Ken Bruland’s research group has had the good fortune to receive NSF support from the Chemical Oceanography Program for the last four decades. Lately the focus of our research has dealt with interactive influences of bioactive trace metals (with an emphasis on iron) and phytoplankton; examining both the influence of micronutrient trace metals on the structure and function of phytoplankton communities, and the influence of microorganisms on trace metal speciation, distributions, and biogeochemical cycling. I am submitting here an Accomplishment Based Renewal (ABR) proposal that builds on the track record of our research group, and hopefully will extend our research for a final 2.5-year funding cycle with a new field program. This will be the final proposal of Bruland’s research group. Bruland’s last two students, Claire Parker and Ralph Till, will finish their Ph.D. during this funding cycle, and Ken Bruland and Geoffrey Smith will be retiring. If funded, it will be their ‘last hurrah.’ Accomplishment Based Renewal Proposals are unique and rare in our field. In an ABR proposal the Project Description is replaced with the following items:

1. Copies of up to six reprints of publications during the preceding 3 to 5 year period resulting from research supported by NSF:
2. Information on human resources development at the post doc and graduate levels; and
3. Brief summary (not to exceed four pages) of plans for the proposed support period.

The six publications highlighting previous NSF funded research that will be examples of our research group’s accomplishments are listed below and a brief explanation of the papers and authors (graduate students and post docs are in bold) follows:


A recently completed grant from the Chemical Oceanography Program was entitled “Mixing of iron-rich coastal waters with nutrient-rich HNLC waters leading to enhanced phytoplankton biomass: a focus on the northwest Gulf of Alaska” (OCE-0526601). A major field effort was mounted in late summer of 2007 on the RV Thomas Thompson examining the role of Sitka and Kenai anticyclonic mesoscale eddies in delivering Fe to the High Nutrient Low Chlorophyll (HNLC) regions of the Gulf of Alaska. This field effort, led by Bruland’s research group, also allowed a number of collaborative interdisciplinary research activities to occur. The grant supported Ph.D. theses of Matt Brown and Sherry Lippiatt. Key papers in their Ph.D. theses are the #1 and #2 publications used to justify this ABR:

Another grant that resulted in publications during the last 5 years was entitled “Coupling of trace metal micronutrients and phytoplankton dynamics – a focus on the Bering Sea and the role of iron” (OCE 0137085). A major field effort was mounted in late summer of 2003 on the RV Kilo Moana. This field effort, led by Bruland’s research group, also allowed a number of collaborative interdisciplinary research activities to occur. This grant supported the Ph.D. theses of Ana Aguilar-Islas, Kristen Buck and Matt Hurst. Two of their key papers used to justify this ABR are publications #3 and #4. Maeve Lohan was a post doc during this time and a key paper with Maeve as first author was publication #5.
Bruland has an NSF grant (just ending) that is the foundation for this ABR proposal. The grant, entitled “The California Current transition zone off northern and central California: an extensive region exhibiting Fe-limitation and moderate chlorophyll” (OCE-0849943), included two field efforts off central and northern California in May 2010 and August/September 2011 on the RV Point Sur examining the role of Fe in upwelling regions off northern and central California. Dondra Biller is using this grant for the bulk of her Ph.D. thesis that she plans to finish by the end of this calendar year. Dondra Biller was the first author on a recent paper that is publication #6. Two newer graduate students, Claire Parker and Ralph Till, used the last field effort of this grant to gain valuable research experience and begin to define their Ph.D. theses, the bulk of which will be carried out on this new ABR proposal.

**Human Resources Development:** NSF funding during this period under discussion has supported the Ph.D. theses of six graduate students; Matt Hurst (now an Associate Professor at Humboldt State University), Ana Aguilar-Islas (now an Assistant Professor at the University of Alaska, Fairbanks), Kristen Buck (now a researcher at the Bermuda Institute of Ocean Sciences), Sherry Lippiatt (now a NOAA researcher based in Almeda, CA coordinating the response to the Japan debris issue), Matt Brown (now an Assistant Professor at Flagler College in Florida), and Dondra Biller in the finishing stages of her Ph.D. at UCSC. In addition, Maeve Lohan was a post doctoral researcher during some of this time and is now an Associate Professor (Reader) at Plymouth University, UK. Four of the graduate students and the post doc are women. Claire Parker and Ralph Till would be supported to finish their Ph.D. research with this ABR funding.

