Fe redox status and its bioavailability in the East China Sea shelf break area

Koki Yamanaka[1], Yoshiko Kondo[1], Natsuho Fujita[2], Yudai Sunahara[1], Hajime Obata[3]

[1]Graduate School of Fisheries and Environmental Sciences, Nagasaki University
(Koki Yamanaka Email: bb53120020@ms.nagasaki-u.ac.jp)
[2]Faculty of Fisheries, Nagasaki University
[3]Atomosphere and Ocean Research Institute, The University of Tokyo

1. Introduction

Iron is recognized as an essential element for marine phytoplankton (Sunda., 2012). Dissolved iron in seawater exists in various forms such as organic complex iron, inorganic ions, iron hydroxide and inorganic colloidal iron. The bioavailability of Fe is controlled by its chemical speciation in seawater. The reduced form of Fe, Fe(II), is more bioavailable than Fe(III)-ligand complexes, the existence of Fe(II) has important implication on Fe biogeochemical cycles. It is thought that many phytoplankton cannot directly take up Fe(III)-ligand complexes into cells, but take up Fe(II) generated by photochemical reactions occurred on the surface of the ocean and reduction reactions on the surface of biological cells (Shaked et al., 2005). But Fe(II) is rapidly oxidized by O_2 and H_2O_2 in seawater and its half-life in seawater is very short, known to vary from minutes to hours (Santana-Casiano et al., 2005). Therefore, it is important to elucidate the mechanism of Fe(II) production and disappearance in seawater in order to improve the efficiency of iron utilization by phytoplankton in the ocean.

In this study, we investigated in the upper 500 m of the East China Sea shelf break area where the dissolved iron concentration and the chemical form of iron are expected to change due to the influence of surface currents such as the Kuroshio and Taiwan warm currents and the continental shelf. The purpose was to understand the relationship between the distribution of Fe(II) and its half-life and marine environmental characteristics.

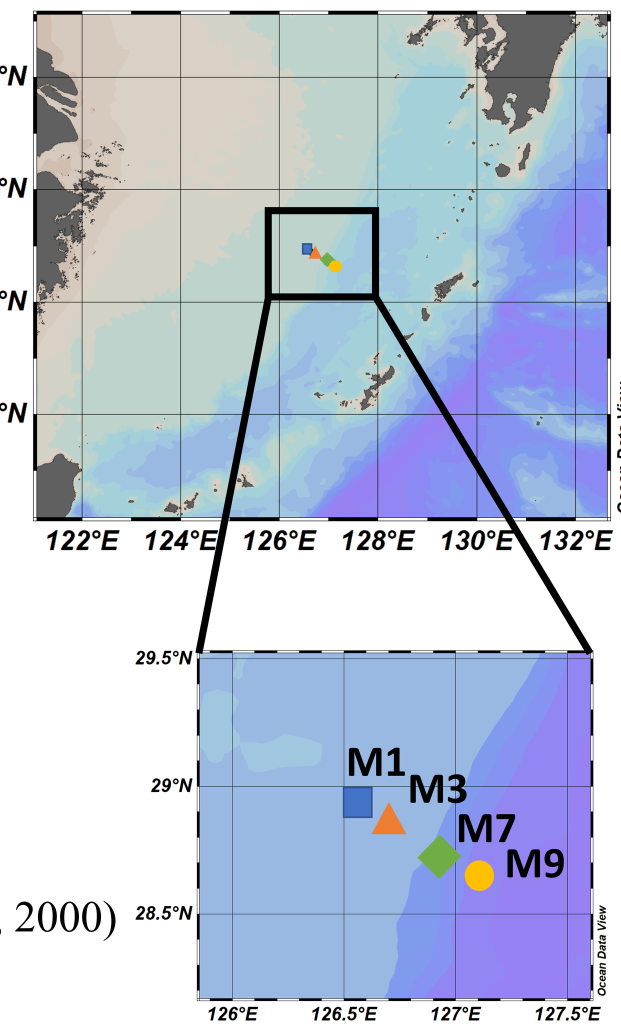
2. Methods

【Research cruise】
- T/S *Nagasaki-Maru* NS33 cruise (July 10-18, 2019)

