Quadruple sulfur isotopes in 2.7 Ga sedimentary pyrites from the Yilgarn Craton, Western Australia, explained by simultaneous dissociation of SO_2

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We report the results of a multi-S isotope study of early-diagenetic pyrite nodules from the 2.69 Ga carbonaceous Kapai Slate, and late diagenetic bedded pyrite samples from interflow shales and cherts of the Kambalda Domain, Yilgarn Craton, Western Australia. The best-fit $\Delta^{36}S$-$\Delta^{33}S$ lines for both the nodules and bedded pyrites have $\Delta^{36}S/\Delta^{33}S$ slopes close to the Archean reference array (ARA) (*1*), and positive intercepts on both the $\Delta^{36}S$ and $\Delta^{33}S$ axes. Rigorous statistical tests show that the probability of any of the best-fit lines passing through the origin is low to negligible. The observed $\Delta^{36}S$-$\Delta^{33}S$ linear fractionation lines and their non-zero intercepts can be produced by the dissociation of SO_2 in the atmosphere by natural ultraviolet light of different wave lengths: 1) Photoexcitation, which has a fractionation line with a slope of $\Delta^{36}S/\Delta^{33}S$ of +0.6, occurs in the bandwidth of 250-330 nm (*2*), and 2) self-shielding ($\Delta^{36}S/\Delta^{33}S$ = -4.6) (*3*) or mutual-shielding ($\Delta^{36}S/\Delta^{33}S$ = -1.9) (*2*) photolysis in the 190-220 nm bandwidth, depending on the partial pressure of SO_2. To produce the linear relationship between $\Delta^{36}S$ and $\Delta^{33}S$, the two dissociation processes are required to occur simultaneously in a single reservoir in order that the fraction contributed by the end-member process remains constant across the full range of $\Delta^{33}S$ values. We suggest this process should be called Simultaneous Dissociation and have calculated the fraction of S contributed by photoexcitation end-member required to produce the measured $\Delta^{36}S/\Delta^{33}S$ values of the linear arrays, and positive intercepts on the $\Delta^{36}S$ axis, when the other end-member is self-shielding or mutual-shielding photolysis.

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