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"PRISTINE", a new high volume sampler for ultraclean sampling of trace metals and isotopes

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ABSTRACT

Many trace elements like Mn, Fe, Co, Ni, Cu and Zn are essential for marine life, some trace elements are of concern as pollutants, e.g. Pb and Hg, while others, together with a diverse array of isotopes, are used to assess modern-ocean processes and the role of the ocean in past climate change. GEOTRACES is an international program that aims to measure the distribution of trace elements and isotopes throughout the world oceans to improve our understanding of their marine biogeochemical cycles. To contribute to GEOTRACES a new sampler system was developed at NIOZ allowing efficient sampling of large volumes of seawater under ultraclean conditions. The 24 "PRISTINE" samplers each with a volume of 24.4 L are made of a high-purity polymer Polyvinylidene Fluoride (PVDF) and are opened and closed using a butterfly-valve closing mechanism. The samplers are mounted on an all-titanium frame and deployed using a poly-aramide hydrowire (Super Aram) with internal power/signal conductors. Upon recovery the complete frame is immediately placed in its own clean-air laboratory unit. Samplers are (i) always closed when onboard, (ii) always mounted on the frame without the need for hand-carrying heavy samplers, and (iii) can be deployed again with minimal (manual) preparation. The PRISTINE ultraclean sampling system was used for the first time during the GA02 GEOTRACES cruises in the West Atlantic Ocean (2010–2012). During 60 full ocean depth stations all 24 samplers closed with a 100% success rate. Sampling proved to be much faster, less labor intensive, and ultraclean. A comparison of salinity, temperature, nutrient and oxygen data collected with the rectangular titanium frame with PRISTINE samplers and a traditional CTD frame with Niskin samplers showed that the CTD systems functioned equally well, that the PRISTINE samplers took discrete seawater samples without any inward leakage of seawater during the up-cast, and that no atmospheric oxygen contaminated the seawater samples in the PRISTINE samplers after return on deck. The excellent agreement between 13 trace elements sampled with PRISTINE and sampled during the cross over occupation of US-GEOTRACES at the Bermuda BATS site (32°N, 64°W) shows its suitability for ultraclean trace element and isotope sampling (see accompanying paper).

1. Introduction

Trace elements like Mn, Fe, Co, Ni, Cu and Zn are necessary constituents in many metabolic functions of marine organisms (de Baar and LaRoche, 2003; Morel and Price, 2003). Other trace elements like for example Pb and Hg are toxic. Trace elements play key roles in ocean ecosystem functioning, biological production, and the biogeochemical cycles of nutrients and carbon. Therefore, to understand the Earth's system and how global climate change will affect this system, it is important to understand the marine biogeochemical cycles of these trace elements. In the sedimentary record, trace elements and their isotopes also form important tools to investigate environmental conditions and changes in the past. However, the large-scale oceanic distributions of these trace elements and isotopes in the modern oceans and the processes that govern their distributions are still poorly known.

The GEOTRACES project is an international project that aims to improve our understanding of biogeochemical cycles and large-scale distributions of trace elements and isotopes in the marine environment and establish the sensitivity of these distributions to changing environmental conditions (Henderson et al., 2007). The objective is to elucidate important biogeochemical processes, sources and sinks that determine the distributions of bio-essential and other trace elements in the

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world oceans. Advances in clean sampling protocols and equipment as well as analytical techniques now allow for the high resolution sampling of a wide range of trace elements and isotopes along full depth transects across the world's oceans.

To contribute to GEOTRACES, a new sampler system "TITAN" was developed at NIOZ in 2005 allowing efficient sampling of seawater under ultraclean conditions (de Baar et al., 2008). A rectangular shaped all-titanium frame was developed and fitted with a CTD system in a titanium housing and 24 conventional newly purchased GO-FLO samplers of 12 L volume each. To guarantee trace metal clean sampling each GO-FLO sampler was coated internally with Teflon. The use of GO-FLO samplers (General Oceanics) made of PVC and internally coated with Teflon has been an accepted method for trace metal clean sampling ever since its first application more than 30 years ago (Bruland et al., 1979). To reduce the risk of contamination the GO-FLO samplers stayed closed while on board and only opened after deployment at 20 m depth. After recovery, the complete TITAN frame was immediately placed inside a clean-air laboratory unit for sub-sampling and remained there until its next deployment. This complete system has been used successfully during several cruises in the Arctic, Antarctic and Northeast Atlantic Ocean with a total of 113 full depth casts. The system proved clean to sample for dissolved Fe (Klunder et al., 2014), the organic complexation of Fe (Thuróczy et al., 2011), dissolved Al (Middag et al., 2009), dissolved Mn (Middag et al., 2013), dissolved Zn (Croot et al., 2011), the organic speciation of Zn (Baars and Croot, 2011), dissolved Cd (Baars et al., 2014) and the stable isotope composition of dissolved Cd (Abouchami et al., 2011, 2014; Xue et al., 2013) and Zn (Zhao et al., 2014).