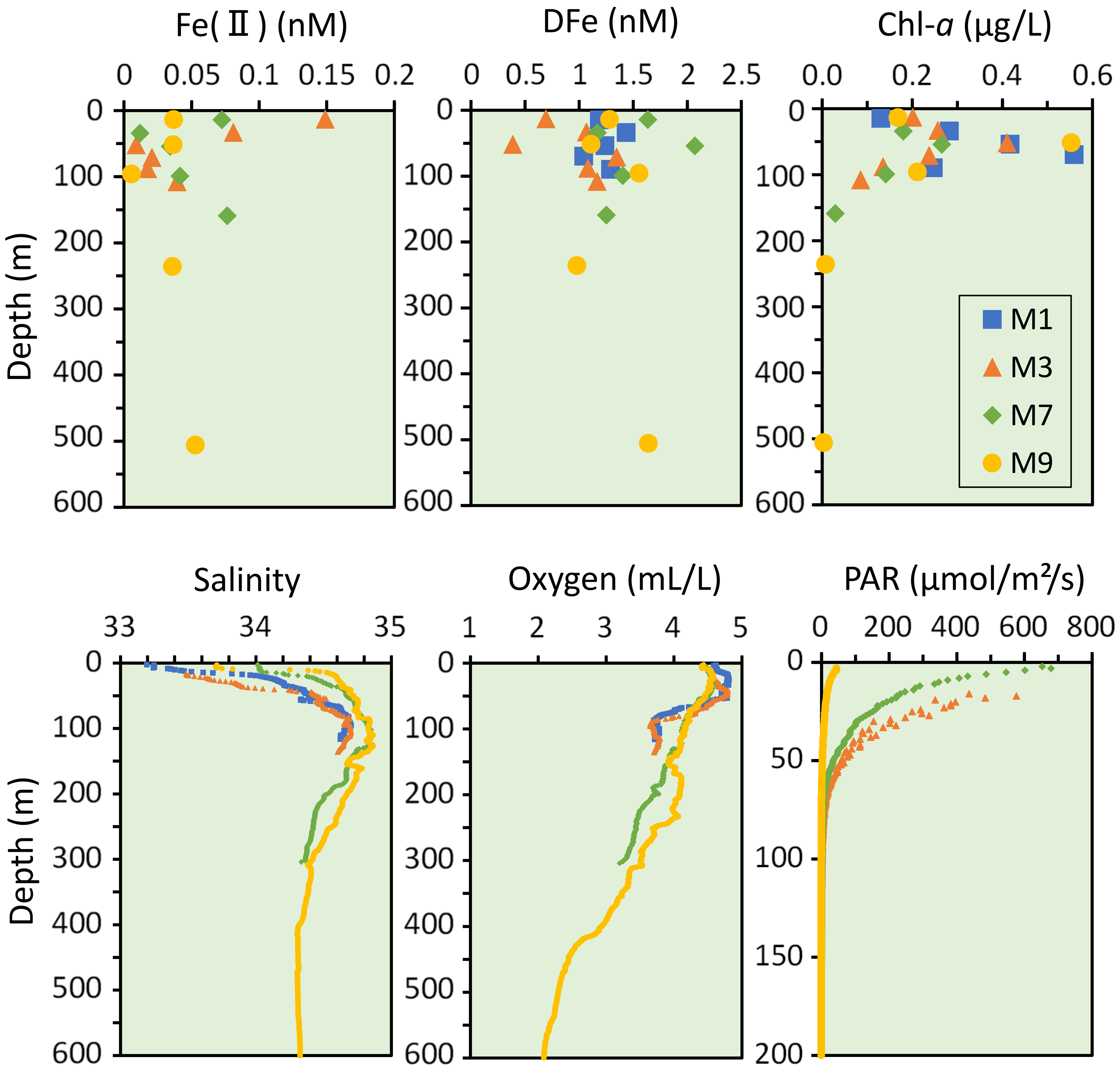
【Trace metal clean sampling】
- 12 L Niskin X bottle: 13-506 m (5 or 6 layers/station)

