

The bi-stability of organic haze in the Archean atmosphere

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Methane has long been a postulated component of the Archean atmosphere, but very little direct evidence exists for this contention. Ecosystem models predict that modest fluxes of methane into reducing atmospheres would result in high concentrations [1], while models of the evolution of atmospheric redox on the early Earth suggest important roles for methane associated with the rise of oxygen [2, 3]. Here, we expand previous photochemical modeling efforts [3, 4] by linking changes in methane concentration to observable geochemical signatures. In a suite of reducing model atmospheres, we increase concentrations of methane until an organic haze forms. Using particles which scatter using both classical Mie physics as well as newly postulated fractal scattering behavior [5], we find that the Archean atmosphere would exhibit bi-stability between a “clear skies” case and one with a thin organic haze. The photochemical modeling further demonstrates that the presence of the thin organic haze would significantly affect the fractionation of minor isotopes of sulfur (mass-independent fractionation of sulfur or S-MIF) by both UV opacity effects and by changing the redox chemistry of S species in the atmosphere. The prediction of an Earth system with correlated changes in methane concentration and variations in S-MIF is evident in new data from the Campbellrand-Malmani platform of South Africa [6], which indicate multiple appearances of organic haze due to a methanogen-driven high CH₄:CO₂ ratios [4] in the late Neoproterozoic. These combined results provide stronger evidence for a role for methane in the Neoproterozoic atmosphere, and support arguments that the Great Oxidation Event may have been related to the disappearance of a large biological flux of methane [3].

[1] Kasting et al. (2001) *Origins of Life and Evolution of the Biosphere* **31**, 271-285. [2] Catling et al. (2001) *Science* **293**, 839-843. [3] Zahnle et al. (2006) *Geobiology* **4**, 271-283. [4] Domagal-Goldman et al. (2008) *Earth and Planetary Science Letters* **269**, 29-40. [5] Wolf and Toon, (2010) *Science* **328**, 1266-1268. [6] Zerkle et al. (2012) *Nature Geosciences* (in press).

How does the continental crust get really hot?

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Evidence for the physical conditions under which the Earth's crust can generate large volumes of magma is provided by metamorphic rocks that represent the solid residue of partial melting and chemical differentiation. Many of these rocks preserve mineral assemblages stabilised at very high-temperature and moderate pressure conditions that lie above the dry solidus for most crustal rock types. These ultra-high temperature (UHT) metamorphic rocks can only be formed after substantial degrees of partial melting and, although originally regarded as isolated thermal anomalies, there is increasing evidence that continental crust has attained UHT conditions repeatedly in time and space. Our ability to quantify this metamorphic record as absolute temperature-depth information has increased dramatically over the last 40 years with improved thermodynamic constraints on the pressure-temperature stability of mineral assemblages. At the same time, development of mathematical models for the thermal behaviour of continental crust has allowed us to compare pressure-temperature data from real metamorphic rocks with geothermal gradients predicted for simple tectonic settings, and identify possible causes of elevated metamorphic temperatures. While these thermal models can reproduce conditions recorded by the majority of metamorphic rocks, UHT metamorphism remains difficult to replicate with standard numerical models for orogenesis. In this contribution, we examine a number of heat sources that might account for these extreme temperatures and investigate the link between UHT metamorphism and magma generation.