Dramatic oceanic sulfur-isotopic shift event at the Early Eocene

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Oceanic sulfate is a huge reservoir of sulfur on the earth surface with its residence time as long as >10 myr. Paytan et al. (1998: Science) showed temporal variation of sulfur isotope value ($\delta^{34}S$) of oceanic sulfate that was summarized based on the analytical results of pelagic barite from deep sea sediments. They revealed conspicuous positive $\delta^{34}S$ shift (17 to 22‰) within a short period of time (~1 myr) across 50 Ma.
Ogawa et al. (2009: EPSL, 285) reported continuous deposition of pyrite-rich sediments through 55 to 45 Ma from ACEX core (IODP EXP. 302) and suggested deposition of vast quantity of pyrite on the sea floor of Arctic Ocean during Eocene that could explain 3‰ of positive $\delta^{34}S$ shift of entire ocean. However, it was still inconsistent with the enigmatic positive shift mentioned above from the standpoint of its duration and size. The temporal variation of oceanic sulfate is also required to be verified through this interval.
The objective of this research is to clarify the global temporal variation of $\delta^{34}S$ of oceanic sulfate through Early-Middle Eocene and discuss the inconsistency between duration and magnitude of positive $\delta^{34}S$ shift between $\delta^{34}S$ fluctuation shown by Paytan et al. (1998) and that expected from ACEX data.
Continuous $\delta^{34}S$ record of pelagic calcareous ooze or micritic carbonate collected by ODP, IODP is obtained from analyses of CAS (carbonate-associated sulfate). We tried to acquire $\delta^{34}S$ values of both barite and CAS from identical sample but it could be achieved only from single sample of equatorial Pacific. Enough CAS data have been obtained from ODP Sites 1258, 1259 (Equatorial Atlantic) and Sites 1262, 1263, 1265, 1267 (South Atlantic) to draw a temporal variation of $\delta^{34}S$ with CAS for Early-Middle Eocene. The fluctuation exhibited considerable decoupling with that of Paytan et al. (1998) showing gradual shift over >5 myr with the magnitude smaller than 5‰ instead of abrupt change as large as 5‰. The time interval for $\delta^{34}S$ shift is concordant with that for pyrite deposition on Arctic seafloor and well explained by outflow water from Arctic discussed by Ogawa et al. (2009). Abrupt $\delta^{34}S$ shift at 50 Ma shown in Paytan et al. (1998) could reflect local heterogeneity of sulfur isotopic composition of oceanic sulfate around eastern equatorial Atlantic during this period.

Keywords: sulfur isotope, Eocene, sulfur, sulfate ion, barite

