Precambrian paleosols and atmospheric CO2 levels

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Received 3 November 2005; received in revised form 13 February 2006; accepted 19 February 2006

Abstract

Precambrian atmospheric pCO2 levels were previously estimated using a simple thermodynamic model based on the mineral assemblage in paleosols. In addition to theoretical flaws with that model, recalculation of pCO2 levels using more recent thermodynamic data gives significantly lower values. A new model based on the mass balance of weathering in paleosols gives consistent results from three separate ∼2.2 Ga old paleosols. The calculated pCO2 value of 23 × 3 ÷ 3 times present atmospheric levels is insufficient to overcome the “faint young Sun” paradox, suggesting that another greenhouse gas such as CH4 was present at elevated levels relative to the present atmosphere to account for the discrepancy. Applying this new approach to other Precambrian paleosols a Proterozoic pCO2 curve is generated, which indicates consistently high pCO2 from 2.5 to 1.8 Ga ago, and a substantial drop in atmospheric pCO2 at some time between 1.8 and 1.1 Ga ago.

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Keywords: Precambrian; Paleosols; CO2; CH4; Proterozoic

1. Introduction

There has been a large amount of speculation about the composition of the Earth’s Precambrian atmosphere based on unusual sedimentary deposits such as banded iron formations (BIFs) and possibly detrital uraninite and pyrite (for contrasting views see Minter, 1999; Phillips and Law, 1997), as well as on the basis of deposits such as paleosols (e.g., Holland and Zbinden, 1988) that are not restricted to the Precambrian. When they have not been pervasively altered (e.g., by potassium metasomatism; Palmer et al., 1989), paleosols offer the most direct evidence of past environmental conditions because they formed at the Earth’s surface, in direct contact with the atmosphere. Holland (1994) and his colleagues (Pinto and Holland, 1988; Holland and Zbinden, 1988; Holland et al., 1989) have suggested semi-quantitative methods for estimating Precambrian oxygen and carbon dioxide levels based on a number of simplifying assumptions. Estimates of atmospheric carbon dioxide levels before ∼2.2 Ga ago were further constrained by a simple thermodynamic model, based on greenschist–siderite equilibrium, to have been less than 100 times present levels (Rye et al., 1995), an amount insufficient to account for the “faint young Sun” paradox (Kasting, 1993), which has led recent investigators to propose that elevated methane levels may have provided the additional greenhouse component necessary to maintain equable surface temperatures throughout Earth’s history (Pavlov et al., 2000, 2003). In this study, I examine the shortcomings of the simple thermodynamic model, propose an alternative method of calculating atmospheric carbon dioxide concentration using mass balance in paleosols, and generate a pCO2 curve for 2.5–1.0 Ga ago.

2. CO2 Paleoharometry

Rye et al. (1995) suggested that the equilibrium relationship between siderite and reduced iron silicates (SIS
herein) in paleosols could be used to constrain Precambrian atmospheric $p_{\text{CO}_2}$. They argued that the lack of siderite in Precambrian paleosols limits atmospheric $p_{\text{CO}_2}$ since reduced iron silicates should precipitate instead of siderite if $p_{\text{CO}_2}$ is low. Greenalite was selected by Rye et al. (1995) because it is a simple low-temperature metamorphic iron silicate suitable to Precambrian paleosols, many of which have been altered by greenschist facies metamorphism at $T \geq 300^\circ$C (Rye and Holland, 2000a,b). Siderite is not decarbonated under common conditions of metamorphism up to, and including, greenschist facies metamorphism (Rye et al., 1995).

