

Non-photochemical variations of D33S and D36S in natural environment

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Non-mass-dependent (NMD) sulfur isotope fractionation recorded in pre-2.3 Ga sedimentary rocks provides strong evidence for oxygen-free early atmosphere (Farquhar et al. 2000), because photochemical reactions are the only known mechanisms for producing large NMD so far. The NMD signal has been expressed as non-zero D33S ($= d33S - 0.515 \times d34S$) and D36S ($= d36S - 1.90 \times d34S$) values, representing deviation from reference mass dependent relationship. However, recent investigations pointed that no large NMD has been observed in a period from 3.0 to 2.8 Ga (D33S: less than 0.3 permil; Ohmoto et al. 2006). Two mutually-conflicting interpretations are available to explain the small D33S values: 1) No NMD signal was preserved, because oxygen content of the atmosphere increased tentatively at around 2.9 Ga (Ohmoto et al., 2006) or 2) weak NMD signal was preserved, because atmosphere was still anoxic, but chemically different from other Archean (Farquhar et al. 2007). The main problem is how to distinguish weak photochemical signature with small D33S from normal mass dependent relationships. Now, it is essential to understand variations of D33S and D36S produced by mass dependent processes in nature. Recent high precision analyses of some Phanerozoic pyrites demonstrated that small non-zero D33S (less than 0.3permil) can be produced by mass-dependent processes, for example mixing, transportation and microbial sulfate reduction (Ono et al., 2006), though we have not yet understood natural variation of D33S and D36S values in various modern environments. We have developed a fluorination and multi-GC technique, which allow us quadruple sulfur isotope analyses ($32S/33S/34S/36S$) with precisions of ± 0.5 , ± 0.01 , and ± 0.2 permils for $d34S$, D33S and D36S, respectively. In this presentation, we report high precision analysis of various types of sulfur compounds in modern deep-sea hydrothermal systems, stratified lakes (Nakagawa et al. this meeting), seawater and river water, as well as sulfur, sulfide and sulfate reagents. All these modern sulfur compounds show D33S values from -0.1 to +0.2 permil. Hence, photochemical origin is valid for large D33S over 0.5 permil recorded in several Archean sedimentary rocks. Moreover, various non-biological sulfur compounds show characteristic negative correlation of D36S/D33S with slopes about -8, whereas sulfide and sulfate produced or consumed by microbial processes exhibit distinctive D36S/D33S slopes from less than -15 to -4. All these D36S/D33S ratios are significantly lower than those observed in laboratory experiments of SO_2 photolysis ($D36S/D33S = -0.9$; Farquhar et al., 2001) and are different from those observed in 3.0 to 2.8 Ga sedimentary pyrites (Tsuruoka et al. this meeting). Hence, we conclude that the small NMD signatures of this age record photochemical fractionation, hence, supporting anoxic atmosphere at 2.9 Ga. Our results also indicate that D36S analysis is helpful not only for distinguishing photochemically-induced NMD fractionation from other mass dependent processes, but also for decoupling abiological and different types of microbial reactions.