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Titan: A new facility for ultraclean sampling of trace elements and isotopes in the deep oceans in the international Geotraces program

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Abstract

Towards more rapid ultraclean sampling of deep ocean waters for trace elements, a novel rectangular frame was constructed of titanium, holding two rows of 12 samplers, as well as various sensors. The frame is deployed to deep ocean waters by an 8000 m length Kevlar wire with internal power and signal cables. Closing of each sampler is by seawater hydraulics via silicone tubings connecting each sampler with a central 24 position Multivalve. Upon recovery the complete frame with 24 samplers is placed inside an ultraclean laboratory van, where water is drawn via filters into bottles. Previously the clean sampling of ocean waters has been very time-consuming by attachment of individual ultraclean bottle samplers one by one to a metal-free (e.g. all-Kevlar) hydrowire. The novel Titan system is 3–4 times faster and permits routine collection of deep ocean sections while economizing required shiptime. In a test of the new system in November 2005 in the Canary Basin excellent low dissolved Fe concentrations (~0.1 to ~0.4 nM) are consistent with values obtained of individual samplers on a simple wire, and previous values in a pilot study of 2002 in the same basin, as well as published dissolved Fe values elsewhere in the northeast Atlantic Ocean.

Keywords: Sampling; Clean; Titanium; Trace metals; Oceans

1. Introduction

The distribution of trace metals and other trace elements in the world oceans has been, and still is, one of the grand challenges in oceanography. Having been encouraged by remarkable findings of metal-rich hot salty waters at the bottom of the Red Sea (Brewer et al., 1965), soon attention was focused on the remarkable chemistry in anoxic waters of the Black Sea. Here a dramatic increase of dissolved manganese (Mn) was found going from about 0.5–5 nM within the oxic surface waters to as high as a maximum of about 8–9 μM in the anoxic deep waters (Spencer and Brewer, 1971). In later expeditions these values and remarkable trends for dissolved Mn were nicely confirmed and further investigated (Haraldsson and Westerlund, 1988; Lewis and Landing, 1991). Similarly the dissolved iron (Fe) showed a strong increase, albeit less dramatic than Mn, from the oxic into the deeper anoxic waters (Spencer and Brewer, 1971) of the Black Sea. In the later studies this

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trend was also reported, with varying depths and intensities of the dissolved Fe maximum (Haraldsson and Westerlund, 1988; Lewis and Landing, 1991).

1.1. The GEOSECS program

Thus when the very ambitious GEOSECS program started, the sampling and detection of a suite of trace elements (Fe, Cu, Zn, Co, Sb, Cs and U) was also vigorously pursued at an initial GEOSECS-II test station (Brewer et al., 1972). However these earliest results have eventually become superseded (Campbell, 1983) by the first reliable data collected some years later. The increased awareness of the need for clean techniques of sampling, filtering and analyzing seawater for trace metals, led to the criterion of oceanographic consistency, as first mentioned for Cu versus nutrients in surface water samples collected along a transect (Boyle and Edmond, 1975). Next, the first convincing vertical profiles of dissolved metals Cd (Boyle et al., 1976), Ni (Sclater et al., 1976), Mn (Bender et al., 1977), Cu (Boyle et al., 1977), and Al (Hydes, 1979) were reported. These later GEOSECS samples (Campbell, 1983, his Table 44.2) were collected with standard 30 L Niskin samplers mounted on a Rosette. Nevertheless routine sampling and analyses still were extremely difficult, and within the GEOSECS program complete ocean vertical section distributions for trace elements were realized merely for one: the apparently less contamination-prone 'non-metallic' earth-alkaline element Ba (Bender et al., 1972; Bacon and Edmond, 1972; Chan et al., 1977). Moreover the sampling system did not permit (Bruland, 1983) uncontaminated samples to be collected for certain very contamination-prone trace metals, notably Zn (Bruland et al., 1978), Fe or Pb.

1.2. Clean sampling for Pb

Quite independently the zealous and successful efforts of Clair Patterson to determine lead (Pb) in seawater, led to development of a new deep-water sampler with which samples could be collected free from contamination by the ship and hydrowire (Schaule and Patterson, 1981). This allowed Patterson and co-workers to quantify and understand the natural cycling of Pb in the exterior biosphere of our precious planet, and discover the major perturbations of this cycle due to severe global contamination by mankind. In combination with his previous first-ever reliable dating of the 4.55 million years age of the whole planet by Pb isotopes (Patterson, 1956), the achievements and contributions of Patterson cannot be underestimated; yet outside the scientific community they have been (Bryson, 2004).

1.3. Clean sampling for several metals

The deep-sea sampler of Patterson and Schaule was a marvelous breakthrough, yet each time-consuming lowering yields only one sample to be collected. However Bruland et al. (1979) took another approach by mounting several internally Teflon-coated GO-FLO (General Oceanics) non-metallic water samplers one-by-one on a Kevlar (non-metallic) hydrowire. By detailed comparison with Patterson's sampler no significant differences were observed for Zn, Cu, Ni and Cd (Bruland et al., 1979). Soon afterwards the classical article on these four trace metals and their co-variances with major nutrients did appear (Bruland, 1980). This was followed by the first-ever reliable data on dissolved Fe (Landing and Bruland, 1981) as confirmed soon afterwards relying on the same Teflon-coated GO-FLO sampler approach (Gordon et al., 1982) and eventually published (Landing, 1983; Landing and Bruland, 1987). All previous reported values of dissolved Fe in seawater, from year 1874 onwards (as reviewed by De Baar, 1994) had become obsolete. The approach of mounting several individual GO-FLO samplers, one after another, on the Kevlar hydrowire was more efficient than doing one sample at a time, and has become the standard method for sampling trace metals (trace elements) in the oceans.

This article is focused on trace-metal-clean sampling devices. Nevertheless one must realize that breakthroughs were also very much dependent on the awareness of inadvertent contamination by common plastics (e.g. Patterson and Settle, 1976; Moody and Lindstrom, 1977), and the parallel developments of several clean analytical methods, notably the very successful dithiocarbamate/solvent extraction procedure (Kinrade and van Loon, 1974; Danielsson et al., 1978; and independently Bruland et al., 1979).

The revolutionary 1975–1983 era led to discoveries of several more 'oceanographically-consistent' vertical profiles of many trace elements, for example of Ce and the other lanthanides, independently by Elderfield and Greaves (1982) and by the group of Peter Brewer (De Baar et al., 1983, 1985). With the comfort of hindsight we now realize that the review by Brewer (1975) on minor elements in sea water, did appear in print one year before the revolution started (Boyle et al., 1976), and the quantum leap in knowledge of trace elements necessitated a new review chapter within less than a decade (Bruland, 1983).

1.4. The Fe age in oceanography

Just a few years later Fe was shown to be a limiting trace element for phytoplankton growth, first in the