mathrm{nmol\,kg^{-1}}$. Unlike other nutrient-type metals, there is no significant interocean fractionation for iron; the deep waters do not continue to accumulate iron as they travel from the Atlantic to the Pacific. This can be explained by a balance between regeneration of iron from biogenic matter and subsequent removal by scavenging; the residence time of iron is estimated to be quite short, on the order of 100–500 years (**Table 1**). An alternate hypothesis, that organic ligands control the solubility of iron and set the deep water concentration at $0.6\,\mathrm{nmol\,kg^{-1}}$ has also been proposed.

Dissolved iron enters the ocean via atmospheric, fluvial, hydrothermal, and sediment pathways. Rapid removal of iron from fluvial and hydrothermal

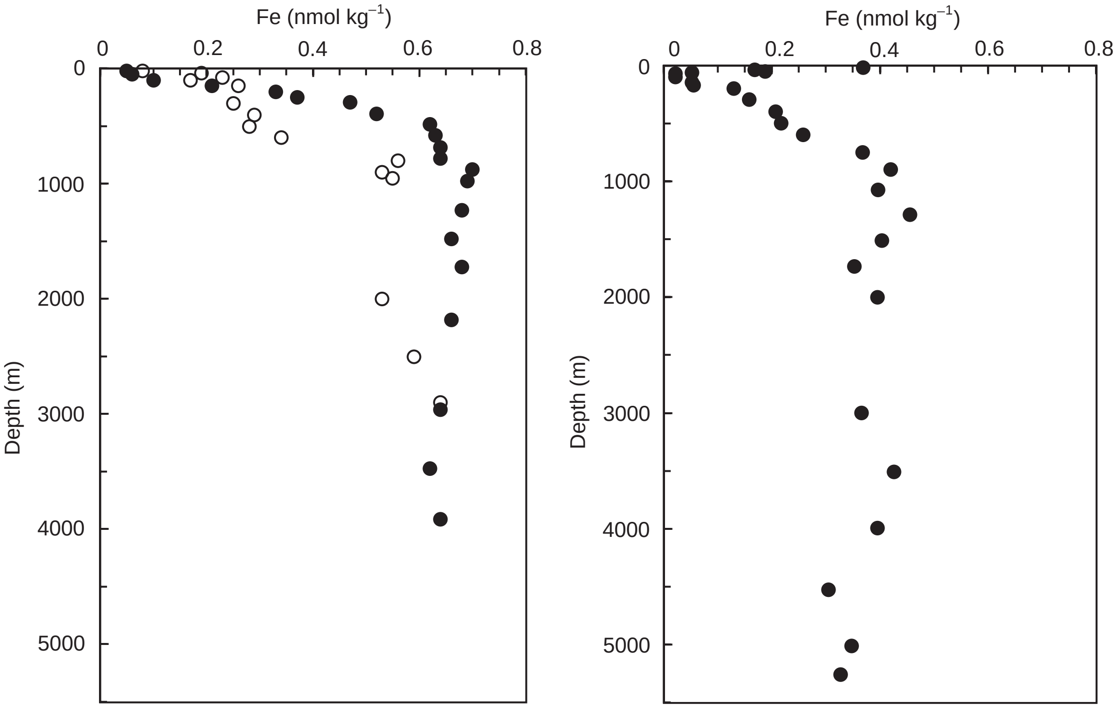

Figure 8 Depth profiles of dissolved iron in (A) the North Pacific (solid symbols; 50°N 145°W; Martin *et al.*, 1989) and the North Atlantic (open symbols; 47°N 20°W; Martin *et al.*, 1993), and (B) the central North Pacific (28°N, 155°W; Bruland *et al.*, 1994).

sources limits the extent of their influence. Sediments can provide a more significant source; the flux of iron out of reducing sediments is large. Upwelling over the continental shelf brings elevated iron levels to the surface in many coastal regions. Atmospheric dust is the dominant source of iron to the surface of the open ocean. Owing to the low and nearly uniform levels of dissolved iron in surface waters, which do not follow variations in dust patterns, as dissolved aluminum does, the importance of this source has been questioned. The input of iron from atmospheric sources was observed in the central North Pacific by Bruland and colleagues. During a time of unusually strong stratification, when the upper half of the sunlit waters were cut off from the nutrient supply, the removal of iron by phytoplankton was limited to the lower half of the photic zone, thus allowing the build-up of iron from atmospheric dust in the upper waters (**Figure 8**).

