

## Trace metal drawdown during a Cretaceous oceanic anoxic event: Implications for global redox conditions

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The global redox state of the oceans during periods of widespread organic-carbon deposition is an essential part of our understanding of Earth's important climatic feedbacks. The Cretaceous is renowned for several global organic-carbon burial events marked by coeval positive carbon isotope excursions now widely known as oceanic anoxic events (OAEs). Here we present a high-resolution compiled data set from Demerara Rise spanning the Cenomanian-Turonian boundary event (~93.9 Ma) or OAE 2, which shows a dramatic drawdown of redox sensitive trace elements. Organic carbon contents are high throughout the entire section analyzed, and, importantly, Fe speciation implies the locality was dominantly euxinic (i.e., anoxic and sulfidic bottom waters) before, during, and after the event. Molybdenum (Mo) and vanadium (V) are effective paleoredox proxies for tracing oceanic euxinia and anoxia, respectively. The drawdown of Mo coincides with the onset of OAE 2, suggesting a global expansion of reducing and sulfidic conditions. Significantly, though, the drawdown of these two redox sensitive elements is offset by 100 kyr, with V preceding Mo. The decline in V enrichment prior to Mo implies an expansion of low oxygen but non-euxinic conditions prior to the OAE. Numerical geochemical box modeling for Mo suggests that euxinia must have covered >2% but <10% of the global seafloor to explain enrichments that were only 25% of those seen before and after the event. Mo and V drawdown may have impacted the nitrogen cycle and thus patterns of primary production, and this feedback may have contributed to the termination of the OAE.

## Chemical compositions of soluble aerosols around the last termination in the NEEM (Greenland) ice core

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The polar ice cores provide us with reconstruction of past atmospheric aerosols. Soluble aerosols in both Arctic and Antarctic ice cores are well discussed by using the proxy of ion concentration/flux, however, there are few studies about chemical compositions of soluble aerosols in ice cores. Using sublimation method [1], here we show differences in the compositions of sulfate and chloride aerosols around the last termination in the NEEM ice core.

A total of 43 samples were distributed from NEEM ice core section from 1280 to 1580 m. Soluble aerosols were extracted from the samples by sublimation system [1]. Constituent elements and diameter of each non-volatile particle were measured by SEM-EDS. By using a method in ref. [2], we assumed chemical compositions of sulfate and chloride aerosols.

We divided the last termination into 4 stages by focusing on the temperature; Holocene, Younger Dryas (YD), Bølling-Allerød (B-A) and Last Glacial Period (LGP), and compared the mass ratio of sulfate and chloride aerosols in each stage. During the cold stage in YD and LGP, CaSO<sub>4</sub> accounted large percentage of sulfate aerosols. On the other hand, during the warm stage in Holocene, Na<sub>2</sub>SO<sub>4</sub> accounted large percentage of sulfate aerosols. In B-A, percentage of Na<sub>2</sub>SO<sub>4</sub> is almost as same as that of CaSO<sub>4</sub>. Since CaSO<sub>4</sub> is considered to be formed at first among sulfate salts in the atmosphere, these results is probably controlled by Ca<sup>2+</sup> concentration. Mass ratio of NaCl/Na<sub>2</sub>SO<sub>4</sub> decreased from LGP to Holocene (Fig. 2f), which indicate that sulfatization of NaCl increased toward Holocene.

[1] Iizuka *et al.* (2009) *J. Glaciol.* **55**, 552-562. [2] Iizuka *et al.* (2012) *Geophys. Res.* **117**, D04308.