Limits on the partial pressure of H_2 in the Archean atmosphere during weathering of basaltic minerals

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It is widely recognized that the Archean atmosphere was anoxic with a partial pressure of $H_2(g)$ in the range 10^{-6} - 10^{-3} bars and $CO_2(g)$ $10^{-2.5}$ - $10^{-1.5}$ bars [1]. The existence of detrital minerals like siderite ($FeCO_3$) and pyrite (FeS_2) in Archean sedimentary rocks [2] also suggests similar atmospheric characteristics [3]. However, quantification of weathering processes involving the proposed anoxic atmosphere are needed to assess which minerals might form and the resulting water chemistry. Here, models were constructed to simulate rainwater and weathering processes at 25 °C, 1 atm under present-day and Archean atmospheric conditions. The simulations for the present-day used world-average rainwater resulting in the expected weathering products, including hematite, smectite and chalcedony, with calcite and sepiolite at large extents of reaction, and waters dominated by Na^+-Ca^{2+}-Mg^{2+}-SiO_2-HCO_3^--Cl^--SO_4^{2-} species. For the simulation of Archean rainwater, we varied the levels of $pH_{2,g}$ over a wide range of $pCO_{2,g}$ values. At the highest H_2 levels suggested by atmospheric models, the predicted aqueous carbon-species in rainwater are dominated by dissolved hydrocarbons. This result suggests that a more realistic upper limit on the $pH_{2,g}$ would be about $10^{-4.0}$ - $10^{-3.5}$ bars. A lower limit of 10^{-6} bars, with $pCO_{2,g} = 10^{-2}$ bars, from the atmospheric models is consistent with siderite stability relative to magnetite. To simulate weathering, we assumed $pH_{2,g} = 10^{-5}$ bars, $pCO_{2,g} = 10^{-2}$ bars. In contrast to the present-day results, the weathering products included pyrrhotite and siderite, along with smectite, chalcedony, calcite and sepiolite. Pyrrhotite formed because we permitted the model aqueous solutions to become supersaturated with respect to pyrite. The waters were again dominated by Na^+-Ca^{2+}-Mg^{2+}-SiO_2-HCO_3^--Cl^-, but had highly variable amounts of Fe^{2+} and HS^-, and trace amounts of dissolved N were present as NH_4^+. Our models predict that Fe(II) minerals such as pyrite or siderite would either form or persist during weathering, indicating that the proposed H_2-bearing atmosphere is consistent with the detrital mineral records. Linking the atmospheric models with weathering processes also leads to a more complete picture of riverine input to the Archean oceans involving reduced Fe, S and N species.

[1] Catling & Claire (2005), *Earth Planet. Sci. Lett.* **237**, 1-20. [2] Rasmussen & Buick (1999), *Geology* **27**, 115-118. [3] Sverjensky & Lee (2010), *Elements* **6**, 31-36.