

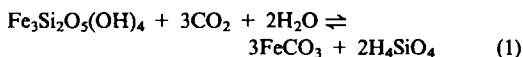
O₂ and CO₂ in the Late Archaean and Early Proterozoic atmosphere

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There is now abundant and convincing evidence for a major increase in the O₂ content of the atmosphere between 2.25 and 2.06 Ga (see for instance Holland, 1994, and Karhu, 1993). The behaviour of iron during soil formation indicates that P_{O₂} was ≤ 1% P.A.L. (2 × 10³ atm) before 2.2 Ga and has been ≥ 15% P.A.L. (0.03 atm) since 1.9 Ga. In pre-2.2 Ga paleosols Fe²⁺ released from parent basalts during weathering moved downward and was reprecipitated in part as one or more ferrous silicates. These have since been converted into high-Fe²⁺ chlorites (see for instance Button, 1979 and Macfarlane, Danielson, and Holland, 1994). Siderite has not been found in any of these paleosols, although dolomite has been recorded in a 2.6 Ga paleosol developed on ultramafics (Martini, 1994). The precipitation of an iron silicate suggests that P_{CO₂} in pre-2.2 Ga soils was below the stability boundary of siderite. Greenalite is the simplest iron silicate that might have been the precursor of high-Fe²⁺ chlorite.

At equilibrium between siderite and greenalite



and

$$K_1 = \frac{a_{\text{H}_4\text{SiO}_4}^2}{P_{\text{CO}_2}^3} \quad (2)$$

A rather uncertain value for K₁ can be calculated on the basis of good solubility data for siderite (Greenberg and Tomson, 1992, and Bruno, Wersin and Stumm, 1992) and estimated thermochemical data for greenalite (Eugster and Chou, 1973). Fortunately the value of 10^{-0.2} for K₁ estimated on this basis agrees satisfactorily with values based on the composition of groundwaters in the Biwabik iron formation, which contains both siderite and greenalite.

The minimum P_{CO₂} in groundwaters from five sideritic sedimentary rocks in Pennsylvania, Virginia, and Kentucky that contain a variety of clay minerals is only slightly higher than that at the siderite-greenalite boundary. This suggests that P_{CO₂} in pre 2.2 Ga paleosols was less than c.

10^{-2.4} atm even if the original Fe²⁺-silicate in these paleosols was not greenalite. The P_{CO₂} of the atmosphere above these paleosols must have been equal to or greater than that at the site of Fe²⁺-silicate precipitation. If the diffusion of CO₂ into these soils was rapid, the CO₂ gradient in the soils was small, and P_{CO₂} in the atmosphere was about ≤ 10^{-2.4} atm. If CO₂ diffusion was slow, atmospheric P_{CO₂} was significantly greater than in the paleosols but probably less than c. 10^{-1.8} atm. Such values of P_{CO₂} are much lower than those needed to compensate for the lower solar luminosity 2.25–2.75 Ga, the age range of the paleosols that have been studied to date (Kasting, 1992). Even if mass loss from the early Sun raised solar luminosity above that estimated by standard evolution models, the effects of mass loss would have been very minor 2.75 Ga, i.e. 1.8 Ga after the formation of the Earth (Doyle et al., 1994). It is therefore likely that one or more greenhouse gases in addition to CO₂ were present in the Earth's atmosphere prior to 2.25 Ga. Methane is the most likely candidate. Recent work (Sagan et al., 1994) suggests that the red haze in the atmosphere of Titan is due to a photochemical smog of tholins. A similar smog on Earth might have served as a sufficient screen to protect CH₄ in the troposphere from decomposition by solar ultraviolet radiation. Such a model of the Earth's atmosphere demands that O₂ was completely absent prior to 2.25 Ga, and that the period between 2.25 and 2.06 Ga witnessed a truly major compositional change from mildly reducing to highly oxidizing.

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