**II. An iron limitation mosaic within the central California Current System (cCCS).**

**Background:** Over a decade ago, Hutchins and Bruland (1998) reported that phytoplankton communities in the central California coastal upwelling region off the Big Sur coast were Fe-limited. We observed that upwelled waters along the Big Sur coast required the addition of dissolved iron to initiate a phytoplankton bloom and drawdown nitrate, whereas Monterey Bay waters exhibited diatom blooms in a period of 4 to 5 days with a large build up of chlorophyll and a complete drawdown of nitrate without any additional input of Fe. Bruland et al. (2001) suggested that Fe supplied during winter floods could be a major external source of Fe to these coastal waters since much of the river-derived particulate iron is deposited on mid-shelf mud-belts where it could then be a source of Fe during subsequent spring and summer upwelling seasons. Further studies by the research groups of Ken Johnson (Johnson et al., 1999; 2001; Fitzwater et al., 2003; Chase et al., 2005a), Zanna Chase (Chase et al. 2005b; Wetz et al. 2006; Chase et al., 2007), Ken Bruland (Bruland et al., 2005; Hurst and Bruland, 2008) and collaborative studies with Dave Hutchins (Hutchins et al. 1998, Firme et al., 2003, Hutchins et al., 2002) have shown the importance of an additional external supply of iron from shelf sediments in allowing extensive blooms of large diatoms to occur in coastal upwelling regions.

Chase et al. (2007) provided an interesting extension of this concept. They argued that a combination of winter stream flow and shelf width accounts for over 80% of the spatial variance in summer chlorophyll within 50 km of the West Coast of North America. They attributed this relationship to the role of rivers as suppliers of the micronutrient iron and described the continental shelf as a ‘capacitor’ for riverine iron, charging during the high-flow winter season and discharging during the upwelling season. Ware and Thomson (2005) had noted a poleward increase in Chl a, which they speculated to be driven by a poleward increase in river runoff. However, productivity along the West Coast is dominated by the spring/summer upwelling season, a time when river discharge is minimal in this region. Chase et al. (2007) suggested that the gradient in Chl a is driven by a poleward increase in winter runoff, which supplies iron to the shelf. A concomitant poleward increase in shelf width can act to effectively retain Fe at depths where spring and summer upwelling can supply this external source of Fe to the surface for use by phytoplankton. This meridional gradient in shelf width has broad implications for higher trophic levels since there is a documented significant correlation between fish yields and phytoplankton standing stock (Chl a) in this same region (Ware and Thomson, 2005).

In studies off central and northern California, we have identified a number of coastal upwelling regions with a relatively narrow continental shelf and minimal river input where we observed elevated macronutrients but such low concentrations of dissolved and leachable particulate iron as to limit productivity (unpublished data from our ending NSF grant, Firme et al., 2003). The upwelling region adjacent to the Big Sur coast is not unique in being Fe-limited within the California Current System.
(CCS). Another such area is the upwelling region from Cape Mendocino to south of Pt. Arena. Figure 1 presents a satellite image of Chl a for the month of June. Both the Big Sur coast and the region between Point Arena and Cape Mendocino show up as relatively low chlorophyll regions (1 to 3 µg/L) even though they are both regions of intense upwelling. Coastal upwelling areas with phytoplankton blooms (on the order of 30 µg/L) are in red. These high chlorophyll regions are areas where rivers supply a large source of iron in winter flood events and where a relatively broad shelf acts as a capacitor to trap this iron in winter months and make it available during spring and summer upwelling periods. These regions of extensive phytoplankton blooms with high Chl a include the near shore regions in the Gulf of the Farallones and the well studied regions of Monterey Bay and Bodega Bay.

**Proposed Research:** We propose a major field effort during June/July of 2014 with the RV Thomas Thompson or equivalent size ship. Our proposed research will have the overall goal to Characterize the Fe and nutrient environment (dissolved Fe, labile particulate Fe, Fe-binding ligands, nitrate, phosphate and silicic acid) in the three CCS zones. We believe the CCS consists primarily of three zones: i) a mosaic of coastal upwelling regimes with varying characteristics ranging from Fe-replete regions over a broad shelf with a substantial external input of Fe to Fe-deplete regions over a narrow shelf without adequate external Fe inputs; ii) an eddy-rich, often Fe-limited transition zone where upwelling within cyclonic eddies and wind-curl induced offshore upwelling also brings elevated nutrient concentrations to the surface to fuel the transition zone productivity but without adequate Fe to allow for blooms of large diatoms; iii) a nitrate-limited oligotrophic California Current region further offshore with very low chlorophyll. Underway, near real-time, shipboard measurements of dissolved Fe (Lohan et al., 2006) and nutrients will enable high-resolution characterization. We will also collect trace metal samples on the surface transects and vertical profiles to return to UCSC for analysis of a suite of other trace metals such as Zn, Cd, Co, Ni, Fe, Mn, Pb, and Cu (Biller and Bruland, 2012).

