Glossary

Advection Horizontal water motion.

Bioavailable metals Dissolved and particulate metals that are accessible to organisms during normal metabolic activity.

Bioaccumulative metals Metals that can be regulated and reside in the organism and are added to over its life.

Biomagnified metals Metals that are not regulated by organisms that can acquire an even larger body burden of metals.

Bioturbation Reworking of bottom sediment by burrowing marine organisms.

Diagenesis Release of particulate metals into the dissolved phase under suboxic conditions.

Flushing time The time required for an existing body of water to be exchanged with surrounding water.

Upwelling Vertical, upward movement of water at the shelf break, often tidally induced.

See also

Aeolian Inputs. Anthropogenic Trace Elements in the Ocean. Anti-fouling Materials. Atmospheric Input of Pollutants. Estuarine Circulation. Land–Sea Global Transfers. Metalloids and Oxyanions. Ocean Margin Sediments. Pollution: Effects on Marine Communities. Pore Water Chemistry. Refractory Metals. Regional and Shelf Sea Models. River Inputs. Temporal Variability of Particle Flux. Transition Metals and Heavy Metal Speciation. Trapped Particulate Flux. Shelf-sea and Slope Fronts.

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METALLOIDS AND OXYANIONS

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Introduction

The concentrations and distributions of dissolved trace elements (typically called trace 'metals,' though not all trace elements are metals) in the world's oceans are due to a complex interaction between their purely chemical behavior (e.g., acid/base properties, oxidation state, solubility), the way in which they are delivered to the ocean (atmosphere, rivers, submarine hydrothermal vents), biological reactions, and water circulation (e.g., currents). To organize this somewhat chaotic and confusing situation, the kinds of trace element behavior are classified into four types: conservative, nutrient-like or recycled, scavenged, and hybrid or mixed. A conservative trace element behaves like the major dissolved elements that make up the bulk of the ocean's salinity (e.g., Na^+). These elements are only effected by the physical processes of mixing, or the addition (dilution) or removal (evaporation) of water. Since there are no chemical or biological reactions that affect these elements, they have rather uniform concentrations with ocean depth. In contrast, the nutrient-like trace element is taken up by phytoplankton in surface waters during photosynthesis (like the nutrient nitrate), and this organic matter-bound element begins to gravitationally settle into deep waters. However, organic matter is a precious commodity in the open and deep sea, so many levels of the food web (bacteria to zooplankton) consume this organic detritus, releasing some fraction of the bound trace element back into the water column. This recycling makes the nutrient-like trace element concentration lower at the surface and higher at depth, with the exact shape of the profile depending on the rate at which it is recycled. Many dissolved trace elements have high charge to atomic radius ratios, and electrostatically adsorb to particle surfaces; this process is loosely termed 'scavenging.' Thus, scavenged elements have distributions that depend on the number and type of particles (e.g., clay, phytoplankton) and the mode of introduction (e.g., atmosphere, hydrothermal vents). An excellent example of this interaction is given by lead, which is very particle-reactive and is introduced from atmosphere, with the resulting distribution showing a surface maximum and rapid decrease with depth. Finally, many trace elements display features of both scavenged and nutrient-like elements, with the distribution of the micronutrient iron being a good example (particle reactive, but also recycled).

Most of these classifications were developed for the metals that are cations (positively charged) in solution, but there are elements in periodic groups IVA, VA and B, VIA and B, VIIA, and VIII that actually form oxygen-containing anions. In general, these elements display their maximum potential oxidation state in sea water, and in aqueous solution undergo hydrolysis (e.g., $Mo^{+6} + 4H_2O \rightarrow MoO_4^{2-} + 8H^+$). The metalloid elements (antimony, Sb; arsenic, As; germanium, Ge; selenium, Se; tellurium, Te) all exist as oxyanions, as do the transition metals chromium (Cr), molybdenum (Mo), osmium (Os), rhenium (Re), tungsten (W), and vanadium (V). In addition to existing as anions, most of these trace elements can be found in multiple oxidation states (e.g., As(III) and As(V)), ensuring that the oxyanions probably have the most diverse behaviors of any trace elements in the ocean. Interestingly, the form in which an oxyanion exists in sea water, the 'chemical speciation,' strongly affects its biological and chemical reactivity.

In this review, the oceanic distributions of each element will be discussed in terms of its purely chemical properties, known biological behavior, and general geochemical considerations (inputs and outputs). The focus will be primarily on the dissolved ions rather than those associated with particles, since these are free to move with the water molecules and are available to the first trophic level in the ocean, phytoplankton. Because deeper waters in the Pacific Ocean are much older and have undergone more mixing than those in the Atlantic, most data will come from the Pacific to focus on the biological and chemical processes affecting the element, and not the mixing of different water masses. In addition, all concentrations will be expressed in fractions of a mole per liter rather than as mass per liter. This allows direct comparisons between elements (i.e., atom to atom) and is consistent with the principles of chemical and biological reactions (e.g., to make CO_2, it takes one atom of C and 2 atoms of O). As trace elements, the concentrations units will be nanomoles per liter ($nmol\,l^{-1}$; $10^{-9}\,mol\,l^{-1}$), picomoles per liter ($pmol\,l^{-1}$; $10^{-12}\,mol\,l^{-1}$), and femptomoles per liter ($fmol\,l^{-1}$; $10^{-15}\,mol\,l^{-1}$). Nevertheless, low concentrations do not mean that the oxyanions are unimportant as either essential or toxic compounds, or as useful ocean tracers; these points will be highlighted below. To provide a logical order to this presentation, the periodic table will be followed from left to right.

