Origin of sulfur isotopic anomalies in the present-day atmosphere and new insights into the Archean sulfur cycle

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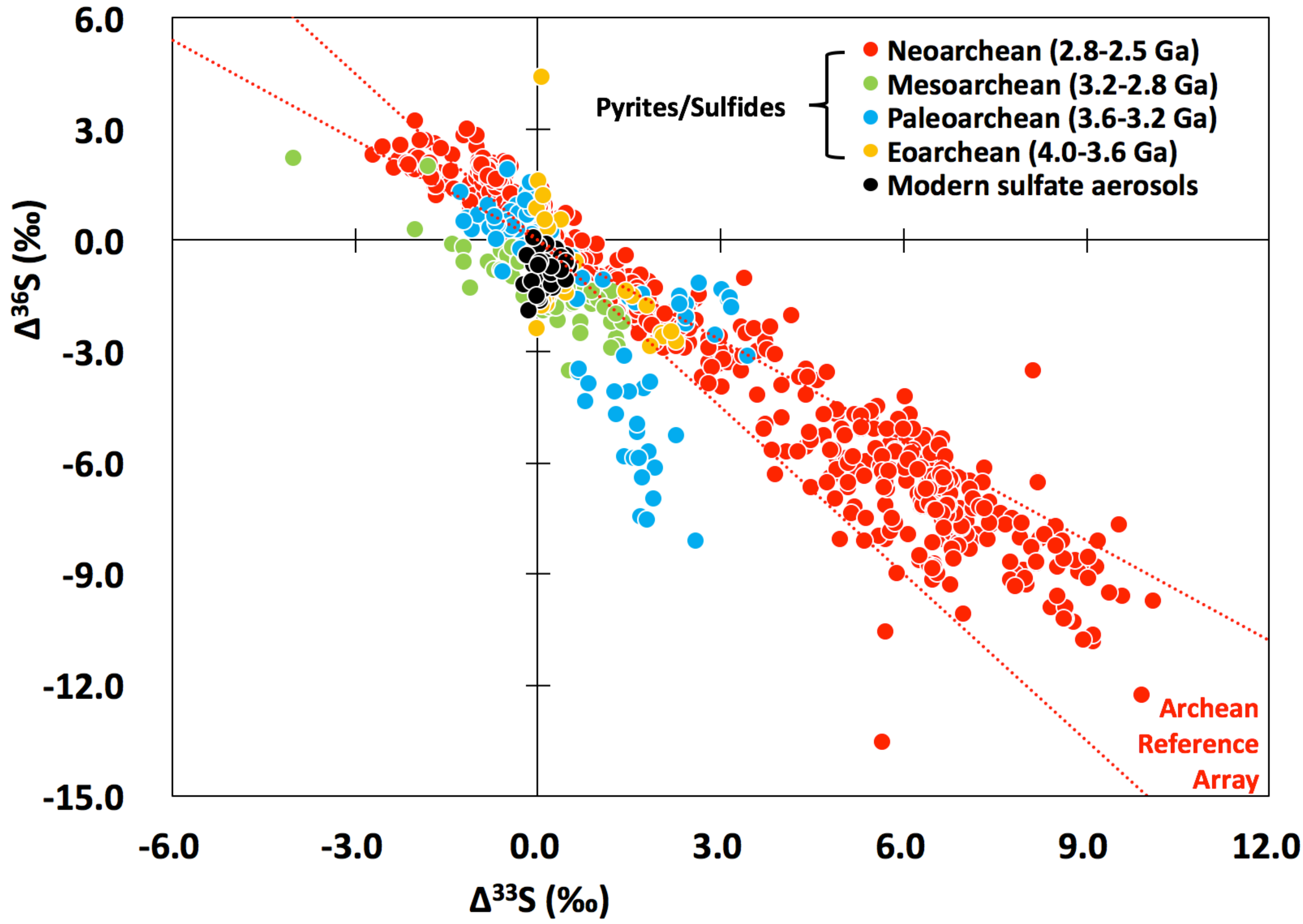
The observation of mass-independent compositions of quadruple sulfur stable isotopes (S-MIF) in Archean rocks and Martian meteorites provides a unique probe of the oxygen and sulfur cycles in the primitive terrestrial and Martian atmospheres, which are essential for understanding the origin and early evolution of life. The mechanistic origin of S-MIF however contains some uncertainties. Even for the modern atmosphere, the primary mechanism responsible for the S-MIF observed in nearly all tropospheric sulfates has not been identified. Without a complete understanding for the origin of S-MIF in modern atmospheric sulfates, interpretation of S-MIF signals preserved in geological and meteoritic samples possess embedded uncertainties.

Here we present the high-sensitivity measurements of a fifth sulfur isotope, stratospherically produced radioactive ^{35}S, along with all four stable sulfur isotopes in the same sulfate aerosols to further define sources and mechanisms on a field observational basis. The five-sulfur-isotope approach provides strong observational evidence that S-MIF signatures in tropospheric sulfates are concomitantly affected by two processes: an altitude-dependent positive ^{33}S anomaly, likely linked to stratospheric SO_2 photolysis, and a negative ^{36}S anomaly mainly associated with combustion. Our first quadruple stable sulfur isotopic analysis in various representative Chinese coal samples (formed in the Carboniferous, Permian, and Triassic periods) and SO_2 emitted from combustion displays essentially normal ^{33}S and ^{36}S within analytical error, suggesting that the observed ^{36}S anomaly in tropospheric sulfates is originating from a previously unknown S-MIF mechanism during combustion instead of coal itself. In addition, we also present a 200-year atmospheric sulfur isotopic anomalies record from the Mount Everest. Along with previous field-based and chamber-based measurements, the first long-term atmospheric sulfur isotopic anomaly record obtained from a non-polar region indicates that a negative ^{33}S anomaly may originate from combustion processes as well.

The chemical physics of S-MIF processes during combustion remain inadequately described, but recombination reaction of elemental sulfur, which is a strictly thermal reaction, is a highly likely mechanism. Because formation of gaseous/solid elemental sulfur related to volcanism has been observed in both terrestrial and extraterrestrial bodies (such as Io), it is plausible, and cannot be ruled out, that the thermal origin of S-MIF may also occur in the Archean volcanism. The fundermental chemical physics of S-MIF in two distinct processes (photolytic and thermal reactions) and their interplay, which was not explored together in the past, may be another ingredient for providing deeper understanding of the evolution of Earth's atmosphere and life's origin.

Keywords: mass-independent fractionation, atmospheric sulfur cycle, recombination reactions, Δ33S , Δ36S, sulfate aerosols



6.0
3.0
0.0
-3.0
-6.0
-9.0
-12.0
-15.0
Δ36S (‰)
-6.0
-3.0
0.0
3.0
6.0
9.0
12.0
Δ33S (‰)
Pyrites/Sulfides
Neoarchean (2.8-2.5 Ga)
Mesoarchean (3.2-2.8 Ga)
Paleoarchean (3.6-3.2 Ga)
Eoarchean (4.0-3.6 Ga)
Modern sulfate aerosols
Archean Reference Array

