

## Incorporation of trace elements by diatom frustules: Significance of sediment-trap observation in the Southern Ocean

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Diatoms contribute to more than half of the primary production of the oceans and it is well established that the formation and dissolution of diatom opal governs the distribution of dissolved silica in ocean columns (Nelson et al., 1995). Owing to the physical and chemical difficulty in isolating diatom opal from clays (Shemesh et al., 1988; Beck et al., 2002), however, it is difficult to clarify the trace composition of opal and thus to understand how diatoms contribute to the ocean circulation of trace elements. To date, no direct determination of rare earth elements (REEs) in diatoms has been made, and the role of diatoms has not been considered in the circulation of REEs (Sholkovitz et al., 1994; Oka et al., 2009; Siddall et al., 2008; Arsouze et al., 2009; Tachikawa et al., 2003).

The recent study, based on the dissolution kinetics of diatom silica frustules and the incorporation theory of silicic acid complexes, unveiled the composition of diatom frustules and identified the role of diatoms in the oceans (Akagi et al., 2011; Akagi, 2013). Diatoms incorporate metal-silicate complexes, silicate minerals as well as dissolved silica, to form their silica frustules. They recycle rare earth elements in the water column and disintegrate silicate minerals to change rare earth elements in refractory silicates to readily dissolvable forms. Diatom frustules are no longer regarded as pure hydrated silica, but impure matter able to transport some elements to the deep water. In the Bering Sea diatoms are found to incorporate island-arc matter with a high  $\epsilon\text{Nd}$  value (Akagi et al., in press). Diatoms are important in distributing this high  $\epsilon\text{Nd}$  signature to the ocean. This new insight may affect the interpretation of the Nd isotope variation recorded in ferromanganese crusts and foraminifera, which synchronizes with the glacial-interglacial periodical variations.

The new insight on diatom frustules has been established based mainly on sediment trap samples from the Bering Sea, a rather special sea, and ocean chemists tend to treat the insight a rather exceptional case. To generalize the insight, the same line of study should be extended to the sediment trap samples from more normal oceans such as the Southern Ocean.

To date, the possibility of silicic acid complex formation with metal ions has not been explored in the research on marine chemistry. Some elements classified as high field strength elements, HFSEs, are considered to be in the form of OH complex in seawater (Byrne, 2002). Most of elements classified to high field strength elements (HFSEs) have a valency of 3+ or 4+, and considering their thermodynamic properties, it was found that they are likely to have fairly high complex formation constants with silicic acid (Wang et al., 2009; Wang and Xu, 2001). Although silica has been long studied, this study is the first to discover the possibility that it is an important carrier of many elements in marine chemistry. To establish this view, again, studies using trap samples from the Southern Ocean would be highly requested.

Keywords: diatom frustules, trace elements, sediment trap, Southern Ocean