To allow the clean sampling of larger volumes of seawater for a whole suite of trace elements and their stable isotopes, a new sampler system was developed at NIOZ in 2010. The TITAN frame is now fitted with 24 "PRISTINE" samplers each with a volume of 24.4 L. When designing the new PRISTINE samplers, all drawbacks from the existing GO-FLO samplers were dealt with and eliminated. The PRISTINE samplers are made from intrinsically clean PVDF whereas GO-FLO samplers are made of Teflon coated PVC. The PRISTINE samplers do not require an internal pre-cleaning step with dilute acid as sometimes performed with GO-FLO samplers. The PRISTINE samplers use a butterfly valve system allowing a large opening at the top and bottom whereas the GO-FLO bottles open and close using a small rotating ball-valve system. The butterfly valve system ensures better flushing, the secure and reliable closing of the samplers, and the use of a seawater filled hydraulic closure system versus stainless steel springs. Furthermore, the PRISTINE samplers have no dead spaces and can be fully drained, thus preventing any risk of missing any sedimented particulate fraction. Finally, the PRISTINE samplers can be prepared for deployment without handling them in less than 3 min, versus at least half an hour of full human contact labor with the GO-FLO bottles.

The TITAN frame fitted with the PRISTINE samplers has now been successfully used during 8 research cruises along the whole West Atlantic Ocean, in the Mediterranean Sea and the Black Sea, totaling over 130 full depth hydrocasts. In this article we present the PRISTINE samplers and use some of the data from the West Atlantic Ocean to show its suitability for large scale trace metal clean sampling of large volumes of seawater. An accompanying article shows in a more extensive way that this trace metal clean sampling system has been successfully involved in the inter-comparison of a suite of 13 trace elements sampled during a cross-over station at BATS between the Dutch GA02 GEOTRACES cruise in 2010 and the US GA03 GEOTRACES cruise in 2011 (Middag et al., 2015–in this issue).

2. Materials and methods

2.1. The PRISTINE samplers

2.1.1. Materials of the PRISTINE sampler

All metal parts of the PRISTINE samplers are made of unalloyed (pure) grade 2 Ti. The rationale for using Ti which is also used in the TITAN frame (de Baar et al., 2008) is that Ti is a relatively inert metal that withstands corrosion in the seawater environment. It is also relatively easy to shape Ti into custom-made products. We did consider graphite-epoxy (carbon fiber) as it is the least corrosive in the galvanic series, but this is only economical for production in series using costly molds. The use of metals like aluminum (Al), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), silver (Ag), cadmium (Cd), tin (Sn), platinum (Pt), mercury (Hg) and lead (Pb) was avoided as these are the metals we are interested in to measure in the marine environment and would therefore form a contamination risk. An external coating to separate the parts made of these metals from the seawater could be applied, however, coatings tend to get physical damage or cracks or may be porous. Moreover, seawater is corrosive to many metals and corrosion may occur invisible under the coating. Although Ti is also a trace element of interest in the oceans, it is shown that there is no detectable Ti contamination from the PRISTINE samplers or from the Titan frame (Middag et al., 2015–in this issue).

The large volume PRISTINE samplers are made of the polymer Polyvinylidene Fluoride (PVDF). Ultra-high purity grade PVDF is produced in a clean room environment by Georg Fischer Piping Systems (Herzogenburg, Austria) and available under the commercial brand name SYGEF® Plus. Major customers are the semi-conductor and the pharmaceutical industry, both requiring high purity production processes. The PVDF is free of additives, pigments or stabilizers and has a white opaque appearance. We chose to use PVDF because low purity plastics contain almost all of the trace metals of interest as either impurities or sometimes intentionally as a catalyst or stabilizer in the production process. For example, Cd is used as a catalyst in many plastics and Al is sometimes used as a catalyst in the production of polyethylene, whereas Sn is used as a stabilizer in PVC. Coating low purity PVC with Teflon spray has been the practice for GO-FLO samplers or lever-action type Niskin or Niskin-X samplers. However, also here cracks or porosity in the coating may expose the underlying low purity PVC.

2.1.2. Construction and operation of the PRISTINE sampler

The samplers are designed in a way that once the sampler is closed, the seawater sample is only in contact with the high purity PVDF, the two flat silicone O-rings and the polytetrafluoroethylene (PTFE, Teflon) of the two small valves for draining (lower) and inlet (upper) of N_2 gas. To construct the PRISTINE samplers, PVDF piping with a length of 1080 mm, an external diameter of 180 mm and an internal diameter of 162 mm was used (Fig. 1). PVDF sheets with a thickness of 60 mm were used to construct two end-pieces that were hot plate welded on both ends of the straight pipe, together forming the main body of the sampler (Fig. 1). Note that each end-piece has an internal 135° angle ring surface extending 7 mm inwards that serves as the resting surface for the round, flat silicone O-ring in the closing lid to completely seal the closed sampler (Fig. 1). Furthermore, there are two external extensions (Fig. 1). One extension is used to attach 2 titanium levers and the actuating cylinder used to drive the third central Ti lever. The second extension is to implement the small PTFE valve to drain the bottle for sample or pressurize the bottle with N_2 gas. The bottom PTFE draining valve is positioned in such a way that the sampler can be completely drained. Furthermore, two PVDF mounting rings are fitted on the outside around the sampler body just above and just below the lower and upper end-pieces to fix the PRISTINE sampler to the titanium frame using Ti bolts.

The lids are also cut from 60 mm PVDF sheets. Each round lid has a groove around its circumference in which a flat sealing ring is placed which is cut from silicone elastomer (polysiloxane) (Fig. 1). We chose a flat silicone ring because a flat ring adjusts to unconformities as small dents or imperfections in the roundness of the sampler body while still maintaining a reliable seal. The samplers are closed while on board and during deployment through the ocean surface. At 5–10 m depth the lids start to open automatically, using the outside water pressure as a driving force. Because the bottom lids on each sampler experience a 0.13 Bar higher pressure to open than the top lids, the