Four examples of specific goals that Bruland’s research group will address are:

1. **Determine whether the high concentrations of strong Fe(III)-binding organic ligands observed in the benthic boundary layer (BBL) and playing an important role in allowing elevated dissolved Fe concentrations to exist in the BBL are humic-type ligands with a continental source released from the riverine-derived mud belt sediments.** We (Claire Parker) will utilize methods developed by Laglera and van den Berg (2009) and Laglera et al. (2011) to determine the concentrations and importance of humic-type compounds in the BBL as a component of the Fe(III)-binding ligands (Buck et al., 2007).

2. **Determine concentrations of both dissolved Fe(III) and Fe(II) in the benthic boundary layer samples.** We have observed that when the dissolved O2 concentrations drop below 50 µmol kg\(^{-1}\) that Fe(II) can be kinetically stabilized in these low pH, low temperature and low oxygen hypoxic waters and exist at elevated concentrations greatly increasing the total dissolved Fe concentrations. Dissolved Fe(III)
will be determined using the approach of Lohan and Bruland (2008), while dissolved Fe(II) will be determined using the method of Blain and Treguer (1995). Lohan and Bruland (2008) have shown that in the hypoxic waters off Oregon and Washington that this is an important mechanism to greatly increase the dissolved Fe in the BBL and in upwelled waters. The Fe(III) concentrations are capped as the Fe(III)-binding organic ligands are titrated. In the severely hypoxic waters, however, Fe(II) can provide an additional significant source of dissolved Fe to the BBL.

3. Examine the exchange between particulate and dissolved forms of Fe and the biological accessibility of the elevated concentrations of leachable particulate Fe found in the benthic boundary layer and upwelled into surface waters. Here we (Ralph Till) will utilize the stable isotope tracer method presented in Hurst and Bruland (2007). The low abundance $^{57}$Fe stable isotope (natural abundance of 2.1%) can be used as a tracer (using an enriched $^{57}$Fe tracer with 97.6% abundance) and added to the soluble phase. Hurst and Bruland (2007) in a study using this tracer approach over the Bering Sea shelf estimated that the net removal of 2.0 nM dissolved Fe by phytoplankton over a 4.8 day period was associated with 2.9 nM of regenerated particulate Fe to the dissolved phase and an overall removal of 4.9 nM dissolved Fe. In four pages we are not able to list other specific objectives.

4. Study the role of cyclonic and anti-cyclonic eddies in supplying nutrients and iron to the eddy-rich transition zone of the California Current. Coastal upwelling with subsequent advection offshore will be contrasted with offshore, wind-curl induced upwelling and the role of eddies in supplying nutrients and iron to the CCS transition zone.

In addition to our research group’s overall and specific goals, we plan to fill the ship with collaborating scientists. Many of these scientists will have already funded grants that their students and post docs are working on and this proposed field effort (where all the nutrient data and trace metal data is provided by our research group) will be ideal support data for them. We have a strong track record of doing this. A few new proposals will be submitted if this proposal is funded and ship time is secured. For example, Adrian Marchetti will plan to submit a proposal examining luxury uptake of Fe by diatoms and the unique role certain diatoms possess due to their distinct Fe-related physiology.

III. Broader Impacts.

Outreach and Education: The proposed budgets will provide partial funding for two graduate students at UCSC; Claire Parker and Ralph Till. They will be trained in advanced analytical methods to measure trace metals in seawater – for both near real-time measurements on board the research ship and post-cruise at UCSC. In addition to the formal course offerings, they will also receive course training in a curriculum that includes i) scientific communication skills, ii) careers in marine science, and iii) grant writing.

A broader outreach goal of this project is to facilitate teaching and learning on marine science-related topics through translating our research objectives into educational materials that can be used for K-12 and the general public. To accomplish this, we will team with the Seymour Discovery Center at the Long Marine Lab, UCSC. This Discovery Center receives 14,000 visitors each year and we have budgeted funding to develop an interactive display on limiting nutrients and phytoplankton bloom development in the CCS.

Broader Impacts: There is a great deal of interest in the CCS because of its importance in terms of phytoplankton productivity and the support of higher trophic levels. Ware and Thomson (2005) have documented a significant correlation between fish yields and phytoplankton standing stock (Chl a) in this region. Until now, the emphasis in studies of the CCS has been on relationships between physics and biology. This proposal inserts the important role of micronutrient chemistry into the picture. This ABR will also serve an important role in securing ship time in advance and providing logistical support for other collaborative studies. Bruland’s research group has an excellent track record of taking the lead in providing ship time and supporting collaborative field studies that have been dependent upon us for: i) the collection of large volumes of clean seawater for various experiments, ii) providing shipboard dissolved Fe and macronutrient data to assist in sampling strategy and experimental design, and iii) providing trace metal and nutrient data for the subsequent interpretation of results. This is extremely valuable and cost effective for collaborating scientists since with the hydrography, nutrient and trace metal data provided, they can focus on their complimentary research efforts. Four pages is only enough to provide a flavor of what will be accomplished. This proposal is justified by our research group’s track record.