

## Particulate Chemical Signatures during VERTIGO.

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### 1.0 INTRODUCTION

The Nozaki (1997) chemical periodic table representation of vertical profiles of the elements in the North Pacific ocean is now compelling introductory chapter material for marine biogeochemistry textbooks (Sarmiento and Gruber, 2006). The profiles synthesized in the table represent 30 years of effort in the post GEOSECS era by numerous investigators (Bruland 1980a,b, Boyle et al, 1977, 1981... and hundreds of references). The profiles clearly indicate a variety of direct and accidental involvements in the biological carbon cycle.

Knowledge of the large scale oceanic distributions of dissolved trace metals -- seemingly well determined as implied by the Nozaki figure -- is in fact severely limited in the world's oceans. Knowledge of particulate trace metal abundances is even more severely limited. Most is known about the major particle associated trace elements Fe and Mn (e.g. Landing and Bruland 1987, Bishop and Fleisher 1987). Early work extending the suite of particulate trace metals and isotopes includes (Bacon et al. 1976, Bishop et al., 1977, Bishop, 1988, Sherrell and Boyle 1992, Jeandel et al. 1995).

Lam et al, (2006), Lam and Bishop (submitted) have seen clear evidence of long distance transport of shelf derived acid labile iron particles into the interior of both eastern and western N Pacific oceans. The east to west enhancement of biology and the strength of the biological carbon pump can be explained by stronger than previously recognized lateral -- just below the surface layer (and thus stealthy) -- transports of iron and other reactive species from the continental margin. Such transports appear to eclipse dust iron supply.

### Particle Studies Using the Multiple Unit Large Volume in-situ Filtration System

#### MULVFS.

Since its inception, the Multiple Unit large Volume in situ Filtration System has evolved in capability and reliability. Now it is a virtually 'turn key' system able to support multi-investigator studies of collected particulate samples. The present system collects particles and dissolved materials using three independently metered flow paths (Fig. 2).

Briefly, MULVFS consists of 12 electrically powered pump units deployed simultaneously to kilometer depths using a specialized electromechanical cable and winch system. Each light-weight pump unit collects size-fractionated particulate matter samples using its main filter holder assembly. Approximately 10,000 liter volumes of sea water are filtered under a suction of <0.8 atm over four to five hours (total ship time per cast is ~7-8 hours) through a 25.4 cm diameter filter series consisting of 51  $\mu\text{m}$  polyester (or 53  $\mu\text{m}$  Nitex) square mesh prefilter, and a pair of identical Whatman QMA quartz fiber filters (approximate pore size of about 1  $\mu\text{m}$ ). The three particle size fractions represented by these filters are >51, 1-51, and '< 1 $\mu\text{m}$ '. The < 1  $\mu\text{m}$  fraction is non quantitative but represents compositional systematics of particles in the larger sub micron particle class. The >51  $\mu\text{m}$  samples contain particles contributing mostly to particle sedimentation and the

<51  $\mu\text{m}$  size fractions represent the slowly sinking material that in most cases dominates particulate matter concentration. Exceptions to this general rule occur in the euphotic zone where >51  $\mu\text{m}$  phytoplankton can be found at times.

The amounts of material retained on the main flow channel's (Fig. 2A-1) 1-51  $\mu\text{m}$  QMA filter ranges from 100-300 mg. Replicate analysis samples of 1/50th of the filter area of this filter reproduce absolute elemental composition typically at several percent (see Bishop et al. 1977, 1985). To the unaided eye, the samples are uniform. The prefilters collect 10-150 mg quantities of material. Due to the somewhat heterogeneous nature of aggregate particles water column, replicate subsamples of the same prefilter usually repeat at 10%. The second flow path (Fig. 2A-2), with 1000-2000 liter water flow has been used for Mn treated radionuclide adsorption cartridges or for entirely separate multi-stage filter holders (one provided by Tom Trull (Australia) is shown in Fig. 2A-2). A third, separately metered flow path (Fig. 2A-3) enables as many as 6 small 47 mm filter holders or absorbers to be co-deployed. We use two of these 6 places for quantification of >0.4  $\mu\text{m}$  Si and major trace elements (Ba, Mn...), the latter to cross check particle capture efficiency of the main QMA filters (for those interested, the short answer is that fine micron/submicron size Mn and Ba particles show less than 10% difference between the 0.4  $\mu\text{m}$  and <1  $\mu\text{m}$  QMAs).