【Collected samples】
- Dissolved Fe(II) (<0.2 µm): Onboard determined
- Dissolved (<0.2 µm) Fe: Stored at pH1.7 (over 3 monthes)

【Analytical Methods】
- Fe(II): Flow injection-based luminol chemiluminescence detection (Bolster et al., 2018)
  Adding DTPA to mask Fe(II) to determine baseline
  Detection limit: 0.005- 0.019 nM
- DFe: cathodic stripping voltammetry (Croot & Johansson., 2000)
  - Detection limit: 0.041 nM

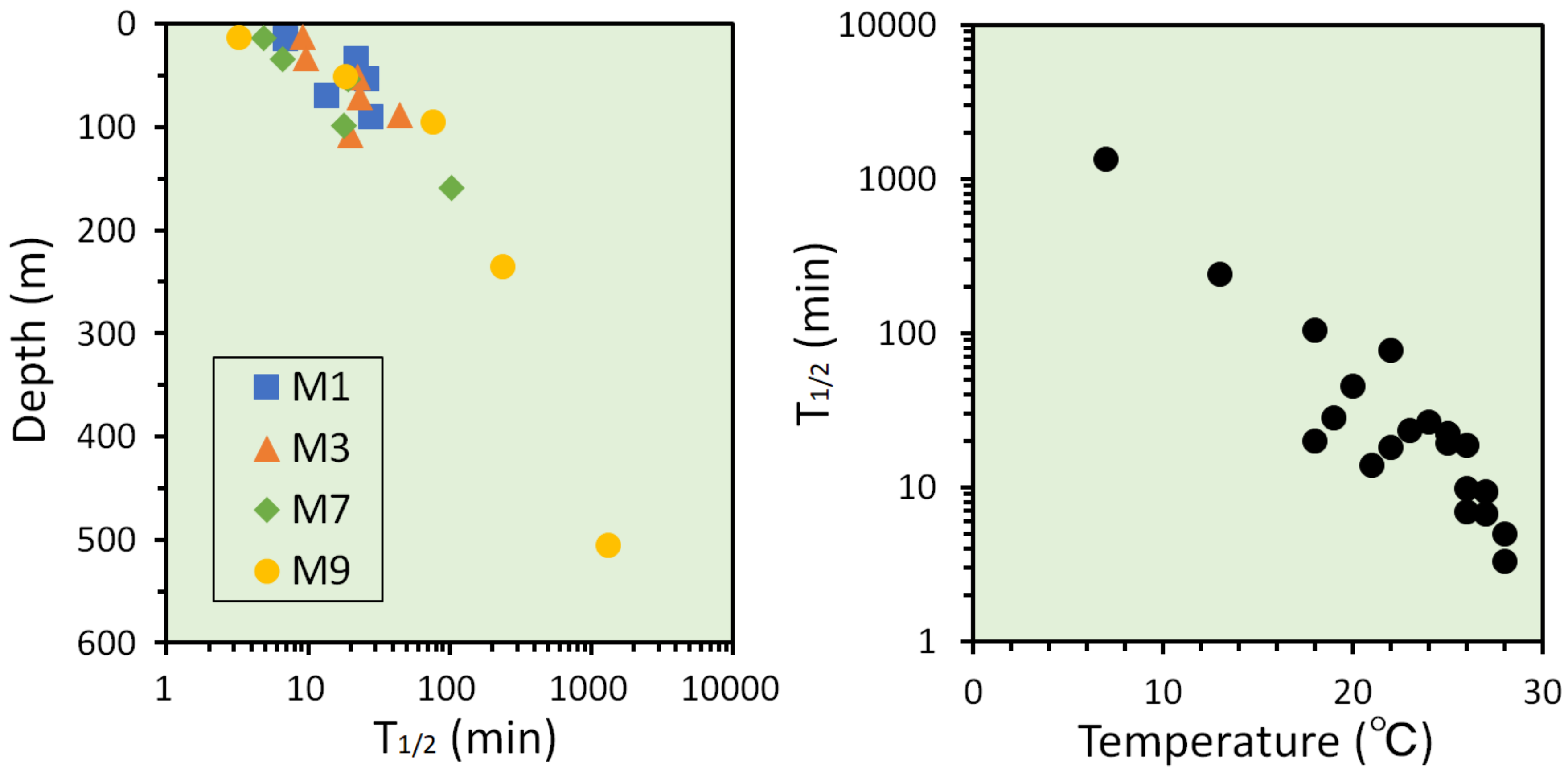


3. Vertical distributions of Fe(II) and other parameters



- The Fe(II) and dissolved Fe concentration were distributed in the range of 0.006- 0.150 nM, 0.39- 2.1 nM.
- From the relationship between PAR and Fe(II), Fe(II) observed in the surface layer during the daytime is considered to be due to the photochemical reaction.
- On the surface of the East China Sea shelf break area, it was considered that the light intensity had a strong influence on the bioavailability of iron.
- Fe(II) concentration was higher than the total dissolved iron concentration level (0.1 nM) in the open ocean surface water such as high-nutrient low-chlorophyll regions.

4. Fe(II) half life



- Fe(II) half-life tended to increase with depth and was basically correlated with temperature.
- Fe(II) observed in the aphotic zone was considered to be the effect of organic matter decomposition in the mesopelagic zone and long-term storage of Fe(II) supplied from sediments in a reduced environment.
- The Fe(II) half-life in the photic zone was 3-22 minutes, which was longer than that of the eastern South Pacific subtropical open ocean surface water (~1 min, Kondo & Moffett., 2015).

5. Summary

The maxima of Fe(II) were observed in the surface layer, comprising up to 21% of dissolved Fe. High Fe(II) in the surface water could be derived from photochemical reaction.

