Characterization of Fe in Marine Particulates via Micro-XAS: Possibilities and Limitations

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Introduction

Fe is a key limiting nutrient to primary production in several areas in the ocean. Since iron is both a micronutrient and a particle-reactive element, its geochemistry is controlled by uptake into biological organisms and reactions with solid surfaces [1, 2]. Studying particulate iron is thus central to understanding the biogeochemical cycling of this element.

The handful of measurements of particulate iron in the ocean [3, 4] uses standard wet chemistry techniques. Here, we examine the possibilities and limitations of using synchrotron x-ray absorption microspectroscopy (micro-XAS) to characterize the Fe content and valence ratio in a unique collection of marine particulates. Our goal at the APS was to perform exploratory work to examine the iron content, distribution, redox state, and bonding environments in single cells and marine aggregates (marine snow and fecal matter) collected from two seasons that demonstrated a large difference in phytoplankton species composition.

Methods and Materials

All work was done at beamline 13-ID at the APS in June 2001. We used marine particulate samples collected from Station PAPA (50°N, 145°W) in the subarctic Pacific from winter and spring 1996. These samples came from an archive of size-fractionated marine particles (1-53 μm on quartz fiber filters and >53 μm on polyester mesh filters) that were collected by using the multiple-unit large-volume *in situ* filtration system (MULVFS) [5]. This collection technique allows large samples of trace-element-clean particulates to be collected and results in minimal disturbance to the morphology of the aggregates. Individual cells or aggregates of particles from a depth of 46 m in February and 36 m in May were subjected to micro-XAS.

Several ways of mounting samples in front of the beam were explored. Initially, marine particulates on their original polyester mesh filters (>53 μm) were mounted directly. This mesh showed significant levels of Ti and Mn, making it impossible to study Mn in our samples (an element of interest). However, the high Ti in the mesh was a useful way of locating the position of the beam relative to the sample, since our samples have negligible Ti.

Organisms were also isolated from polyester filters by using a micromanipulator attached to a light microscope and deposited electrostatically onto a Kapton® slide mount. The Kapton exhibited a significant Fe background relative to the low Fe signal from our samples, however. Clean silica disks looked like a possible clean substrate, but we did not pursue them further because of the desire to measure Si from the particles. Double-stick tape was a convenient way of removing individual organisms from the quartz filter (1- to 53-μm fraction). In addition, the tape exhibited a low metal background. Unfortunately, the glue on the double-stick tape melted in the beam, resulting in too much sample movement during the course of a spectroscopic scan. Results presented below are from particulates on their original polyester mesh filters.

We attempted to collect spectra for x-ray absorption near-edge structure (XANES) and extended x-ray absorption fine structure (EXAFS) analyses of Fe in individual cells to compare Fe content and coordination between individual species of phytoplankton. For larger aggregates, we mapped the distribution of several elements (Fe, Ca, Mn, Ti) by using 5-μm steps to examine their spatial heterogeneities and correlations.

Results and Discussion

The most interesting and unexpected results were from 2-D element maps of marine aggregates. We found small (no more than several micrometers in diameter), discrete Fe-rich particles embedded in a large aggregate (400 μm) collected during the late winter from the upper water column of the subarctic Pacific, giving rise to heterogeneous “hot spots” of iron within the aggregate (Fig. 1, top). Because of difficulties encountered in finding an appropriate sample substrate, we did not collect XANES spectra of

these hot spots to determine the nature of the embedded iron.

Most of the Ca in our sample was from coccolith $CaCO_3$, which are 1 to 2 μm in size and are well dispersed throughout the aggregate. The Ca element map thus gave a good indication of the topology of our aggregate (Fig. 1, bottom). There appeared to be no correlation between the location and intensity of the Fe hot spots and the amount of bulk matter present, as deduced from the strength of the Ca signal. Aggregates are typically composed of fragments of phytoplankton, bacteria, fecal matter, and biogenic detritus. The lack of correlation between Fe and Ca suggests that the tiny micrometer-sized Fe-rich particles were probably captured independently from ambient seawater as particles aggregated.

We encountered a drift of the beam position in collecting XANES and EXAFS spectra, presumably because of the vibration and movement of the flexible sample substrate relative to the beam. This drift was enough to render scans of the smaller particles and heterogeneous targets unusable. Attempts to eliminate this motion did not work well.

The levels of iron in individual coccolithophore or diatom cells examined were at or near the detection limit. The mounting substrate with the lowest level of Fe was also flexible (double-stick tape) and therefore not suitable for the collection of spectra for XANES and EXAFS analysis. The coccolithophores were also roughly the same size as the beam (several micrometers in diameter), making them a difficult target.

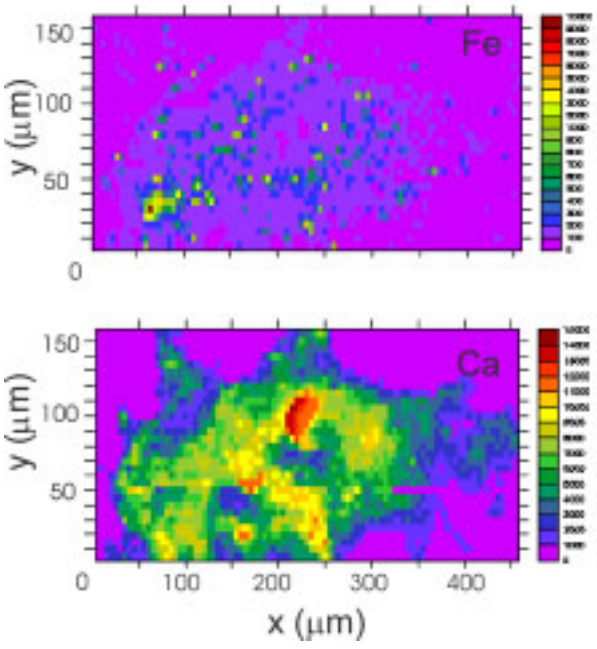

FIG. 1. Distribution of Fe (top) and Ca (bottom) in a marine aggregate collected from Station PAPA in February 1996. Scale bar shows raw counts per pixel. Pixel size is 5 μm. Dwell time was 1 s per scan.

In summary, micro-XAS holds promise for the characterization of Fe in marine particulates, but technical challenges remain to be solved. From previous bulk chemical analyses, we knew that these samples contained low levels of Fe, but use of micro-XAS revealed new information about the unexpected spatial distribution of Fe within marine aggregates. This distribution raises many interesting questions about the cycling and bioavailability of iron in the upper water column and demonstrates the extent to which our understanding of iron in marine particles is incomplete. We still need to overcome certain technical challenges so that we can further probe the chemical nature of the aggregate-associated Fe. Our biggest difficulty was finding a background substrate that was sufficiently trace-metal-clean and rigid enough to prevent sample movement. These problems will have to be solved in order to collect sufficiently high-quality data for XANES and EXAFS analyses to determine Fe redox state and bonding environments. Only then can we fully exploit the capabilities of micro-XAS.

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