For the recent VERTIGO project each 12 pump MULVFS cast generated ~60 distinct samples; each main sample was further split 4 to 6 ways (Fig. 2C). 5 deployments of MULVFS were carried out during the VERTIGO occupation of station ALOHA; 4 casts were completed during occupations of station K2.

## 2.2 Sample analysis.

Sine 1992 we have began a routine program of ICP-MS analysis of the major, minor, and trace metals leached from MULVFS samples by 0.6 N HCl at 60 C over 24 hours. This treatment does not depart significantly from that of Bishop et al, (1977) except that all sample preparation, at sea processing and shore based analysis was accomplished using trace metal clean techniques and wherever possible in a class 100 environment. Methods for Si are described by Bishop et al. (1977). C and N results were determined as described by Buesseler... MULVFS sampling and analysis protocols are described in supplemental materials.

## 2.2 VERTIGO: Iron transports from the continental margin in the Subarctic NW Pacific.

During the VERTIGO 2005 occupation of station K2 (Figure 1) near Japan, we discovered shallow and intense subsurface maxima of both particulate Fe and Mn; concentrations exceeded OSP levels by nearly a factor of ten Lam and Bishop (in review). Synchrotron XRF and ICP-MS analysis once again confirmed that substantial quantities of the particulate iron was acid labile and not silicate bound. The Mn peak at 135 m was found on an isopicnal that out crops at the depth of the Kamchatka continental shelf and at the depth of the Kuril-Kamchatka island arc sill which separates the Sea of Okhotsk from the N Pacific Ocean. Some material could be derived directly from the Sea of Okhotsk. A number of other lines of evidence including the temporal variability of Fe and particles near the depth of the Fe maximum rules out the importance of dust supplied iron to the area near K2 --- nearly 500 km from the closest shelf/sill.

## 2.3 Results and discussion of VERTIGO: ALOHA -vs K2.

The major, minor and trace element chemistry of MULVFS sample collections during VERTIGO occupations of ALOHA and K2 is shown in (attached 4 figures). The VERTIGO goal was to contrast particle abundances and fluxes in the (100-1000 m) twilight zone in differing productivity regimes.

Particulate P distributions showed approximately three times more fine material in the surface waters at K2 than at ALOHA. The real difference was in the  $>51 \mu\text{m}$  size fraction where P abundances at K2 exceeded ALOHA levels by a factor of ten.

Biogenic Si was  $\sim 50$  times more elevated (nearly  $2 \mu\text{M}$ ) in K2 surface waters compared with ALOHA ( $\sim 50 \text{ nM}$ ), consistent with relative differences in sedimentation fluxes inferred for the two areas (Honda et al. 2002).

Biogenic Ca occurred at similar levels at ALOHA and K2 but was concentrated more in near surface waters at K2 in the  $> 51 \mu\text{m}$  fraction. Day/night pairs of MULVFS profiles separated in time by  $\sim 10$  days showed a significant decrease for Ca in the  $>51 \mu\text{m}$  fraction and also factor of two decrease over ten days of  $1-51 \mu\text{m}$  fraction in the 100-300 m depth interval.

Trends of decreasing particulate Ca and Si in the  $>51 \mu\text{m}$  fraction match trends of decreasing sedimentation described by Buesseler et al. (in review). The profiles collected just 36 hours apart replicated extremely well in the biologically dynamic waters of K2. The relatively rapid changes over 10 days at K2 contrast with a very static - non varying distributions seen at ALOHA.

Strontium in particles can occur at high concentrations when Acantharia are present. This was true for station ALOHA where Sr was found at particularly elevated concentrations in the  $> 51 \mu\text{m}$  fraction. A strong concentration decrease with depth of  $>51 \mu\text{m}$  Sr is consistent with dissolution and mechanical fragmentation of Acantharian shells with depth (Bishop et al., 1977).

