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$\Delta^{34}S^{18}O$ systematics of modern sulfate

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In this study, ^{34}S-^{18}O clumping in sulfate are newly used to constrain the sulfur and oxygen cycling. Quantitative conversion from sulfate sample into SO_2F_2 is conducted by the reaction with $BaSO_4$ and F_2 at 280°C for 3 h in a nickel reaction vessel. The produced SO_2F_2 was purified and measured by high-mass-resolution mass spectrometer (MAT253 ULTRA). The fluorination method was applied to measure seawater, river water and hot spring water to elucidate the $\Delta^{34}S^{18}O$ systematics of modern sulfate. First, several seawater sulfate samples show constant $\Delta^{34}S^{18}O$ value, which is indistinguishable from that of the international sulfate standard NBS127 (modern marine evaporite). This suggests that $\Delta^{34}S^{18}O$ of gypsum/anhydrite could preserve seawater signature after precipitation. River water sulfate found to exhibit high $\Delta^{34}S^{18}O$ value up to +4.5‰ relative to seawater sulfate ($\Delta^{34}S^{18}O$ = 0‰ by definition). The high $\Delta^{34}S^{18}O$ could be a distinctive signature for sulfate derived from oxidative weathering. On the other hand, sulfate in hot spring water always shows low $\Delta^{34}S^{18}O$ value from –1.0‰ to –0.5‰, which may reflect high temperature hydrothermal origin. These results suggest that the ^{34}S-^{18}O clumping in seawater sulfate is modified from the river input potentially through microbial sulfate reduction and/or hydrothermal activity. In summary, the $\Delta^{34}S^{18}O$ of marine sulfate deposit could be useful to trace biogeochemical evolution of seawater.