The Elements

Vanadium

In oxygenated sea water with an average pH of 8, vanadium should be found in the $+5$ oxidation state, which undergoes hydrolysis to form vanadate, HVO_4^{2-}. In sea water with no oxygen ('anoxic') such as found in the Black Sea, V(V) can be reduced to V(IV) which is more reactive than V(V), and as a consequence, anoxic sediments have elevated concentrations of vanadium relative to sediments underlying oxic waters. Thus, sedimentary vanadium may act as a historical tracer of anoxic conditions. Vanadium has also been studied in sea water because it is enriched in fossil fuels and may be a potential pollutant. In this respect, vanadium does not have any established biological function, although the chemistries of phosphate and vanadate are similar, and therefore vanadate might be taken up into soft tissues (e.g., lipids) along with phosphate. The depth profile of dissolved vanadium in the North Pacific Ocean (**Figure 1A**) shows a surface concentration of $\sim 32\,nmol\,l^{-1}$ and an increase into deep waters to $\sim 36\,nmol\,l^{-1}$. This slight surface depletion has also been observed at other locations in the Pacific and Atlantic Oceans and, based on their similarity to the depth profiles of phosphate, it appears that vanadium is taken up by phytoplankton in surface waters. This type of behavior is also found in estuaries where river and sea waters mix, and both phosphate and vanadium show removal. This means that processes at the ocean margins (e.g., in estuaries) reduce the amount of vanadium

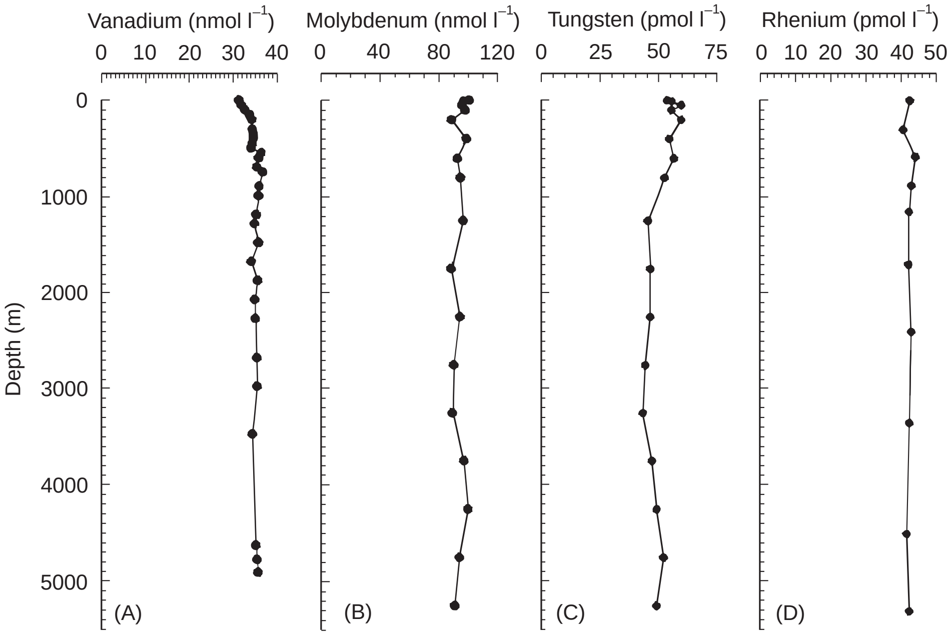

Figure 1 (A) Dissolved vanadium in the North Pacific Ocean, 11°N, 140°W. (Data from Collier RW (1979) Particulate and dissolved vanadium in the North Pacific Ocean. *Nature* 309: 441–444.) (B) Dissolved molybdenum in the North Pacific Ocean, 30°N, 159°50′W. (Data from Sohrin Y, Isshiki K and Kuwamoto T (1987) Tungsten in North Pacific waters. *Marine Chemistry* 22: 95–103.) (C) Dissolved tungsten in the North Pacific Ocean, 30°N, 159°50′W. (Data from Sohrin Y, Isshiki K and Kuwamoto T (1987) Tungsten in North Pacific waters. *Marine Chemistry* 22: 95–103.) (D) Dissolved rhenium in the North Pacific Ocean, 24°16′N, 169°32′W. (Data from Colodner D, Sachs J, Ravizza G, Turekian K, Edmond J and Boyle E (1993) The geochemical cycle of rhenium: a reconnaissance. *Earth and Planetary Science Letters* 117: 205–221.)

entering the oceans from rivers. In contrast, hydrothermal vents do not appear to be substantial sources or sinks of vanadium to the deep ocean.

