Multiple sulfur isotope signatures in Archean sulfates: implications for early Earth atmospheric evolution

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In an anoxic world, sulfate is rare or absent and therefore unlikely to be preserved in the geological record. It is intriguing, therefore, that several sulfate deposits were formed during the Archean, period dominated by reducing conditions. Known Archean sulfate deposits occur as barite ($BaSO_4$) associated with felsic volcanic rocks in Western Australia, India and South Africa at about 3.5, 3.4 and 3.2 Ga. How sulfate appeared in the oceans during the early Archean when oxidative weathering was absent remains unresolved. Does it reflect a period of unique conditions for the preservation of sulfate, an exceptional period of intense sulfate aerosol production, or an unexpectedly active biological sulfur cycle?

In the present work, we performed SIMS analyses of the four sulfur isotopes in the 3.2 and 3.5 Ga-old sulfates from Mapepe (South Africa) and Dresser (Western Australia) Formations. This in situ approach allows us to investigate the diversity of Archean sulfate texture and isotopic heterogeneity with unprecedented resolution, and from then on to deconvolute the ocean and atmosphere Archean sulfur cycle. Our data define a bimodal distribution of $\delta^{34}S$ values at ~ +5 and +9‰, which is matched by modern sulfate aerosols. The peak at +5‰ is associated with barites of different ages and host-rock lithology displaying a wide range of $\Delta^{33}S$ between -1.77 and +0.24‰. These barites are interpreted as primary volcanic emissions formed by SO_2 photochemical processes with variable contribution of OCS shielding in an evolving volcanic plume. The $\delta^{34}S$ peak at +9‰ represents close to zero $\Delta^{33}S$ barites with strongly negative $\Delta^{36}S$ values, which are best interpreted as volcanic sulfate aerosols formed from OCS photolysis. Our results tend to support the view of a photochemical pathway, specific to the early reduced atmosphere, taking place near the point of volcanic emission. Moreover, we also identify variability within the Archean sulfate isotope record that suggests persistence throughout Earth history of photochemical reactions characteristic of the present-day stratosphere (i.e. SO_2 and OCS photolysis).