Effect of ocean acidification on bioavailability of iron bound to natural iron-complexing ligands

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Ocean acidification will affect the chemistry and biology of future oceans, and may change the availability of iron to phytoplankton. Iron is a limiting micronutrient in large oceanic regions, including High Nitrate Low Chlorophyll (HNLC) subarctic Pacific, and a critical factor in many nearshore regions such as the coastal California upwelling system. Most of the iron dissolved in seawater is known to be strongly complexed by natural organic ligands. The potential effect of a decrease in pH on iron availability is mainly due to changing the chemical equilibria among free, inorganic iron species and the organic complexes. The limited data on how ocean acidification affects iron availability imply that phytoplankton respond to ocean acidification differently in different ocean regions with a mechanistical link to differences in the character of the iron-complexing organic ligands.
We performed laboratory culture experiments using a marine diatom *Thalassiosira* sp. isolated from the HNLC water of the western subarctic Pacific, and its growth responses at low and high pH/pCO_2 were compared between surface waters collected from the western and eastern subarctic Pacific and subsurface water of the California coastal upwelling region. Before the inoculation of iron-limited diatom cells, the filtered seawater was spiked with 0.5 nM $FeCl_3$ and allowed to equilibrate for 24 hour with natural iron-binding ligand, and pH/pCO_2 was manipulated by bubbling the CO_2:air mixed gases.
The specific growth rate of diatom in the surface water from the western subarctic Pacific (Stn. K2) decreased with decreasing pH from 7.9-8.0 to 7.5-7.6. The observed increase in the consumption ratio of silicic acid and nitrate (Si/N) supports decreased iron availability at lower pH. Opposite trend was observed in the subsurface water of California coastal region. Decreasing the pH increased the specific growth rate, indicating increased iron availability. The relatively low growth rate observed at higher pH suggests that diatoms can not efficiently use iron bound to natural iron-complexing ligands in the subsurface water. The effect of pH in experiments using surface seawater collected from the eastern subarctic Pacific (Stn. P) was not statistically significant, but there was an increasing trend in the specific growth rate with decreasing pH. These results suggest that ocean acidification over the next century will alter the availability of iron in these surface waters differently and may affect future primary production.

Keywords: Ocean acidification, Iron, Phytoplankton, Organic ligand

