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North Pacific nutrient response to the initiation of Northern Hemisphere Glaciation

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We have investigated the Si isotope composition in marine diatoms over the abrupt change in opal accumulation in North Pacific records accompanying the intensification of Northern Hemisphere Glaciation at 2.7 Ma. Sigman *et al.* have demonstrated marked changes in the nitrogen isotope composition over the same time interval and suggested the change is due to a decrease in the rate of exposure of nutrient-bearing deep water at the subarctic Pacific surface. As diatom production is largely dependent on the availability of silicic acid, a change in nutrient supply would also likely have affected the Si isotope composition of marine diatoms.

The stable Si isotopes of cleaned biogenic silica were measured by the Nu1700 High-Resolution Multi-Collector-ICP-MS at ETH Zürich, in dry plasma mode, to obtain both $^{30}Si/^{28}Si$ and $^{29}Si/^{28}Si$ isotope values. MC-ICP-MS has two major advantages over gas source mass spectrometry; firstly, safer methods not requiring the extremely hazardous fluorinating gas, and secondly, faster analytical protocols, with less chemical processing and much quicker analyses (even allowing for many duplicated analyses). We have adapted cleaning methods, and chemical purification techniques to aid the analyses of Si by ICP-MS.

We observe large variations in the Si isotope composition recorded in the biogenic opal over this time period, related to changes in the opal accumlation rates and nitrogen isotope composition. Initial results show an inverse correlation between the Si and N isotope variations. This observation likely results from a decoupling between the nitrogen and silicon cycles on glacial/interglacial timescales. The results demonstrate that Si isotopes can be used as indictors of biogenic Si utilisation.