Bismuth

Bismuth (Bi) exists in the $+3$ oxidation state in sea water, probably as the reactive cationic oxyhydroxide species, BiO^+ and $Bi(OH)_2{}^+$, with a minor contribution from $Bi(OH)_3$. Dissolved bismuth ranges from 25 to 450 fmol kg^{-1}, with the lowest concentrations in the deep North Pacific and the highest at mid-depth (600 m). Vertical profiles of bismuth are complex, as shown in **Figure 9**. They typically show high surface water concentrations, thought to reflect the dissolution of aerosol particles. Dissolved bismuth then decreases beneath the surface as a result of removal via scavenging onto particles, and increases again to a mid-depth maximum (500 fmol kg^{-1} in the Pacific; 370 fmol kg^{-1} in the Atlantic) at 600 m. Concentrations below 600 m decrease to their lowest values at the bottom, from scavenging in deep waters. The mid-depth maximum is roughly associated with the oxygen minimum and is possibly due to the dissolution of manganese phases, which may transport bismuth. In North Atlantic surface waters, bismuth varies between 200 and 400 fmol kg^{-1}, with a distribution consistent with a major atmospheric source. The residence time of bismuth, based on fluvial, atmospheric, and volcanic input to the upper ocean, is estimated to be very short – about 20 years. This estimate seems too short in light of the large enrichment seen for bismuth relative to aluminum in sea water (**Table 2**, **Figure 1**). The lower deep water concentrations in the Pacific are consistent with an increase in scavenging as water ages.

Thorium

Thorium (Th) is a naturally occurring radioactive element with four primary isotopes; ^{232}Th