Chromium

Owing to its use in many industrial processes and its high toxicity, considerable attention has been paid to chromium in group VIA. The two primary oxidation states of chromium are +6 and +3, which hydrolyze in water to form chromate, CrO_4^{2-}, and $Cr(OH)_3$, respectively.

Thermodynamic calculations show that chromate is the expected form in oxygenated sea water, while the insoluble Cr(III) species would predominate in very low-oxygen (so called 'suboxic') or anoxic waters. However, it is important to note that thermodynamic calculations only predict elemental speciation at equilibrium (when the rates of formation and destruction are balanced), but they do not consider the rates of conversion themselves. For example, Cr(III) should not exist in oxygenated sea water, but its rate of oxidation to Cr(VI) is slow (days to months), meaning that Cr(III) can persist in oxic water ('kinetic stabilization'). In the eastern North Pacific Ocean, Cr(VI) displays a surface concentration of $\sim 3\,\mathrm{nmol\,l^{-1}}$ (**Figure 2A**), but then decreases rapidly to a minimum of $1.7\,\mathrm{nmol\,l^{-1}}$ at 300 m depth and increases below this to levels of 4–5 $\mathrm{nmol\,l^{-1}}$ in the deeper waters. While chromate appears to display a mixture of scavenged and nutrient-like behavior, the Cr(VI) minimum occurs at the same depth as the widespread suboxic zone in the eastern Pacific. Indeed, at other sites in the North Pacific without a suboxic layer, Cr(VI) has only nutrient-like profiles. Thus, the data in **Figure 2A** suggest Cr(VI) to Cr(III) reduction, and correspondingly, Cr(III) shows a maximum at the same depth (**Figure 2B**), although the increase in Cr(III) ($\sim 0.6\,\mathrm{nmol\,l^{-1}}$) is not as great as the Cr(VI) depletion ($\sim 1.3\,\mathrm{nmol\,l^{-1}}$). This is likely due to the higher reactivity of Cr(III), which would be scavenged by particles, decreasing its concentration. While this all might seem in agreement with thermodynamic predictions, the existence of Cr(III) in fully oxygenated surface and deep waters (**Figure 2B**), argues that Cr(III) is kinetically stabilized (slow to oxidize).

Molybdenum

Because many trace elements such as iron function as essential nutrients in the ocean, considerable attention was paid to molybdenum, since it is a

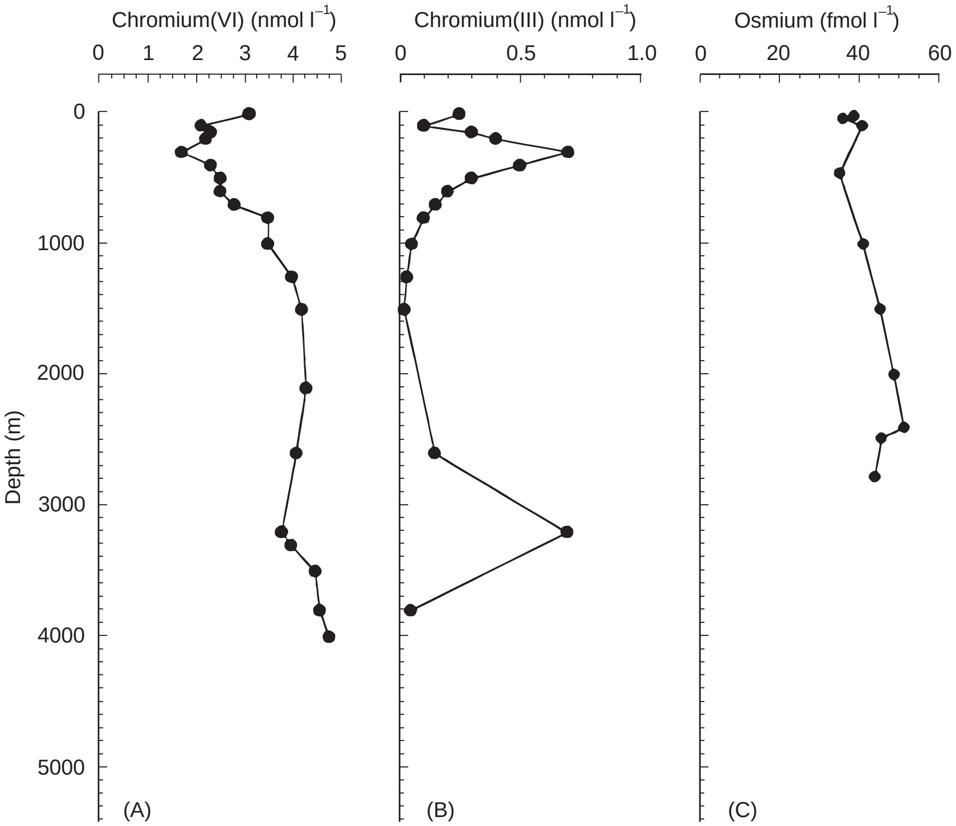

Figure 2 Dissolved Cr(VI) (A) and Cr(III) (B) in the eastern North Pacific Ocean, 23°N, 115°W. (Data from Murray JW, Spell B and Paul B (1983) The contrasting geochemistry of manganese and chromium in the eastern tropical Pacific Ocean. In: Wong CS *et al.* (eds) *Trace Metals in Seawater*, NATO Conference Services 4: *Marine Science* vol. 9, pp. 643–668. New York: Plenium Press.) (C) Dissolved rhenium in the eastern North Pacific Ocean, 9°46′N, 104°11′W. (Data from Woodhouse OB, Ravizza G, Falkner KK, Statham PJ and Peucker-Ehrenbrink B (1999) Osmium in seawater: vertical profiles of concentration and isotopic composition in the eastern Pacific Ocean. *Earth and Planetary Science Letters* 173: 223–233.)