Barium has been used as a proxy for paleo productivity and the formation of particulate Ba in the water column appears to take place in aggregate (fecal material... marine snow) microenvironments and fragmented diatom frustules and is this an indicator of particle export (Bishop 1988). Buesseler et al. (submitted) found particle mass fluxes at K2 to be 10 times more elevated than at ALOHA. The abundances of Ba in the  $>51 \mu\text{m}$  fraction parallels this trend exactly.

Manganese in the  $1-51 \mu\text{m}$  fraction displayed the classic signature of material rapidly delivered from the continental margin sediment sources (section 2.2). Interestingly, the  $>51 \mu\text{m}$  particle fraction shows peak concentrations at depths shallower than the  $1-51 \mu\text{m}$  Mn peak. It appears that particle packaging organisms feeding near the 135 m Mn maximum are migrating vertically and producing Mn enriched fecal material at shallower depths. This is another mechanism where by reactive elements can be transported vertically and fuel biological processes in the euphotic zone.

In Figure X we have only shown profiles of  $<1 \mu\text{m}$  P. We have not plotted  $<1 \mu\text{m}$  Ca, Sr, Ba or Mn - since levels of these latter elements only several percent of those of the  $1-51 \mu\text{m}$  fraction. The same is not true for Cd and Zn as depicted in Figure 5, thus all three size fractions are presented.

Cadmium at station K2 shows concentration trends with time and depth that almost exactly parallels that for P; thus Cd and P appear strongly correlated as they are in the water column. Surprisingly, The particle Cd:P molar ratio is five times elevated ( $1.5 \times 10^{-3}$ ) relative to the dissolved Cd:P ratios in the N Pacific ( $0.3 \times 10^{-3}$ ). In contrast particulate Cd and P at ALOHA are only correlated in the  $>51 \mu\text{m}$  fraction (and that ratio is sub oceanic at  $0.1 \times 10^{-3}$ ). In the  $1-51 \mu\text{m}$  fraction at ALOHA Cd appears most closely correlated with Ca (Cd:Ca  $\sim 1.25 \times 10^{-5}$ ). Kremling and Stru (2001) report Cd:P variations from 0.1 to  $\sim 0.7 \times 10^{-3}$  in the North Atlantic. K2 is twice as extreme.

Zinc in the silica-rich  $>51 \mu\text{m}$  fraction K2 has a clear biotic signature with a Zn:P molar ratio of 0.025 and a Zn:Si molar ratio of  $0.13 \times 10^{-3}$  (dissolved Zn:Si  $\sim 0.05 \times 10^{-3}$ ; Bruland (1980a)).

At K2 both Zn and Cd co-occur in particles above ratios that their dissolved oceanic distributions systematics would imply.

Cobalt at K2 shows both biotic and abiotic phase associations. The biotic signature is found in the Si-rich > 51  $\mu\text{m}$  material in the surface layer. The > 51  $\mu\text{m}$  concentration trends in deeper waters follow Mn. A clear abiotic behavior in <51  $\mu\text{m}$  material evidenced by the close match to the profile systematics for Mn. Unlike Zn and Cd, Co in the <1  $\mu\text{m}$  fraction showed virtually no profile. The story for Co at ALOHA is very different. Although there is a clear Mn association in the 1-51  $\mu\text{m}$  fraction, there is also a clear biotic (surface enhanced) signature in both the 1-51 and < 1  $\mu\text{m}$  fractions. Saito et al. (2004) recently found a biological behavior for Co. Clearly more knowledge of the element's distribution would illuminate the rules for it's behavior and role in biotic carbon cycle processes.

Elements determined in our sample collection but not described above include Al, Cu, Ni, Nd, Pb, and U.

Aluminum is interesting since the element exhibits labile behavior (under our acid leach conditions). Profiles correlate strongly with Fe and the mole ratio of Al/Fe is  $\sim 1.3$ . No known silicate has this composition. We suspect that the particulate Al is a hydrous oxide phase much like the majority of the Fe we detect. The notion of a "refractory Al" does not apply to these samples.

