

Unique Late Archean Atmosphere due to Enhanced Volcanic and Biological ActivitiesY. Ueno^{1,2,3}, S.O. Danielache⁴ and Y. Endo¹¹Department of Earth and Planetary Sciences, Tokyo Institute of Technology, Meguro Tokyo 152-8551, Japan²Earth-Life Science Institute, Tokyo Institute of Technology, Meguro Tokyo 152-8551, Japan <ueno@elsi.jp>³Precambrian Ecosystems Laboratory, JAMSTEC, Japan.⁴Faculty of Science & Technology, Sophia University, Japan.

Late Archean may be characterized by increasing continental volume and large igneous provinces as well as by onset of oxygenic photosynthesis [1,2]. Enhanced biological production at that time may not have readily resulted in oxidizing atmosphere, and rather caused increasing biological methane in the atmosphere [3,4], that is supported by anomalously ¹³C-depleted organic carbon recorded in the Late Archean sequence [5]. The large volcanic input into CH₄-bearing very reducing atmosphere may cause unique atmosphere of habitable planet.

In order to test the scenario, we have developed a sulfur isotopic model by improving our atmospheric reaction model [6,7]. The improvements to our model includes the addition of hydrocarbon chemistry, chemical formation and deposition of organic sulfur haze, together with newly determined high-accuracy ultraviolet absorption cross sections of SO₂ isotopologues for reproducing the geological record. The “Sulfur Mass-Independent Fractionation” (S-MIF) has been useful to monitor chemistry of the Earth’s early atmosphere. Sedimentary sulfides exhibit exceptionally large variation of $\Delta^{33}\text{S}$ values in the latest Archean, from 2.7 to 2.5 Ga, compared to older period. The maximum scatter of S-MIF may indicate anomalous chemistry of atmosphere or climatic system of the late Archean Earth, though the primary cause of the large MIF is still poorly understood.

Our model results suggest that after a volcanic injection of SO₂ into the Archean atmosphere, a significant fraction of the sulfur is converted into carbonyl sulfide (OCS) and could be accumulated in an atmosphere over a timescale of 10 years, if background atmosphere is reducing enough to yield hydrocarbon haze and volcanic sulfur input is large and episodic. Such model could explain the large $\Delta^{33}\text{S}$ scatter observed in the Late Archean sedimentary rocks. Moreover, isotopically fractionated two reservoirs (i.e. atmosphere and ocean) can be mixed episodically and thus possible to explain the observed small scale heterogeneity of S-MIF even within a hand specimen level. Combined greenhouse effect by the CH₄ and OCS could have resulted in warm Late Archean climate. Furthermore, subsequent oxidation event of this highly reducing atmosphere may have been more significant for cooling than previously thought, thus could have been the trigger of global-scale glaciation at around the earliest Proterozoic.

References: [1] Sessions et al. (2009) *Current Biology* 19, R567–R574, [2] Ernst (2007) *Episode* 30, 108–113. [3] Hoeler et al. (2001) *Nature* 412, 324–327. [4] Pavlov et al. (2001) *Geology* 29, 1003–1006. [5] Hayes (1994) *Early Life on Earth*. pp. 220–236. [6] Danielache et al. (2008) *J Geophys Res* 113, D17314. [7] Ueno et al. (2009) *PNAS* 106, 14784–14789.