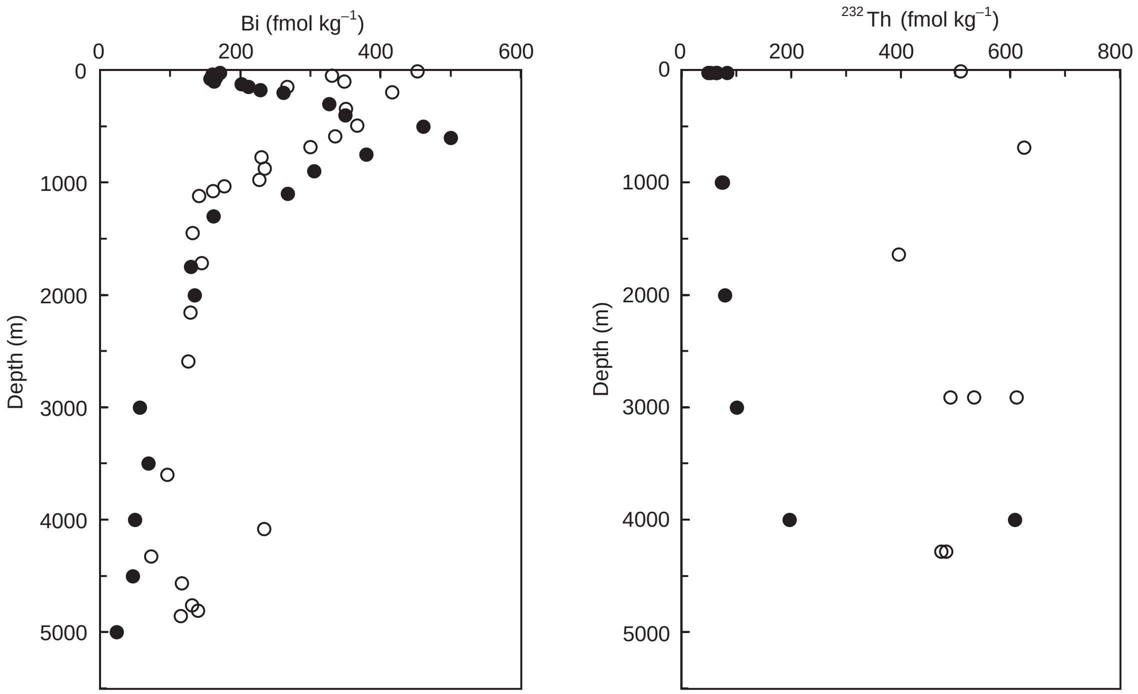

Figure 9 Depth profiles of (A) bismuth in the central North Pacific (solid symbols; 28°N 155°W; Lee *et al.*, 1985/86) and in the western North Atlantic (open symbols; near Bermuda; Lee *et al.*, 1985/86), and (B) ^{232}Th in the western North Pacific (solid symbols; 23°N 158°W; Roy-Barman *et al.*, 1996) and in the eastern North Atlantic (open symbols; 51°N, 43°W; Chen *et al.*, 1986).

($t_{1/2} = 14 \times 10^9$ y), ^{234}Th ($t_{1/2} = 24.1$ d), ^{230}Th ($t_{1/2} = 75\,200$ y), and ^{228}Th ($t_{1/2} = 1.91$ y), in order of abundance. The dominant chemical species of thorium is thought to be the neutral hydroxide, $Th(OH)_4$, but there are no data on the formation constant of $Th(OH)_5^-$. The average concentration of thorium in sea water is 80 fmol kg^{-1} and its residence time, estimated from the scavenging removal of ^{230}Th in the deep sea is 45 years. The only isotope with a primordial origin is the major isotope, ^{232}Th, the others are formed by *in situ* decay. The primary source for ^{232}Th to the oceans is believed to be dust deposition at the sea surface. The vertical profile for ^{232}Th shows a surface minimum (63 fmol kg^{-1}) and a gradual increase to the bottom (200 fmol kg^{-1}), indicating a bottom source as well. Data from the Atlantic are higher (400–600 fmol kg^{-1}) and show no discernible structure. The short residence time and small degree of enrichment in sea water relative to aluminum (**Table 1, Figure 2**) are both due to the high particle reactivity of thorium. It is perhaps surprising that there is any enrichment of Th/Al in sea water.

Discussion

The two indicators of metal reactivity in the oceans (their residence times and the degree of enrichment observed in sea water, relative to aluminum and their abundance in the Earth's crust) do not agree particularly well for the elements discussed here. Short residence times and low sea water/crust ratios are observed for aluminum, iron, and thorium, while longer residence times and higher sea water/crust ratios are observed for gallium, zirconium, and hafnium. The rest are not in agreement, however. Bismuth and indium are both enriched and yet are thought to be rapidly removed. Titanium is not enriched but has an estimated residence time longer than gallium. Niobium and tantalum are not enriched as much as might be expected from their estimated residence times. It must be emphasized that we do not have enough information to place a high degree of confidence on the estimated residence times, or on the validity of using sea water enrichments to infer reduced removal intensity. Differences in the solubility of these elements from continental materials could be significant, but there are many other uncertainties as well.

There have been a number of theories regarding the geochemical basis for the relative reactivity of elements, and the factors that control their sea water concentrations. One theory is that the differential reactivity of strongly hydrolyzed elements may be related to the charge of the hydroxide species that dominates. Those that exist in an anionic form may be less particle-reactive (i.e., they may be less likely to adsorb on negatively charged particle surfaces) and may therefore have longer residence times and be relatively enriched in sea water. The elements with the shortest estimated residence times are bismuth, thorium, aluminum, and iron, all of which are predominantly neutral or cationic in sea-water and, with the exception of bismuth, all of which have extremely low sea water concentrations, relative to their abundance in the Earth's crust. Some elements with intermediate residence times are gallium, hafnium, and zirconium, which are predominantly anionic and enriched in sea water. The other elements have poorly confined estimates of their residence times and are difficult to categorize, but do not appear to follow this trend.