cofactor in the nitrogen-fixing enzyme nitrogenase, and therefore essential for many algae and ecosystems. As a group VIA element like chromium, in oxic sea water dissolved molybdenum should be found in the +6 oxidation state as the hydrolysis product molybdate, MoO_4^{2-}, but in anoxic waters it is reduced to Mo(IV), which in the presence of hydrogen sulfide forms insoluble MoS_2. In fact, molybdenum is enriched in anoxic sediments by this mechanism and, like vanadium, can be used as a sediment tracer of past anoxia. In spite of its crucial biological role, molybdenum in the oxic ocean shows remarkably conservative behavior (**Figure 1B**), with no surface depletion and the highest concentration ($\sim 105\,\mathrm{nmol\,l^{-1}}$) of any of the trace elements examined here. This does not mean that phytoplankton are not taking it up, but rather this uptake is trivial compared to its inputs. Hydrothermal vents also do not remove molybdenum, and the only waters where molybdenum removal is observed are in anoxic basins such as the Black Sea.

Tungsten

Completing the group VIA transition metal series, tungsten is chemically similar to molybdenum and is found in oxic sea water as W(VI) in the form of tungstate, WO_4^{2-}. Owing to difficulties in determining tungsten in sea water, there are few depth profiles for this dissolved element. In the North Pacific Ocean (**Figure 1C**), tungsten displays slightly higher concentrations in surface waters (average of $58\,\mathrm{pmol\,l^{-1}}$) compared to deep waters (average of $49\,\mathrm{pmol\,l^{-1}}$). Dissolved tungsten appears to have a slightly scavenged type of profile, with the surface enrichment likely due to the deposition of terrestrial dust (aerosols). In crustal rocks that are the source of most elements to the ocean by weathering, the abundance of tungsten is about one-third that of molybdenum, but its sea water concentration is over 1000 times less (compare **Figures 1B** and **C**). Since tungsten shows no strong removal in the open ocean, this observation suggests that tungsten must be removed in the coastal ocean. Indeed, profiles of tungsten in estuaries shows strong removal like that of iron; molybdenum shows no such strong removal in estuaries. Thus, while tungsten shows nearly conservative behavior in the open ocean, when the whole land–ocean system is considered, tungsten actually has a very active removal, which lowers its sea water concentration.

Rhenium

Interest in rhenium is for rather esoteric reasons, primarily because one of its radioactive isotopes, and that of its periodic table neighbor osmium, are useful for dating very ancient (>50 billion years) sediments (i.e., the ^{187}Re/^{187}Os ratio). In oxic sea water, Re(VII) is the stable oxidation state and after hydrolysis exists as the relatively unreactive perrhenate ion, ReO_4^-. In the North Pacific Ocean (**Figure 1D**), as well as in the Atlantic, the profile of dissolved rhenium is quite conservative, with an average of $44.3 \pm 0.3\,\mathrm{pmol\,l^{-1}}$. Using the same type of arguments used for tungsten, the very low concentration of crustal rhenium but relatively high sea water concentration (sea water rhenium and tungsten are nearly identical, but crustal tungsten is ~3000 times more abundant than rhenium) suggests that rhenium is very unreactive in the entire ocean system. Nevertheless, in anoxic systems such as the Black Sea, rhenium does show substantial decreases in concentration (nonconservative behavior) that have been attributed to removal at the surface of anoxic sediments. However, in the modern ocean these anoxic systems are too rare to substantially alter the distributions of rhenium in the water column.

Osmium

From the prior discussion of rhenium, it would seem logical to consider the oceanic behavior of the group VIII element osmium in terms of its use as a dating tool. In addition, the ratio of two of its isotopes (^{187}Os/^{186}Os) can trace inputs from extraterrestrial sources (e.g., meteors) and terrestrial sources (i.e., crustal weathering) to the oceans, which are recorded in marine sediments. There is some debate about the exact form of osmium in sea water, but thermodynamic calculations suggest that Os(VIII) as $H_3OsO_6^{2-}$ would be stable in oxic sea water. Determinations of dissolved osmium in sea water are very difficult, especially since osmium concentrations are over 1000 times lower than those of rhenium. Indeed, the profile of osmium in the North Pacific (**Figure 2C**) indicates not only that osmium is found at very low concentrations ($38\,\mathrm{fmol\,l^{-1}}$) in surface waters, but also that its distribution is quite dynamic with depth (minimum at 460 m and rising to $51\,\mathrm{fmol\,l^{-1}}$ in deep waters). This profile is from the eastern North Pacific, which has the distinct suboxic layer, and bears a striking resemblance to that of Cr(VI) in the same region (**Figure 2A**). Thus, osmium may have nutrient-like behavior that is also affected by oxidation–reduction reactions (i.e., reduced to a more particle-reactive (but unidentified) form in the suboxic zone). In this respect, profiles in more oxygenated waters of the Atlantic and Indian Oceans show no such depletion in the upper water column. The nutrient-like distribution does not mean that it is used as a nutrient or nutrient substitute, but rather that it is only carried along in the organic matter cycle.

