Diatom Si isotope variations from the Atlantic Sector of the Southern Ocean (ODP Site 1093) record environmental changes of the last 170 ka

F. WETZEL[1]*, A. SHEMESH[2], B.C. REYNOLDS[1]

[1]Institute of Geochemistry and Petrology, Department of Earth Sciences, ETH Zurich, Switzerland (*correspondence: wetzel@erdw.ethz.ch)

[2]Department of Environmental Sciences & Energy Research, The Weizmann Institute of Science, Rehovot, Israel

A number of recent studies utilized silicon isotopes to trace changes in the biogeochemical cycling of silicon in the paleocean [1, 2]. The main controling process on this cycle is the uptake of silicon by opal-precipitating phytoplankton. Accounting for about 60% of the oceanic primary production, diatoms link the dissolved silicon (nutrient) pool and oceanic CO_2 uptake from the atmosphere. Since the Southern Ocean plays a key role in ocean circulation and deep-sea ventilation, its underlying opal-rich sediments are particularly suitable for studying the link between atmospheric CO_2 variations and phytoplankton nutrient utilization. The degree of surface silicon utilization is to a first order a function of nutrient supply from below and should be reflected in the diatom silicon isotope composition. In combination with carbon isotope ($\delta^{13}C$), nitrogen isotope ($\delta^{15}N$) and micronutrient (esp. Fe) information it is possible to reconstruct the efficiency of the biological pump that determines whether the surface ocean acts as a net source or sink for atmospheric CO_2.

Here, we present down-core (0-170 ka) silicon isotope variations of diatoms from the Atlantic Sector of the Southern Ocean (OPD Site 1093) and examine the impact of glacial-interglacial climate change on the degree of silicon isotope utilization. The results show that the degree of silicon isotope utilization during interglacial periods is different from that of peak glacial periods. During peak glacial periods, silicon utilization is inefficient at a time where an efficient biological pump is assumed to draw down additional atmospheric CO_2, implying a more complex relationship between silicon in frustules and nutrients contributing to organic tissues. In addition, ambiguity exists as to whether the increased efficiency in the biological pump during glacials was, as commonly believed, a contributor to the low atmospheric CO_2 concentrations or a consequence and therefore 'only' a positive feedback.

[1] Ellwood *et al*. (2010) *Science* **330**:1088-1091; [2] Hendry *et al*. (2010) *EPSL* **292**:290-300;

The extent of oceanic anoxic events revealed by correlated Mo- and U isotope records

S. WEYER[1]*, C. MONTOYA-PINO[2], G.W. GORDON[3], B. VAN DE SCHOOTBRUGGE[2], W. OSCHMANN[2], J. PROSS[2] AND A.D. ANBAR[3]

[1]Institut für Mineralogie, Leibniz Universität Hannover, 30167 Hannover, Germany (*correspondence: s.weyer@mineralogie.uni-hannover.de)

[2]Institut für Geowissenschaften, Universität Frankfurt, 60431 Frankfurt a. M., Germany

[3]School of Earth and Space Exploration, Arizona State University, Tempe, Arizona 85287, USA

Isotopic signatures of redox-sensitive trace metals in black shales (e.g. Mo and U) have become a frequently used tool to estimate the extent of anoxic or euxinic conditions in ancient oceans [1-5]. A disadvantage of these tools is that they are sensitive to local redox conditions or other effects [4-6]. Here we show that combining Mo- and U isotopes provide a much more robust approach.

We studied black shales from and around both the Cretaceous OAE2 (Demerara Rise, Central Atlantic ocean) and the early Jurassic T-OAE (Dotternhausen, Germany, and Truc de Balduc, France) and compared our results with those from "recent" sapropels of the Black Sea (unit I and unit II). Samples from all investigated units display a distinct negative correlation of Mo- and U isotope records. This coupling of Mo- and U isotopes is likely generated during black shale formation under variable (redox) conditions.

Samples from the OAE2 and those from below- and above OAE2 together define a single trend of Mo- versus U isotopes. Individual trends are defined by sample suites from different subzones of the lower Toarcian (during- and slightly after the T-OAE). All these trends are significantly shifted towards lighter isotope compositions compared to the trend defined by Black Sea samples, except samples from the *bifrons* zone (the youngest lower Toarcian) which display almost modern Mo- and U isotope records. Our findings indicate significant enhancement of seafloor anoxia (5-10-fold compared to present) during both OAE2 and T-OAE. For both periods, enhancement of seafloor anoxia exceeded the duration of the OAEs, as defined by their $\delta^{13}C_{org}$ excursions.

[1] Arnold *et al*. (2004), *Science* **304**, 87-90; [2] Pearce *et al*. (2008), *Geology* **36**, 231-234; [3] Kendall *et al*. (2009), *GCA* **73**, 2534-2558; [4] Gordon *et al*. (2009), *Geology* **37**, 535-538; [5] Montoya Pino *et al*. (2010); *Geology* **38**, 315-318; [6] Poulson *et al*. (2006) *Geology* **34**, 617-620.