OCS-rich Archean atmosphere

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Currently unsolved main problems of Earth's early atmosphere is: (1) What was the greenhouse gas to have maintained warm climate under faint young sun? and (2) When did the atmosphere become oxic? The two questions link with (3) cause of the Late Archean and Palaeoproterozoic global glaciations, (4) appearance of oxygenic photosynthesis possibly long before oxygen rise, and (5) early terrestrial adaptation without UV-shielding by ozone. The discovery of sulfur-MIF in Archean deposits strongly suggests the Earth's early atmosphere contained virtually no molecular oxygen, and thus may provide some hints of these questions. This hypothesis depends on the fact that SO2 photolysis is the only known process to cause large enough MIF for explaining the geological records. However, the mechanism of MIF by SO2 photochemistry is still poorly understood. We have determined for the first time the UV absorption spectra of 32S, 33S and 34SO2 (Danielache et al., 2008) and use this information in a series of scenarios to constrain the past state of the atmosphere. The calculated isotope fractionations give mass independent distributions that are highly sensitive to the wavelength of UV light. Hence, isotopic fractionation factors of SO2 photolysis can be now predicted as a function of atmospheric concentrations of UV-shielding molecules (O2, O3, CO2, H2O, CS2, NH4, N2O, H2S, OCS and SO2 itself). Although various UV-shielding scenarios can be considered, we found that negative D33S observed in all the Archean sulfate deposits cannot be expected unless carbonyl sulfide (OCS) is present in the atmosphere. Further, we performed numerical simulation of photochemical reactions and found that ppm-level OCS can be accumulated if atmosphere does not contain O2 (much less than 10-5PAL) and is poor in CO2 (CO/CO2 larger than 1). The model calculation of such a reducing atmosphere containing appreciable amount of OCS can reproduce geological sulfur isotope distributions. If Archean atmosphere was OCS-rich reducing condition, greenhouse effect by CO2 cannot be expected. Instead, OCS could be an alternative or even more efficient greenhouse gas to compensate for faint young sun problem, because OCS has absorption bands in the IR window from 8 to 13 micro-meters. Furthermore, OCS also has absorption band in lethal UVC region similar to ozone, thus could be an alternative UV-shielding molecule in an ozone-free reducing atmosphere. This ppm-level OCS may have allowed early terrestrial adaptation even in the Archean. Progressive oxidation of atmosphere must have declined OCS level before rise of O2, thus can explain the cause of the Late Archean glaciation at 2.9 Ga. Also, this OCS decline may have resulted in UV crisis until O2-level increased at about 2.3 Ga. The disappearance of the UV screen may have restricted photosynthesizers into deeper water, explaining the so-called delay of oxygen rise long after appearance of oxygenic photosynthesis.