Germanium

Germanium is a group IVB metalloid, and therefore chemically quite different from the transition metals we have been considering so far. Being directly below silicon in the periodic table, germanium has quite similar chemistry and early studies of phytoplankton that make up their structural skeletons ('tests') of biogenic silica (e.g., diatoms), showed that they take up germanium along with silicon in a relatively constant atomic Ge : Si ratio of $10^{-6}:1$, a value that is nearly identical to the ratio in crustal rocks. Dissolved germanium exists as germanic acid (H_3GeO_4) in sea water just as silicon is found as silicic acid (H_3SiO_4). The depth profile of dissolved inorganic germanium in the North Pacific Ocean (**Figure 3A**) is undoubtedly nutrient-like, and not surprisingly exactly the same as that of silicon (i.e., uptake in the surface by siliceous phytoplankton; recycling at depth by the slow dissolution of biogenic silica). This covariation is the primary reason why there is interest in marine germanium. The Ge : Si ratio derived from crustal weathering inputs to the ocean has a different value from that from hydrothermal vent fluids, and since it appears that the Ge : Si ratio in siliceous organisms records the water column value, the ancient record of crustal weathering versus hydrothermal inputs (i.e., plate spreading) to the oceans can be obtained. Unfortunately, it was discovered that there are methylated forms of germanium in sea water (monomethylgermanic acid, MMGe; dimethylgermanic acid, DMGe) which actually have higher concentrations than inorganic germanium, and for which there are no known silicon analogues. Thus, the two cycles seem to diverge, threatening the usefulness of the Ge : Si tracer. However, the distributions of these two methylated forms are very conservative in the open ocean (**Figure 3B**) and in estuaries. Indeed, methyl-

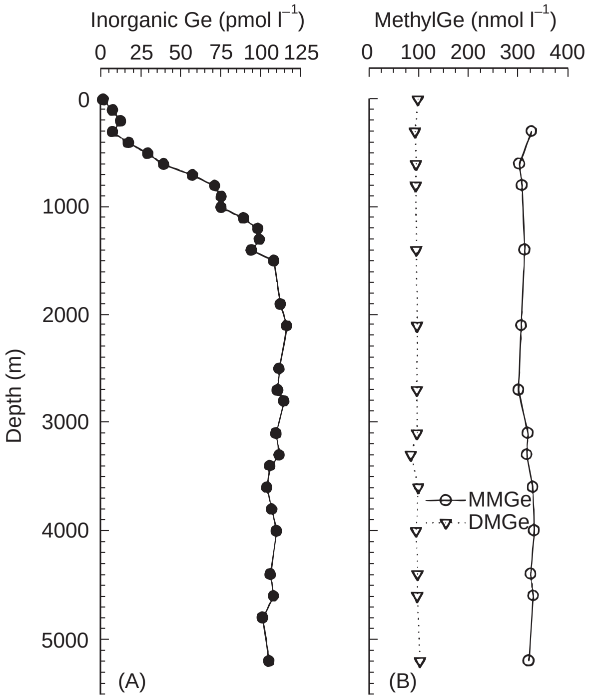

Figure 3 (A) Dissolved inorganic germanium in the North Pacific Ocean, 25°N, 175°E. (Data from Froehlich PN Jr and Andreae MO (1981) The marine geochemistry of germanium: ekasilicon. *Science* 213: 205–207.) (B) Dissolved methylgermanium compounds in the North Pacific Ocean, 25°N, 175°E. MMGe is monomethylgermanic acid and DMGe is dimethylgermanic acid. (Data from Lewis BL, Froelich PN and Andreae MO (1985) Methylgermanium in natural waters. *Nature* 313: 303–305.)

germanium is essentially inert and hence can build up to the observed 'high' concentrations. The source of these compounds still has not been found, although some production in anoxic, organic-rich waters has been documented. Nevertheless, the methylgermanium compounds do not really participate in the germanium cycle, and thus it seems that the Ge : Si ratio can still be used as a weathering versus hydrothermal input tracer.

