

Palaeoclimatology

Archaean atmosphere and climate

Arising from: H. Ohmoto, Y. Watanabe & K. Kumazawa *Nature* **429**, 395–399 (2004)

Ohmoto *et al.*¹ argue that carbon dioxide was abundant in the late Archaean and early Proterozoic atmosphere and that methane was probably scarce, based on a reanalysis of the occurrence of siderite, FeCO₃, in ancient rocks. Here I consider several factors that may undermine their conclusions.

Rye *et al.*² placed an upper limit on atmospheric carbon dioxide partial pressure, *p*CO₂, between 2.2 billion and 2.8 billion years (2.2 and 2.8 Gyr), based on the absence of siderite in palaeosols (soils that are more than 2.5 billion years old). Ohmoto *et al.* discount this result because they argue, quoting my atmospheric models^{3,4}, that the oxygen partial pressure (*p*O₂) was too high to allow siderite to be stable. In doing so, they confuse locally generated *p*O₂ values of up to 10⁻⁶ atm in the immediate vicinity of oxygen oases⁴ with globally averaged values of about 10⁻¹³ atm, and they ignore the much higher partial pressures (10⁻⁵ to 10⁻³ atm) of hydrogen and methane in these model atmospheres. If one includes these latter gases in equilibrium groundwater calculations, then the effective *p*O₂ is below 10⁻⁷⁰ atm and siderite is stable, so the Rye *et al.* conclusions stand.

Ohmoto *et al.* argue that the occurrence of siderite in Archaean/early Proterozoic banded iron formations places a lower limit on atmospheric *p*CO₂ at that time, but this argument is not convincing. Banded iron formations are marine sediments that must have been formed below the wave base as otherwise their laminated texture would not have been preserved. Today, the effective *p*CO₂ in deep water is about three times higher than that in surface water as a consequence of the decomposition of organic matter⁵. If such gradients in dissolved carbon dioxide existed in the Archaean era as well, the *p*CO₂ estimates derived from this procedure will be systematically high by this same amount.

Two other points are relevant. First, atmospheric methane and carbon dioxide levels need not have been inversely correlated. They are inversely correlated only if one can show that the Archaean/early Proterozoic climate was cool. This was clearly the case during the Palaeoproterozoic glaciations at around 2.3 Gyr; however, the surface temperature both before and after that time could have been much warmer. A mean temperature of 70 °C has been proposed for 3.3 Gyr ago⁶. If the Archaean climate was hot, both methane and carbon dioxide could have been abundant. Second, contrary to the assertions by Ohmoto *et al.*, the idea that Archaean methane levels were high was not proposed initially by Rye *et al.*², nor does it rest exclusively, or even primarily, on

the palaeosol evidence for low *p*CO₂. A methane-rich Archaean atmosphere was suggested more than 25 years ago⁷ and was explored during the 1980s by using both photochemical and climate models^{8,9}. If atmospheric oxygen was low^{10,11}, and if methanogens are evolutionarily ancient, high methane levels are predicted, regardless of the particulars of Archaean carbon dioxide levels and climate.

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Archaean palaeosols and Archaean air

Ferrous carbonate, as the mineral siderite, occurs in Archaean palaeosols (ancient soils). Ohmoto *et al.*¹ contend that siderite was not in equilibrium with the oxygen in Archaean air and that its presence in palaeosols provides little constraint on the partial pressure of carbon dioxide in Archaean air. But their argument is invalid because it fails to distinguish the different behaviours of the trivial component oxygen and the significant component carbon dioxide in the partly closed system of soil waters. The presence or absence of siderite in ancient soils is a valid constraint on the carbon dioxide partial pressure (*p*CO₂) in ancient atmospheres.

To illustrate the problem using the approach of Ohmoto *et al.*, I use their lowest oxygen partial pressure (*p*O₂). Solar ultraviolet and lightning would dynamically maintain *p*O₂ at 10⁻¹³ atm (ref. 2). Ohmoto *et al.* correctly state that this is far above the critical *p*O₂ for siderite stability, namely 10^{-65±5} atm. The partial pressure at siderite

stability has only mathematical significance; there is no actual molecule of oxygen in any realizable volume of water at the *p*O₂. Rather, the dissolved oxygen at Archaean *p*O₂ in water, which is about 10⁻¹⁶ mol kg⁻¹, is too small to affect the chemistry of a soil observably, as illustrated by a simple mass balance. Basalt contains about 10% by mass of ferrous oxide, FeO, so it would take 2 × 10¹⁵ kg of oxygen-saturated water to oxidize the ferrous oxide in a kilogram of rock to magnetite, Fe₃O₄. With a typical rainfall of 1 m yr⁻¹, it would require 10¹⁵ years of rain to oxidize a metre of section. This conclusion applies as long as oxygen is a trivial component. Even at a partial pressure of 10⁻⁶ atm, it would take 10⁸ years to oxidize a metre of section.

Rather, the trivial oxygen dissolved in soil water at *p*O₂ = 10⁻¹³ atm reacts with the rock, producing an undetectable amount of ferric iron. This leaves a solution that is quantitatively depleted in oxygen and buffered by ferrous silicates, where siderite is stable if there is enough *p*CO₂. At a higher *p*O₂ of 10⁻⁶ atm, trace oxygen in soil water would produce observable ferric iron before it was exhausted, again leaving a buffer with ferrous silicates. Moreover, if the oxidation reaction is kinetically inhibited at trivial concentrations, the presence of oxygen in the air is irrelevant to the presence of siderite.

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Ohmoto *et al.* reply — The idea of a methane-rich Archaean atmosphere has become popular since Rye *et al.* assumed in their calculation¹ that siderite was absent in pre-2.2-Gyr palaeosols. We have concluded that the absence of siderite in some Archaean palaeosols does not constrain the atmospheric *p*CO₂, but the presence of much siderite in sedimentary rocks does². Sleep's recognition³ that siderite occurs in Archaean palaeosols substantiates our arguments²: although siderite should be absent in well aerated soils of all geological ages, it may form in waterlogged soils where *p*O₂ became less than about 10⁻⁶⁰ atm owing to the abundant anaerobic production of H₂. In fact, we have reported this in a 2.6-Gyr soil profile at Schagen, South Africa⁴: abundant ferric-rich minerals formed while the soil was exposed to air, but ferrous-rich carbonate formed while it was apparently submerged under an anoxic pond.

Cyanobacteria and eukaryotic algae, principal oxygenic photoautotrophs (aerobes), had emerged by about 2.8 Gyr ago⁵ and possibly more than 3.7 Gyr ago⁶.