Conclusion

The elements described here as refractory are not very soluble in water. They have low concentrations in sea water relative to their abundance in the Earth's crust, and short oceanic residence times. They can have extremely large concentration ranges in the oceans. The processes controlling the marine biogeochemistry of these elements are complex, and their distribution types vary considerably. The classic scavenged profile showing a surface maximum is observed only for aluminum, and even then only in some locations. Many of these elements increase gradually with depth, and some have subsurface maxima, mid-depth maxima, or nutrient-type profiles, showing the influence of internal cycles. Some are depleted as deep waters age, others are enriched. To date, there is no unifying theory to explain the distributions and the relative reactivities of hydroxide-dominated elements in the oceans. More information is needed before we are able to fully understand the processes that control these refractory elements in sea water.

See also

Anthropogenic Trace Elements in the Ocean. Metal Pollution. Primary Production Processes.

Further Reading

Alibo DS, Nozaki Y and Jeandel C (1999) Indium and yttrium in North Atlantic and Mediterranean waters: comparison to the Pacific data. *Geochimica et Cosmochimica Acta* 63: 1991–1999.

Amakawa H, Alibo DS and Nozaki Y (1996) Indium concentration in Pacific seawater. *Geophysical Research Letters* 23: 2473–2476.

Brewer PG, Spencer DW and Robertson DE (1972) Trace element profiles from the GEOSECS-II test station in the Sargasso Sea. *Earth and Planetary Science Letters* 16: 111–116.

Bruland KW, Orians KJ and Cowen JP (1994) Reactive trace metals in the stratified central North Pacific. *Geochimica et Cosmochimica Acta* 58: 3171–3182.

Chen JH, Edwards RL and Wasserburg GJ (1986) 238-U, 234-U and 232-Th in seawater. *Earth and Planetary Science Letters* 80: 241–251.

Godfrey LV, White WM and Salters VJM (1996) Dissolved zirconium and hafnium distributions across a shelf break in the northeastern Atlantic Ocean. *Geochimica et Cosmochimica Acta* 60: 3995–4006.

Hydes DJ (1983) Distribution of aluminium in waters of the north east Atlantic 25° N to 35° N. *Geochimica et Cosmochimica Acta* 47: 967–973.

Johnson KS, Gordon RM and Coale KH (1997) What controls dissolved iron in the world ocean? *Marine Chemistry* 57: 137–161.

Lee DS, Edmond JM and Bruland KW (1985/86) Bismuth in the Atlantic and North Pacific: a natural analogue to plutonium and lead? *Earth and Planetary Science Letters* 76: 254–262.

Martin JH, Fitzwater SE, Gordon RM, Hunter CN and Tanner SJ (1993) Iron, primary production, and carbon–nitrogen flux studies during the JGOFS North Atlantic bloom experiment. *Deep Sea Research* 40: 115–134.

Martin JH, Gordon RM, Fitzwater SE and Broenkow WW (1989) VERTEX: phytoplankton /iron studies in the Gulf of Alaska. *Deep Sea Research* 36: 649–680.

McKelvey BA (1994) *The Marine Geochemistry of Zirconium and Hafnium*. PhD thesis, University of British Columbia.

McKelvey BA and Orians KJ (1993) Dissolved zirconium in the North Pacific Ocean. *Geochimica et Cosmochimica Acta* 57: 3801–3805.

McKelvey BA and Orians KJ (1998) The determination of dissolved zirconium and hafnium from seawater using isotope dilution inductively coupled plasma mass spectrometry. *Marine Chemistry* 60: 245–255.

Measures CI, Edmond JM and Jickels TD (1986) Aluminum in the North West Atlantic. *Geochimica et Cosmochimica Acta* 50: 1423–1429.

Measures CI, Grant B, Khadem M, Lee DS and Edmond JM (1984) Distribution of Be, Al, Se, and Bi in the surface waters of the western North Atlantic and Caribbean. *Earth and Planetary Science Letters* 71: 1–12.

Orians KJ and Bruland KW (1986) The biogeochemistry of aluminum in the Pacific Ocean. *Earth and Planetary Science Letters* 78: 397–410.

Orians KJ and Bruland KW (1988a) Dissolved gallium in the open ocean. *Nature* 332: 717–719.

Orians KJ and Bruland KW (1988b) The marine geochemistry of dissolved gallium: a comparison with dissolved aluminum. *Geochimica et Cosmochimica Acta* 52: 2955–2962.