Arsenic

The group VB element arsenic is usually linked with toxicity, and indeed most studies of this element are driven by such concerns. However, arsenic's toxicity is strongly affected by its chemical form and by the actual organisms being exposed. In oxygenated sea water, As(V) in the form of arsenate ($HAsO_4^{2-}$) is the stable form and, because of its nearly identical chemical properties to that of the nutrient phosphate, is highly toxic to phytoplankton. Interestingly, As(III), which can be found in anoxic waters as arsenite ($As(OH)_3$), is not toxic to phytoplankton but is highly toxic to higher organisms such as zooplankton and fish. While this might seem irrelevant (fish do not live in anoxic waters), many phytoplankton have a mechanism to detoxify arsenate by reducing it to arsenite and releasing it to the oxic water column. Other phytoplankton can methylate arsenate to form monomethyl- and dimethylarsenates (MMAs and DMAs, respectively), which are nontoxic. All of these processes make the marine arsenic cycle quite complicated, a feature that is common for all of the metalloid elements. In the North Pacific Ocean (**Figure 4A**) arsenate has nutrient-like behavior, with depletion in the surface and recycling at depth as for phosphate; this is consistent with their chemistries and biochemistries. In surface waters, biologically produced arsenite and methylated arsenic compounds have their maximum concentrations (**Figures 4A** and **B**), and quickly decrease with depth. Again, these distributions are consistent with established biological processes, and therefore they are not due to scavenging (i.e., input from the atmosphere and then adsorption to particles). Moreover, data for methylated arsenic and As(III) at many sites in the world's oceans show that the amounts of these arsenic forms are roughly the inverse of the phosphate concentration – lower phosphate, higher methylarsenic and As(III). This is consistent with laboratory studies of phytoplankton where, under low-phosphate conditions, more arsenate is taken up and more methylated or reduced arsenic is produced in response to this stress. In addition, the fact that As(III) is found in oxygenated sea water at all (i.e., only stable in anoxic waters) demonstrates that its rate of oxidation is slow enough (half-life of months) that it can build up to almost 20% of the total dissolved arsenic in surface waters.

Antimony

Antimony is a group VB metalloid like arsenic but it has more metallic character and the chemistry of antimony is quite different than that of phosphorus or arsenic. Sb(V) is not as strong a Lewis acid as As(V) and in oxic sea water the stable form would be antimonate ($Sb(OH)_6^-$), while Sb(III), like As(III), would be $Sb(OH)_3$ in anoxic waters. Antimony also has methylated forms analogous to those of arsenic (i.e., MMSb, DMSb), although only MMSb has been found in the open ocean. Antimony is not as toxic as arsenic, and since it is used as a plasticizer and is enriched in fossil fuels, most of the interest in antimony has concerned its use as a pollution tracer (e.g. from the burning of plastics). Most of the data for dissolved antimony in the open ocean are from the Atlantic; the profiles in **Figures 4C** and **D** are typical for this element. The major

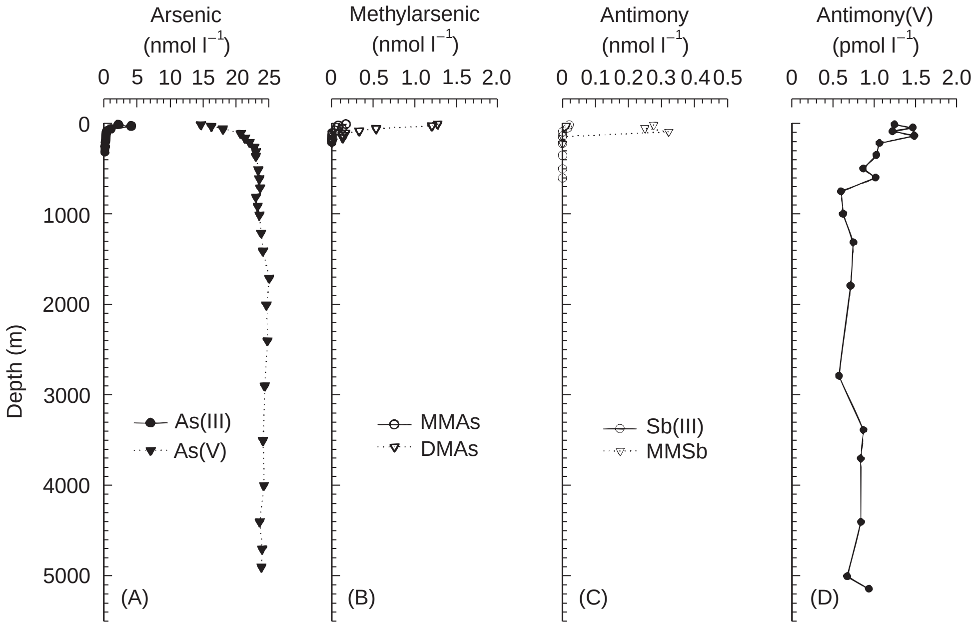

Figure 4 (A) Arsenate (As(V)) and arsenite (As(III)), and (B) monomethylarsenate (MMAs) and dimethylarsenate (DMAs) in the North Pacific Ocean, 30°46′N, 163°30′W. (Data from Andrese MO (1979) Arsenic speciation in seawater and interstitial waters: the influence of biological–chemical interactions on the chemistry of a trace element. *Limnology and Oceanography* 24: 440–452.) (C) Dissolved antimony(III) (Sb(III)) and monomethyl antimonate (MMSb), and (D) antimony(V) in the South Atlantic Ocean, 17°S, 25°W. (Data from Cutter GA, Cutter LS, Featherstone AM and Lohrenz SE (2001). Antimony and arsenic biogeochemistry in the western Atlantic Ocean. *Deep-Sea Research*, in press.)

