In Praise of Marine Chemists

BY FLIP FROELICH
Shortly after the birth of the science of analytical chemistry, over 100 years ago, the art of measuring the chemicals in the sea began with the arduous task of analyzing the six major salts in seawater—sodium, magnesium, potassium, calcium, sulfate, and chloride. It soon became apparent that these four cations and two anions make up the bulk of sea salt, and a few more, like boron, strontium, fluorine, and bromine, were all “conservative.” In other words, the salt composition of seawater was quite boring—the salts in seawater from anywhere in the world ocean contain almost exactly the same proportional composition as seawater from anywhere else—and in direct relationship to its “salinity”—a concept that originated with ocean chemists but was forfeited to ocean physicists when the chemical definition of salinity as a measure of salt mass content got corrupted and was no longer useful to calculate in situ seawater density.

In Nozaki’s 2001 compilation of the vertical profiles of the elements and gases in the periodic chart (Figure 1), it is clear that only a small handful of the vertical profiles we have today are conservative. Most of the trace elements in the interior of the periodic chart—the first, second, and third row transition elements plus the lanthanides (rare earths) and actinides plus the metalloid elements out near the right-hand edge (Ge, As, Se, Sn, Sb, Te)—are not conservative but instead display distinct geochemical behaviors in their vertical profiles. These profile shapes helped to identify the likely vectors carrying each element into the deep sea (e.g., nutrient-like and thus bioactive, downward decreasing and thus scavenged, particulate reactive or surface ocean input, opal and carbonate vs. organic tissue) and hinted at the biochemistry involved (i.e., Ge substituting for Si in opal, Zn and Cd cofactors in carbonic anhydrase). These “smooth profiles” thus became criteria against which to judge the quality of later data sets.

The oldest citations in the Nozaki compilation date from about 1966 (though one from 1961 is the classic Noakes and Hood boron paper). Two 1966 papers (still cited today for the law of conservation) are Morris and Riley (on the bromide/chlorinity and sulfate/chlorinity ratios) and Culkin and Cox (on sodium, potassium, magnesium, calcium, and strontium). A few rare gas papers also first appeared in 1964 and on lives of their own, lives often borrowed from the study of the geochemistry of Earth, the moon, and meteorites. It was as if the ocean had just been discovered and a flotilla of chemists had been set loose to figure it out. The flotilla included Gerald Wasserburg, Harmon Craig, Karl Turekian, Ed Goldberg, Clair Patterson, John Edmond, John Martin, Ken Bruland, Ray Weiss, Ed Boyle—and the list goes on to include their students and grand-students. The major programs that made significant ocean biogeochemistry advances were GEOSECS (Geochemical Ocean Sections Study), VERTEX (Vertical Transport...
an ocean that was unforgiving: they had
to get them out of the ocean and out of
the sampling device and delivered back
home to the lab (that is, storing and
transporting bottles) without transfor-
mation of the seawater contained inside
(no sorption onto bottle walls, no bio-
logical activity, and no contamination
from the accelerators and plasticizers in
the bottles themselves), and then they
had to do the lab work (column concen-
trations and separations of interfering
components and the final analyses, the
analytical chemistry part). Sampling
gear had to be designed, fabricated, and
tested to avoid trace metal contamina-
tion from rusting steel hydro cables,
from painted steel boats (both the hulls,
the houses, and the interior labs), or
from the conductivity-temperature-
depth (CTD) rosette itself (Fe, Co, Ni,
Cu, V, Cr, Mn, Zn …… Al, Ti) or in the
background atmosphere (dust Al and Fe,
ship's stack exhaust, tailpipe fine phase
Pb). Chemists went to sea sheathed in
plastic and bathed in acid. Boyle devised
his “weather vane” water suckers that
clamp onto the wire individually and
sample water “upwind” of the hydro
wire (see Boyle et al., 2014, in this issue).
The Al and Fe groups devised their own
metal-free rosette and its bottles, and
hung them on their own one-of-a-kind
1,000 m Kevlar cable (see Grand et al.,
2014, in this issue). Things that go into
the ocean often don’t come back and are
thus best interpreted as expendable—
as Bill Landing, Chris Measures, and
scientific crew discovered when their
Kevlar cable parted and their rosette
ended up on the bottom in the Southern
Ocean. The worst actor of the elemental
lot—mercury—proved recalcitrant until
recently because of its obtuse speciation
(liquid, vapor, redox, and methylated)
and tendency to stick to anything and
everything (see Lamborg et al., 2014, in
this issue). MeHg is second only to plu-
tonium in its toxicity. Despite decades of
work elucidating the Hg-biomethylation
process by sulfate reducing bacteria in
anaerobic sediments, the open ocean
processes leading to biomethylation and

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Figure 1. Vertical profiles of elements in the North Pacific Ocean. Reprinted from Nozaki (2001) with permission from Elsevier
bioaccumulation of this toxin at the top of the pelagic food chain remained enigmatic. Just last year, the first reliable isotopic values for MeHg in seawater were published (Blum et al., 2013).

Today, this practice of trace element paranoia is universally accepted. Modern lab instrumentation involves mass spectrometers (MC-ICP-MS) with hyphenated front-end chemistries (HG, GC, LC, HPLC, CE, ESI, MALDI—the list is almost endless) with incredible GC, LC, HPLC, CE, ESI, MALDI—the hyphenated front-end chemistries (HG, mass spectrometers (MC-ICP-MS) with modern lab instrumentation involves chemists will need more and better toys to marry the organic and inorganic trace components and isotopes in the sea. [67]

REFERENCES


