Redox evolution of volcanic gas through geologic time

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It has been generally assumed that, before ~2.5 Ga, the global flux of reducing volcanic gas ($F_{\sum red.v} = 1/2F_{H2} + 2F_{H2S} + 1/2F_{SO2} + 1/2F_{CO} + 2F_{CH4}$) was significantly higher than the global oxygen production flux ($F_{p,O2}$), resulting in an anoxic atmosphere. However, this was probably not the case.

Considering the estimates made by various researchers for the fluxes of various volcanic gases, I have estimated today's $F_{\sum red.v}$ to be $(0.5\pm0.3)x10^{12}$ mol/yr, which accounts for only ~5% of today's $F_{p,O2}$ ($\sim 10x10^{12}$ mol/yr); the remaining ~95 % of O_2 consumption is carried out by kerogen and Fe^{2+}-bearing minerals during soil formation. I have also estimated F_i, $F_{\sum redd.v}$ and $F_{p,O2}$ values for the Archean world, taking into consideration of the following possibilities: (1) the total land area was much less (e.g., ~5% land and ~95% ocean); (2) the heat flux was ~3 times higher; (3) fO_2 values for the mantle wedges above subduction zones (i.e., FMQ + 2±1 today) were the same as those of the normal mantle (i.e., FMQ - 1±1); (4) pyrrhotite was ubiquitous in magmas and rocks; and (5) the atmospheric pCO_2 was ~100 PAL. (1)-(4) affect F_i and $F_{\sum redd.v}$ values, whereas (1) and (5) affect $F_{p,O2}$.

The results of computations suggest that the Archean $F_{\sum redd.v}$ could have been as high as $\sim 2x10^{12}$ mol/yr, which is about 4 times higher than today's $F_{\sum redd.v}$. For comparison, the Archean $F_{p,O2}$ ranged from ~7 to ~40 ($x10^{12}$ mol/yr), depending on whether the deep oceans were oxic or anoxic. These values imply that volcanic gas could not have prevented the oxygenation of the atmosphere within <10 Ma since the emergence of cyanobacteria.

SO_2 is a major volcanic gas today, but it was most likely a very minor specie in Archean volcanic gas; thus it was an unlikely source for the anomalous sulfur isotope signatures in Archean sedimentary rocks.

A dismembered Late-Archean anorthositic to charnockitic suite in the Andriamena greenstone-belt, Madagascar

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The Andriamana greenstone belt includes a late-Archean anorthositic to charnockitic suite, which outcrops in the vicinity of two major chromite deposits, associated with minor harzburgites and orthopyroxenites.

The anorthositic rocks comprise coarse-grained leucogabbros grading to noritic gabbros. Based on the An contents of plagioclase, two groups of gabbroic rocks are defined: a high-An group ranging from An_{90} to An_{60} and a low An-group, with compositions grouped around An_{50}. Mantle characteristics are most strongly displayed in rocks bearing calcic plagioclase, which host Al_2O_3-rich orthopyroxenes (up to 6% Al_2O_3) indicative of crystallization at great depth. Charnockitic microgabbros and diorites are particularly rich in incompatible elements. These characteristics were enhanced by magmatic flowage of the charnockitic parental magmas in the crust. Eight samples from the anorthositic to charnockitic suite and associated granites and pyroxenites define a Sm-Nd errorchron with an age of ~2.8 Ga, suggesting significant mantle magmatism and local crustal remobilisation in the Late Archean. Preliminary data obtained from zircons confirm these chronological results.