Sulfur isotope ratios in co-occuring barite and carbonate from Eocene sediments: A comparison study

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The marine sulfur cycle over geologic timescales is closely linked to the redox state of the Earth's surface environments due to the burial of redox-sensitive sulfur species. Fluctuations in the $\delta^{34}S_{sw}$ record have been related to a wide range of global environmental changes, such as oxygenation of the biosphere, bacterial evolution, and mass extinctions. In order to investigate the utility of bulk carbonate as a recorder of seawater sulfate sulfur isotope ratios ($\delta^{34}S_{sw}$), co-existing pelagic barite and bulk carbonate in Eocene sediments from the Equatorial Pacific Ocean (IODP Exp. 320/321 Sites U1331 to U1333) were analyzed for their sulfur isotope ratios ($\delta^{34}S$). The $\delta^{34}S$ from both minerals showed parallel fluctuation throughout the Eocene with carbonate associated sulfate (CAS) values about 0.8‰ heavier than those of barite. A similar offset was observed in CAS $\delta^{34}S$ obtained using species-specific cleaned planktonic foraminifers (Rennie et al., 2018). The consistent results from two distinct minerals suggest that the original $\delta^{34}S_{sw}$ can be derived from bulk CAS analysis, if post deposition carbonate recrystallization is minimal.
Our $\delta^{34}S_{barite}$ data added an important data set in middle Eocene (Lutetian, 47.8 to 41.2 Ma). The data set combined with previous studies showed a ~5‰ increase of $\delta^{34}S_{sw}$ during the Eocene (from 53 Ma to 36 Ma) with the majority of the shift within 7 myr between 53 and 46 Ma. This change is more gradual than previously reported. The timing of this $\delta^{34}S_{sw}$ shift coincides with extensive pyrite burial in the Arctic Ocean, supporting the hypothesis that the 5‰ increase in Eocene $\delta^{34}S_{sw}$ has been caused by ^{34}S-enriched water outflow from the Arctic Ocean as suggested in the previous study.

Keywords: Sulfur isotope, Carbonate associated sulfate, Barite, Eocene

