

Composition of the early precambrian atmosphere and hydrosphere thermodynamic constraints from mineral deposits

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A chemical equilibrium model for the early Precambrian atmosphere and hydrosphere is presented. Thermodynamic calculations based on observed stable minerals and mineral assemblages in banded iron formation (BIF), pyritic, urani-

ferous and auriferous quartz pebble conglomerates, gold-bearing conglomerates of the Tarkwaian in Ghana, and red bed sediments, yield the following conditions:

Before approx. 2350 Ma, the atmosphere was

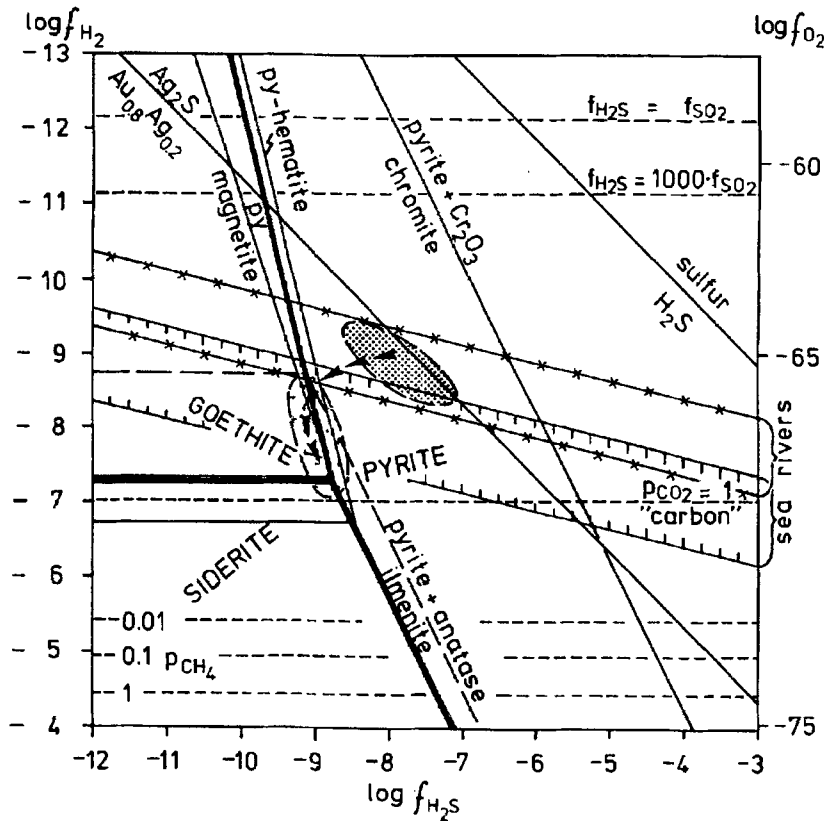


FIG. 1. Hydrogen fugacity vs. hydrogen sulphide fugacity plot (CO_2 -fugacity fixed at 1 bar). Bold lines are phase boundaries between siderite, goethite, and pyrite. Solid lines represent stability field boundaries for the indicated minerals. Dashed lines indicate equilibrium partial pressures of methane, and 'carbon' (graphite) stability boundary at 1 bar CO_2 partial pressure. The two overlapping bands labeled 'sea' and 'rivers' delineate geochemically reasonable combinations of pH and sulphate concentration values (see text). The ovoid areas indicate conditions in ancient river systems (shaded; e.g. Witwatersrand) and in coeval oceans (crosses). Arrows indicate path during mixing of river water and sea water (BIF precipitation).

oxygen-free ($p_{\text{O}_2} \ll 10^{-1}$ bar), consisted mainly of CO_2 ($p_{\text{CO}_2} \leq 1$ bar) and nitrogen, and contained minor amounts of hydrogen sulphide ($p_{\text{H}_2\text{S}} \cong 10^{-7.5}$ bar over continents to 10^{-9} bar over oceans) and hydrogen (p_{H_2} 10^{-9} bar over continents to $10^{-7.5}$ bar over oceans). The high CO_2 partial pressures generated acid rain and surface waters ($\text{pH} \geq 3.9$), and buffered the ocean water to values around $\text{pH} = 6.5$ to 7 . In the oceans, the iron minerals of the various BIF facies ('goethite', pyrite, siderite) in conjunction with the atmospheric CO_2 partial pressure acted as a mineral buffer for $p_{\text{H}_2\text{S}}$ and for the redox state (p_{H_2}). In continental weathering environments, pyrite formation from ferrous iron and atmospheric H_2S , and oxidation of H_2S to SO_4^{2-} are considered the prime redox-controlling mechan-

isms. Figure 1 summarizes some stability relations for typical detrital minerals in Witwatersrand-type conglomerates and in BIFs. River waters previously equilibrated with pyrite precipitated BIF upon mixing with sea water, mainly due to pH changes.

Between 2350 and 2100 Ma, transition from pyritic to iron-oxide-bearing conglomerates indicates that photosynthetic oxygen production rates began to exceed oxygen consumption rates, and that the redox-buffers involving hydrogen sulphide and ferrous iron were overwhelmed. Increased oxidation potentials, and increased surface water pH due to declining atmospheric CO_2 partial pressures, led to immobilization of iron and consequently to continental red bed formation and cessation of BIF deposition.