form of dissolved antimony is antimonate, and it displays a profile consistent with mild scavenging (i.e., maximum of 1.5 nmol l^{-1} at the surface due to atmospheric or riverine input, lower concentrations below the surface layer via adsorption onto particles, some recycling near the sediment–water interface). Measurements of antimony in atmospheric particles (aerosols) and rain show that atmospheric input can explain the surface antimony maximum. Thus, the concentration and behavior of antimony are quite different from those of arsenic. However, MMSb and Sb(III) are found in the surface waters (although the concentration of SbIII is only 0.02 nmol l^{-1}), like the equivalent arsenic forms, but their concentrations do not negatively correlate with the concentration of phosphate (i.e., do not appear to be a result of detoxification reactions). Indeed, it is not clear what mechanisms are producing these forms of dissolved antimony, and bacterial production of MMSb (bacteria are good methylators) and the photochemical reduction of Sb(V) to Sb(III) cannot be ruled out.

Selenium

Selenium is a group VIB metalloid just below sulfur in the periodic table, and its chemistry and biochemistry is very similar to those of sulfur. The interest in this element is based on the fact that this trace element is both essential (e.g., a cofactor in antioxidant enzymes) and toxic, with the chemical form of the element strongly influencing its beneficial or toxic properties. As for sulfur, the most stable oxidation state in oxygenated sea water is Se(VI) as selenate (SeO_4^{2-}), while under suboxic conditions selenite ($HSeO_3^{-}$) would predominate. Selenium forms insoluble elemental Se(0) in anoxic waters, whereas sulfur exists as sulfide (S(II)). Nevertheless, there are numerous organic forms of selenide (Se(-II)) such as selenomethionine, that could be bound in soluble peptides (to be referred to as ‘organic selenide’). There have also been recent measurements of the dissolved gas dimethylselenide ($(CH_3)_2Se$) in surface ocean, which results in a natural selenium input to the atmosphere. Laboratory and field studies have shown that selenite appears to be the most biologically preferred form of dissolved selenium by phytoplankton, while selenate is only taken up in the absence of selenite; data on the bioavailability of organic selenides suggest that these forms are the least available to marine phytoplankton. Depth profiles for dissolved selenium in the eastern North Pacific (**Figures 5A–C**) are from the same region where the chromium and osmium

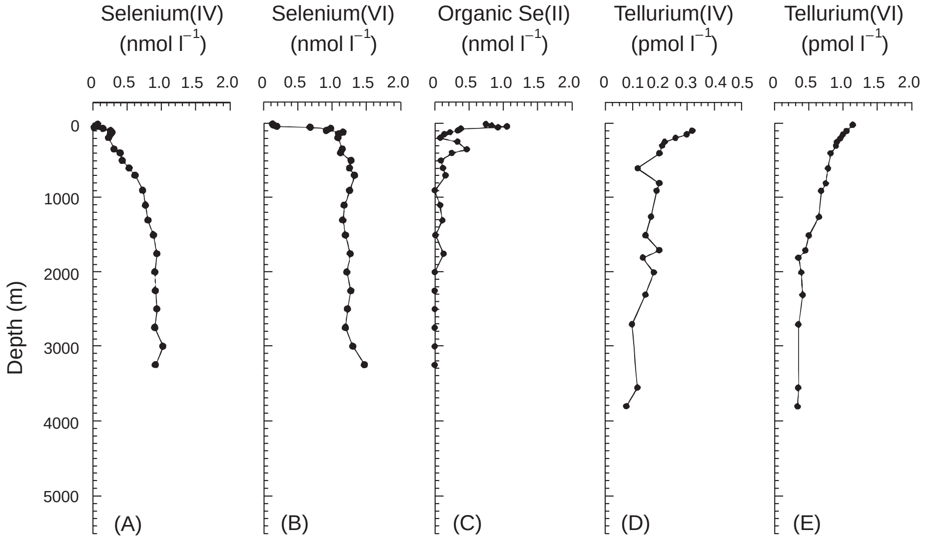

Figure 5 (A) Selenium(IV) (selenite), (B) selenium(VI) (selenate), and (C) organic selenide (organic Se(II)) in the eastern North Pacific Ocean, 18°N, 108°W. (Data from Cutter GA and Bruland KW (1984) The marine biogeochemistry of selenium: a re-evaluation. *Limnology and Oceanography* 29: 1179–1192.) (D) Tellurium(IV) and (E) tellurium(VI) in the eastern North Pacific Ocean, 7°N, 78°40′W. (Data from Lee DS and Edmond JM (1985) Tellurium species in seawater. *Nature* 313: 782–785.)

profiles (**Figures 2A–C**) were obtained, and the water column from ~200 to 800 m is suboxic. In surface waters, both selenite (**Figure 5A**) and selenate (**Figure 5B**) are very depleted, and then show nutrient-like profiles with increasing depth; this is consistent with biotic uptake of both forms, incorporation into organic matter (as organic selenides), and subsequent recycling. In contrast, organic selenide (**Figure 5C**) has a maximum at the surface and in the suboxic zone. Laboratory and field studies using organic matter show that selenium is primarily bound in proteins as organic selenide. When this organic matter degrades, dissolved organic selenide is released, which then sequentially oxidizes to selenite and then very slowly to selenate. This process explains how these unstable forms are introduced to the water column, with kinetic stabilization allowing them to persist. In the suboxic zone, organic selenide is stabilized and a maximum can develop.

