## Understanding Remote Biosignatures Using Earth's Atmospheric Evolution as a Template

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Earth's atmosphere has evolved over time from a weakly reduced, CO2-rich composition to today's predominately N2-O2 mixture. Understanding how Earth's atmosphere evolved may help us understand Earth-like exoplanets when spectroscopic observations of such planets become available. Hadean atmospheric composition is particularly uncertain, as there is only the sketchiest geological record from that time. High concentrations of CO<sub>2</sub> would be expected from impact degassing during accretion. CO may also have been relatively abundant. Once life evolved, both CO and H<sub>2</sub> would have been drawn down, likely leading to the production of CH<sub>4</sub>. High concentrations (~1000 ppmv) of CH<sub>4</sub> could be expected up until the Great Oxidation Event (GOE) at ~2.4 Ga. Depending on the CH<sub>4</sub>/CO<sub>2</sub> ratio, organic haze may also have been present. (Haze is predicted when  $CH_4:CO_2 > 0.1$ .) Following the GOE, O<sub>2</sub> concentrations should have risen, and CH<sub>4</sub> should have declined. Studies of Cr isotopes suggest that Proterozoic O<sub>2</sub> levels were no higher than 0.1% PAL (times the Present Atmospheric Level), although these low values are disputed by other authors. Understanding how abundant O<sub>2</sub> was during this time interval has implications for the evolution of complex life (which requires higher O<sub>2</sub> levels). and for the identification of 'false positives', i.e., abiotic O<sub>2</sub> concentrations that mimic those produced biotically. Some hypothetical abiotic planets, particularly those orbiting M stars, could conceivably develop O2 concentrations exceeding 0.1% PAL.

One of the best indicators of past atmospheric  $O_2$  concentrations is the presence, or absence, of massindependent S-isotope signatures in ancient rocks. New work by C. E. Harman et al., discussed elsewhere in this meeting, suggests that the mechanism for producing this anomalous fractionation has been misunderstood. Sulfur chain formation, not SO<sub>2</sub> photolysis itself, is probably the dominant process. Understanding this process may lead to new insights into Archean atmospheric composition.