Lam's synchrotron XRAY studies of particulate Fe in the NE and NW have challenged the widely held belief that the major source of iron to the HNLC N Pacific ocean (besides upwelling supply) is dust deposition (Jickels et al, 2005). Although there is a western enhancement of dust delivery to the Pacific, especially in the spring, there is little evidence in the suspended particle field for this process to have been a major factor when we have looked (late winter OSP, late summer station K2). Secondly, we hypothesize that the western enhancement of the biological pump at K2 is explained by a stronger Fe delivery from the continental margin to offshore waters.

- By looking at particles directly we have found clear evidence for shifts of Cd:P and Cd - particle phase associations between biologically dynamic NW Pacific waters at K2 and the highly oligotrophic regime at station ALOHA. Cullen et al. (2003) suggest that Fe limitation decreases Cd/P ratios in phytoplankton. Cullen (2006) further has described 'kinks' in the profiles of dissolved Cd:P ratio. The particles themselves provide a more complete story. The K2 vs ALOHA results suggest that phytoplankton at K2 were fully Fe replete while those at ALOHA would have to be extremely Fe stressed.
- Our results demonstrate that direct sampling and analysis of particles reveals the local biogeochemistry of particle fixation, transport and remineralization in the upper 1000 m. Clearly more comprehensive knowledge of particulate matter geochemistry would benefit interpretation of the distributions of dissolved metals in the ocean.
- Note the replication of the 1-51  $\mu\text{m}$  concentration profiles for particulate Mn and Ba is at ALOHA is at the percent level; replication of the >51  $\mu\text{m}$  fraction is about 10%. This is similar to replication statistics for subsamples of individual MULVFS samples.

### **3 Protocols MULTIPLE UNIT LARGE VOLUME IN SITU FILTRATION SYSTEM**

#### MULVFS CAST/sample documentation

Casts will be identified by standard operation number, date, time of start of cast, filtration starting (time, lat, long), filtration (ending time, lat, long), and time of end of cast. Samples in each cast will be identified by nominal wire out depth, pump id, filter holder id, and volume(s) of water filtered. Depth history of samples determined by internally logging CTD located at end of the MULVFS EM-cable.

#### MULVFS pump handling

Where practical, pumps will be covered with plastic between stations, they will be rinsed with fresh water immediately prior to and after each cast. For best results and personnel work load issues, MULVFS units are staged in a protected environment convenient to deck area where they are deployed.

#### MULVFS filter holders

Filter holders and components will be detergent cleaned and acid leached prior to each cruise. They will be rinsed with Milli Q water after each use. They will be covered with plastic until just prior to deployment.

#### MULVFS sample handling

All samples will be processed in a laminar flow clean bench aboard ship. Non-contaminating gloves, subsampling templates, and tweezers will be used. Samples are oven dried at 60 C for 1-2 days. This procedure is described by Bishop et al., 1985. Samples are stored dry in clean polyethylene bags. Samples will be rinsed at sea to reduce the sea salt content ten-fold in order to get decent dry weights. Typical rinse volumes at ~10 cc's. This results in potential loss of organics and labile elements. (This effect is no more than 15% for bulk carbon, Bishop et al. 1986). UNRINSED SUBSAMPLES MAY BE OBTAINED.

#### Filter type and sample identification

We use a series of standard filter types in each Main filter holder [Fig2A-1]: 51  $\mu\text{m}$  polyester screen, and 2 identical Whatman QMA quartz fiber filters (pore size ~1  $\mu\text{m}$ ). These filters are repeatedly batch leached in clean acid (HCl) and MilliQ water rinsed 3 times following Bishop et al. (1985). This procedure is carried out in a laminar flow fume hood. QMA's are precombusted in a dedicated muffle furnace prior to weighing. Filter sets are assigned a unique number YYYYnnn at the time that they are assembled for use. YYYY is the year that the filter batch was leached. This number is a unique identifier through out sample history. At least 1 of every 20 filter sets will be retained in the laboratory for blank purposes.