The Fe(II) half life tended to increase with depth. In this study area, the Fe(II) half-life within the euphotic layers was relatively longer than that in the oceanic region such as the subtropical South Pacific. These results suggested that bioavailability of Fe was high in the East China Sea shelf break area.

6. Acknowledgements

We express our gratitude to the chief scientist Dr. Endo, the captain, crew and scientists who took part in the *Nagasaki-Maru* NS33 cruise for their assistance on board. This study was supported by Grants-in-aid for Scientific Research (C) JP19K12309, Shiseido Female Researcher Science Grant (51000208), and the Interdisciplinary Collaborative Research Program of the Atmosphere and Ocean Research Institute, the University of Tokyo.

7. References

Bolster, K. M., M. I. Heller, and J. W. Moffett, 2018, Determination of iron(II) by chemiluminescence using masking ligands to distinguish interference, Limnology and Oceanography:Methods, 16, 750-759

Croot, P.L., and M. Johansson, 2000, Determination of iron speciation by cathodic stripping voltammetry in seawater using the competing ligand 2-(2-thiazolylazo)-*p*-cresol(TAC), Electroanalysis,12, 565-576

Kondo, Y., and J. W. Moffett, 2015, Iron redox cycling and subsurface offshore transport in the eastern tropical South Pacific oxygen minimum zone, Marine Chemistry, 168, 95-103

Santana-Casiano, J. M., M. Gonzalez-Davila, and F. J. Millero, 2005, Oxidation of nanomolar levels of Fe(II) with oxygen in natural waters, Environmental Science and Technology, 39, 2073-2079

Shaked, Y.,A. B. Kustka, and F. M. M. Morel, 2005, A general kinetic model for iron acquisition by eukaryotic phytoplankton, Limnology and Oceanography, 50, 872-882

Sunda. W.G., 2012, Feedback interactions between trace metal nutrients and phytoplankton in the ocean, Frontiers in Microbiology, 3, 1-22