Orians KJ, Boyle EA and Bruland KW (1990) Dissolved titanium in the open ocean. *Nature* 348: 322–325.

Roy-Barman M, Chen JH and Wasserburg GJ (1996) 230Th–232Th systematics in the central Pacific Ocean: the sources and the fates of thorium. *Earth and Planetary Science Letters* 139: 351–363.

Shiller AM (1998) Dissolved gallium in the Atlantic Ocean. *Marine Chemistry* 61: 87–99.

Sohrin Y, Fujishima Y, Ueda K *et al.* (1998) Dissolved niobium and tantalum in the North Pacific. *Geophysical Research Letters* 25: 999–1002.

Spencer DW, Robertson DE, Turekian KK and Folsom TR (1970) Trace element calibrations and profiles at the GEOSECS test station in the Northeast Pacific Ocean. *Journal of Geophysical Research* 75: 7688.

Taylor SR (1964) Abundance of chemical elements in the continental crust: a new table. *Geochimica et Cosmochimica Acta* 28: 1273–1285.

Whitfield M and Turner DR (1987) The role of particles in regulating the composition of seawater. In: Stumm W (ed.) *Aquatic Surface Chemistry*, Ch. 17, pp. 457–493. New York: Wiley-Interscience.

REGIONAL AND SHELF SEA MODELS

J. J. Walsh, University of South Florida, St Petersburg, Florida, USA

doi:10.1006/rwos.2001.0399

Introduction

Simple biological models of nutrient (N), phytoplankton (P), and zooplankton (Z) state variables were formulated more than 50 years ago (Riley *et al.*, 1949), with minimal physics, to explore different facets of marine plankton dynamics. These N–P–Z models, usually in units of nitrogen or carbon are still used in coupled biophysical models of ocean basins, where computer constraints preclude the use of more complex ecological formulations of global biogeochemical budgets. At the regional scale (**Table 1**) of individual continental shelves (Steele, 1974; Walsh, 1988), however, pressing questions no longer focus on the amount of biomass of the total phytoplankton community, but are instead concerned with the functional types of algal species that may continue to support fisheries, generate anoxia, fix nitrogen, or form toxic red tides.

Regional models that presently address the outcome of such plankton competition must of course specify the rules of engagement among distinct functional groups of P, Z, and larval fish (F) living and dying within time-dependent physical (e.g., light, temperature, and current) and chemical (e.g., N) habitats. Successful ecological models are data-driven, distilling qualitative hypotheses and aliased field observations into simple analogs of the real world in a continuing cycle of model testing and revision. They are usually formulated as part of multidisciplinary field studies, in which the temporal and spatial distributions of the model's state variables, from water motion to plankton abundances, are measured to provide validation data. Here, examples of some state-of-the-art, complex regional biophysical models are drawn from specific field programs designed to validate them. Depending upon the questions asked of regional models, processes at smaller and larger time/space scales (**Table 1**) are variously ignored, parametrized, or specified as boundary conditions.

Statistical models elicit noncausal relationships among presumed independent variables with poorly known probability density functions. Deterministic simulation models in contrast assign cause and effect among the state variables and forcing functions described by a set of usually nonlinear ordinary or partial differential equations, whose solutions are obtained numerically. Within a fluid subjected to such external forcing, the vagaries of population changes of the embedded plankton, along measured spatial gradients, must be described in relation to both water motion and biotic processes.

For example, in a Lagrangian sense – following the motion of a parcel of fluid – the time dependence of larval fish (F) can be written simply as an ordinary differential equation (eqn [1]), where the total derivative is given by eqn [2].

$$\frac{dF}{dt} = (b - d)F \qquad [1]$$

$$\frac{d}{dt} = \frac{\partial}{\partial t} + u\frac{\partial}{\partial x} + v\frac{\partial}{\partial y} + w\frac{\partial}{\partial z} \qquad [2]$$

Mixing is ignored and biotic factors are just the linear birth, b, and death, d, rates of the fish. Because drogues have difficulty following plankton patches, and current meters measure flows at a few fixed locations, it is usually more convenient to