#### Filter Size Fraction Designation

The Polyester screened sample is operationally defined as the >51  $\mu\text{m}$  fraction, the two QM/A filters are defined as the 1-51 and <1  $\mu\text{m}$  fractions, respectively. Comparison of Mn and Ba in 0.4  $\mu\text{m}$  filtered samples obtained using flow path [Fig. 2A-3] are used to crosscheck QMA filtering effectiveness.

#### Filters: process blanks and shipboard blanks:

Process blanks are a set of filters which has been loaded into a filter holder and deployed at depth on one MULVFS pump unit during each cast. This pump is not powered and thus little water passes through the filters (several liters vs 10,000 L of a typical sample). This filter set is processed in an identical way to all samples. One filter set in 30 will be retained unused at sea as a shipboard blank. This blank is similar to laboratory blanks with the sole exception of having been transported from ship to laboratory and back.

#### Large and small particle photography: optical reflectance density distributions:

>51  $\mu\text{m}$  particle size distributions are determined by Digital Photography using standard illumination. Camera response is calibrated with a known photographic gray optical density standard. This method which can resolve 30  $\mu\text{m}$  particles, permits quantification mass loading systematics of 51  $\mu\text{m}$  polyester filters which facilitates subsampling at sea. Assessment of particle loading of the QMA filters also. Lam and Bishop (2006)

#### Dry Weight:

Methodology of Bishop et al. (1976, 1977). 51  $\mu\text{m}$  polyester, and 1  $\mu\text{m}$  QMA filters are preweighed to better than 1 mg in a filtered flow of low humidity air. Unused reference filters are used to track variations in room humidity during weighing. These filters also track variations in dry weight due to humidity differences between the time the filters were originally weighed and after the samples are obtained.

The contribution of sea salt to dry weight values is corrected for by analyzing Na. Na is discriminated against by organisms and therefore is the best estimator of sea salt. Note salt mass to Na mass is 3.61 (not 3.25 as usually assumed); the difference is due to water of hydration of the salts (Lam and Bishop; 2006).

#### Carbon/Nitrogen

Samples are fumed with conc. HCl (to remove carbonates) in closed container overnight. CN elemental analyzer: standards and analyzer blanks by usual procedures. One in every ten samples is repeated, a reference sample is run one each run of 50 samples and standards. >51  $\mu\text{m}$  organic matter is estimated gravimetrically by subtracting inorganic species from dry weight after salt correction. Results are cross checked using P. C and N cannot be estimated >51  $\mu\text{m}$  samples without mechanical removal of material from the filter.

#### ICP-MS acid labile elements:

Li\* | Na\*, Mg\*, Al, P | K\*, Ca\*, Cr, Mn, Fe, Co, Ni, Cu, Zn | Rb, Sr\*, Y, Cd, I | Cs, Ba, Tl, Pb, Bi | Ce, Nd, U\*  
0.6N HCl leach, at 60 C, over night, followed by separation (poretics filtration) of leachate (Bishop et al., 1977). Procedure now employs Seastar ultrapure acids. We have repeat leached samples and have found little added material comes into solution. Analysis by Finnigan Element II ICP-MS. ICP-MS procedures are standard (samples and standards matrix matched, Indium spike, standards mixed in approximate ratios as they occur in samples, individual standards cross checked for presence of other elements). Quality Control for seawater influenced components (\*): repeat analysis of a CASS reference sea water sample of known salinity during each run. Run precision check: 1:10 repeat analysis of samples and reference sample. Bishop et al. (1977, 1985).

#### Silicon (opal)

51 µm prefilter samples are leached in 1M Na<sub>2</sub>CO<sub>3</sub> over night. After filtration, samples are neutralized with HCl and analyzed using methodology of Bishop et al. (1977). 1-51 µm opal cannot be measured on QMA filters but has been estimated gravimetrically (Bishop et al. 1977). More recently, we've used 0.4 µm Poretics filter samples using the parallel sampling capabilities of MULVFS.