Iron (II) variability in the northeast subarctic Pacific Ocean

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INTRO
Iron (Fe) is an essential trace metal limiting productivity in approximately 40% of the global ocean. Fe(II) is considered to be more bioavailable, while Fe(III) is thermodynamically favoured in oxygenated seawater. It is therefore important to understand the controls on speciation in various oceanic environments. We present profiles of dissolved iron in both redox states, measured on three cruises between June 2012 and August 2013 along Line P in the northeast subarctic Pacific Ocean (see map above). Low oxygen concentrations (minimum ~10 μM) prevail in this oceanic region between 500 and 1500 m depth (Fig. 1). While others have observed persistent subsurface Fe(II) maxima associated with oxygen minimum zones (e.g. Kondo and Moffett, 2013), our data indicate that offshore Fe(II) features in the North Pacific are more transient. This observation points to the importance of episodic water column processes — likely associated with remineralization — as drivers of Fe(II) variability in this offshore region.

METHODS
Sampling:
Sampling was conducted from the CCGS John P. Tully using either GO-Flo bottles on a Kevlar line (June 2012) or a trace element-clean rosette system (August cruises). The system consists of an epoxy-coated rosette with sacrificial Mg anodes, 12 x 12 L Teflon™-coated GO-Flo (General Oceanics, Miami FL) bottles, and ~2000 m of 4-conductor Vectran line on a purpose-built winch. At some stations on the June cruise, water from depths less than 37 m was pumped using an air-driven Teflon™ double diaphragm pump through Teflon™-lined, fiberglass reinforced, synthetic tubing into a HEPA flow bench onboard the ship.

Iron (II):
Iron(II) analysis was carried out at sea on unacidified samples using a modified flow injection system with the luminol method. An injection valve was used in 2013 but not in 2012, when a system similar to that of Hansard et al. (2009) was employed. All samples were filtered with an AcroPak 500 filter (0.2 μm) prior to measurement and were analyzed within 2 minutes of sampling. Detection limits ranged from 2-10 pM.

Total iron:
Dissolved Fe was measured on acidified (pH 1.7) filtered seawater in the lab, using a modified flow injection analysis (FIA) method that relies on the detection of Fe(III) with the chemiluminescent reagent luminol (Obata et al. 1993; de Jong 1998). Seawater is treated with H2O2 to oxidize any Fe(II) and is buffered in-line to pH 4 before being passed through a pre-concentration mini-column (1 cm; Global FIA, Fox Island WA, USA) packed with chelating iminodiacetic acid resin (IDA, Toyopearl, AF Chelate 650M). A solution of 0.1 M HCl then elutes Fe(III) from the resin and mixes with 0.96 M HNO3, 0.35 M H2O2 and 0.1 mM luminol con-taining 0.3 mM TEPA. The resulting solution is passed through a 5 mm mixing coil maintained at 35°C before being pumped to the flow cell.

KEY POINTS

OFFSHORE: Fe(II) shows high variability within profiles and among cruises. Local maxima in Fe(II) concentrations:

• ...are transient and coincide with the upper reaches of the oxygen minimum.
• Short-lived, sporadic water column processes such as particle-associated remineralization are a plausible Fe(II) source; vertical supply is key.
• Long-range horizontal transport from shelf sources is an unlikely source for the observed Fe(II).
• Low oxygen serves to stabilize Fe(II), but doesn’t produce it.

NEAR-SHORE: Deep Fe(II) features are persistent.
• P4: Sediment re-suspension is the likely source of deep Fe(II) (Fig. 3), which is stabilized by low oxygen concentrations.
• P12: Sediment signal from P4 might be carried to P12 (Figs. 1 & 4).
• Subsurface feature at P12 in June 2012 may also be sediment-derived, i.e. originate from the shelf (Figs. 1 & 2).

Fig. 2: THERMAL INVERSION in June 2012 in the 100-200 m layer may indicate recent shelf contact of this warm sub-surface water mass. The local Fe(II) maximum at P12 in June 2012 is at a similar depth and may stem from reductive processes in the shelf sediments.

Fig. 3: BEAM ATTENUATION at P4 indicates sediment re-suspension near the bottom. Anoxic conditions in sediments can be a source of Fe(II) to the overlying water (e.g. Lohan & Bruland 2008).

Fig. 4 (left): FE(II) PROFILES GROUPED BY CRUISE, with bottom panels displaying lower profile sections (below ~400 m) plotted against potential density. The deep local maxima observed at the offshore stations (P16-P26) in June 2012 do not fall onto the same density horizon, making long-range transport an unlikely source for the elevated Fe(II). But deep waters closer to shore, e.g. P12 in Aug. 2013, may experience Fe(II) enrichment from the shelf.

Fig. 5 (right): FRACTIONS OF DISSOLVED IRON PRESENT AS FE(II), grouped by cruise. Inset zooms in on %Fe(II) variability near the surface in June 2012. Higher variability in June compared to August may be related to seasonality of vertical particle flux, with remineralization a plausible source for Fe(II).

Fig. 6: DISSOLVED IRON CONCENTRATIONS for June 2012 and August 2013. Inset on the left shows details of the upper 400 m in June 2012. P4 stands out on both cruises with high dissolved iron concentrations at depth, likely related to sediment processes on the shelf and shelfbreak as well as outflow from the Strait of Georgia.

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References
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