Tellurium

Tellurium is a group VIB metalloid like selenium, but its lower position in the periodic table suggests that it has considerably more metallic character than selenium. Thus, Te(VI) exists as $Te(OH)_6$ but, unlike Se(VI), Te(IV) is the stable form as $Te(OH)_4$. There are few data for this element in the ocean, and profiles of tellurium in the eastern North Pacific (**Figures 5D** and E) show that its concentrations are ~1000 times less than those of selenium and both forms of tellurium show strongly scavenged behavior. It is interesting to note that the most abundant form of tellurium is Te(VI), but it is the least thermodynamically stable. Although there are numerous biological reasons to expect reduced species in oxic waters (i.e., as for arsenic and selenium), this observation is somewhat difficult to explain. The elevated concentrations of Te(VI) at the surface, relative to Te(IV), suggest that the atmospheric or riverine inputs of this element are enriched in this form, but virtually no atmospheric data are available to confirm this speculation.

Conclusions

Overall, the classic types of behavior described for trace elements are displayed by the oxyanions. Rhenium, molybdenum, and methylated germanium have conservative, salinity-like distributions with depth. This does not mean that they are truly unreactive, but rather that the reactions affecting them are minor. Vanadium, chromium, osmium, arsenic, and selenium show nutrient-like behavior, although this does not necessarily mean they are biologically required. Tungsten, antimony, and tellurium show scavenged behavior to some degree. Hybrid/mixed behavior was originally defined for trace elements with a single chemical form, but most of the oxyanions can exist in multiple chemical forms, creating a new type of hybrid distributions – oxidation–reduction behavior superimposed upon the other three categories. Finally, the types of behavior found for these elements are strongly affected by both chemical and biological processes, and thus it is appropriate to say that they are 'biogeochemically' cycled.

See also

Aeolian Inputs. Anthropogenic Trace Elements in the Ocean. Atmospheric Input of Pollutants. Carbon Cycle. Conservative Elements. Hydrothermal Vent Fluids, Chemistry of. Marine Silica Cycle. Metal Pollution. Nitrogen Cycle. Platinum Group Elements and their Isotopes in the Ocean. Pollution: Effects on Marine Communities. Refractory Metals. River Inputs. Transition Metals and Heavy Metal Speciation.

Further Reading

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METHANE HYDRATES

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What is Gas Hydrate?

A solid, icelike substance composed of gas and water molecules is called gas hydrate. Water molecules form cage structures in which various kind of gases such as methane, ethane, propane, hydrogen sulfide, and carbon dioxide, are incorporated to form a clathrate structure (**Figures 1** and **2**). Naturally occurring gas hydrate is largely composed of methane and water, and is then properly called methane hydrate but is often referred to as gas hydrate, particularly in the field of earth and ocean sciences. Chemists and petroleum engineers have known about gas hydrates since the nineteenth century. However, most earth and ocean scientists were not aware of the existence of natural gas hydrate (methane hydrate) until it was recovered from a gas field in permafrost in the late 1960s and gas hydrate-related seismic reflectors and gas zonation were identified in deep-sea sediments in the early 1970s. Recent development of marine geological and geophysical surveys have revealed that gas hydrate is widely distributed in deep-sea sediments, and huge amounts of methane are probably trapped as a 'solid gas.' These findings raised three important issues related to human life: gas hydrate could become a potential energy resources, might play an important role in global climatic change, and might cause geological hazards such as slope failures and gigantic gas plumes.

Fundamental Properties

There are three structural types of gas hydrate for which a large number of natural gas molecules have been identified. These are cubic structures known as structures I and II, and the more recently discovered hexagonal structure H. Each structure type is char-

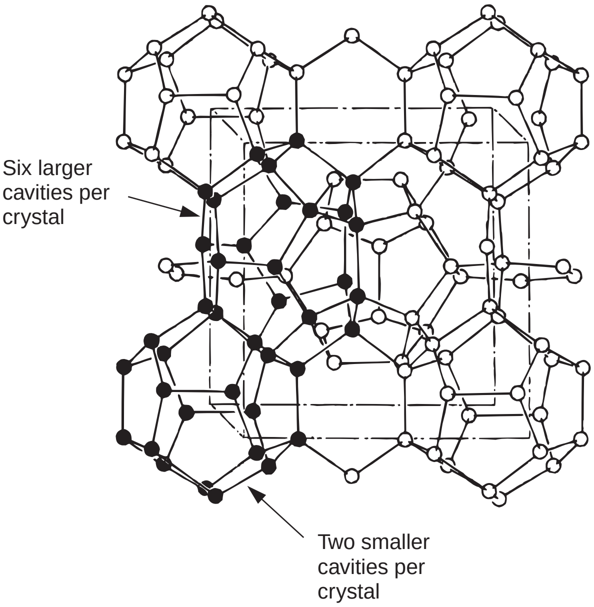

Figure 1 Structure I hydrate lattice composed of six larger cages and two smaller cages. (Hand *et al.*, 1974.)