There are a number of theoretical and geological issues with the simple model of Rye et al. (1995) for determining Archean atmospheric $p_{\text{CO}_2}$ from paleosols. First, using a single equilibrium relationship for all Archean and Proterozoic paleosols is misleading because the mineral assemblage present is not the same in all Precambrian paleosols, and those differences would give different equilibrium results. The presence or absence of siderite is only relevant in cases where the rest of the modeled mineral assemblage is present. Second, greenalite is not known to form authigenically in soils, and it would be better to apply an authigenic iron silicate such as berthierine rather than a mineral in the post-burial metamorphic assemblage. Third, Rye et al. (1995) measured in situ carbon dioxide in banded iron formations (BIFs) as a check on their thermodynamic model results. This provides only weak guidance because the chemistry of a soil formed at the Earth’s surface bears little resemblance to the chemistry of a BIF formed in the ocean, in part because decomposition of organic matter leaves the effective $p_{\text{CO}_2}$ of the deep ocean about three times that of the surface ocean (Kasting, 2004). Fourth, even when a more likely mineral assemblage is used in the calculations including the reduced iron silicate berthierine, which is present in the ~2.2 Ga Waterval Onder paleosol, estimated carbon dioxide levels are inconsistent with geologic evidence as described below. Fifth, the oldest occurrence of siderite in a paleosol, which the SIS paleobarometer would indicate formed under conditions of atmospheric $p_{\text{CO}_2}$ greater than 60–100 times present levels, is ~0.98 Ga, a time for which there is no independent evidence of $p_{\text{CO}_2}$ levels that high (e.g., Retallack and Mindszenty, 1994), suggesting siderite formation may be tied to other factors such as productivity by soil biota (e.g., Sawicki et al., 1995) rather than atmospheric composition. This idea is further supported by anoxic weathering experiments where no siderite was formed from the dissolution of Fe-biotite even at very high $p_{\text{CO}_2}$ levels (1 atm, >2000 PAL) where Rye et al.’s (1995) model would predict siderite stability (Murakami et al., 2004).

3. Equilibrium model results

The original SIS $CO_2$ paleobarometer gives an upper limit of ~100 times present atmospheric $CO_2$ levels based on the following equilibrium between siderite and greenalite:

$$\text{Fe}_3\text{Si}_2\text{O}_5(\text{OH})_4(\text{green}) + 3\text{CO}_2(g) = 3\text{FeCO}_3(\text{sid}) + 2\text{SiO}_2(aq) + 2\text{H}_2\text{O} \quad (1)$$

Rye et al. (1995) used thermodynamic data from Eugster and Chou (1973) and calculated the phase boundary shown in Fig. 1. In their paper, Rye et al. (1995) allowed that Eugster and Chou’s (1973) data for greenalite were poorly constrained. Recalculating the SIS paleobarometer using revised data for greenalite from the computer program SUPCRT92 (Johnson et al., 1992; database updated as SLOP98 by E. Shock) gives a significantly different result (Fig. 1), with Precambrian $p_{\text{CO}_2}$ levels estimated to be only significantly lower than present atmospheric $p_{\text{CO}_2}$ levels (PAL) over a reasonable range of $a_{\text{SiO}_2(aq)}$. Most modern surface waters are near quartz saturation ($a_{\text{SiO}_2(aq)} = 10^{-4.047}$), which, if it was also the case in the Precambrian, would indicate that atmospheric $p_{\text{CO}_2}$ was just $10^{-5.72}$, or 0.006 PAL (Fig. 1). As discussed above greenalite is unlikely to form authigenically in soils, so perhaps the SIS paleobarometer approach is sound, but greenalite is the wrong reduced iron silicate.

Berthierine (thermodynamic data from Fritz and Toth, 1997), a serpentine group ferrous iron silicate that forms in chemically reducing conditions but rarely as a soil mineral (e.g., Sheldon and Retallack, 2002), is part of the mineral assemblage of the ~2.2 Ga old Waterval...
Onder paleosols (Retallack and Krinsley, 1993). A similar expression to Eq. (1) can be written for equilibrium between berthierine and siderite and kaolinite as follows:

$$\text{Fe}_2\text{Al}_2\text{Si}_3\text{O}_{10}\text{(OH)}_4(bert) + \text{SiO}_2(aq) + 2\text{CO}_2(g) = 2\text{FeCO}_3(sld) + \text{Al}_2\text{Si}_3\text{O}_{10}\text{(OH)}_4(kaol)$$

(2)

where kaolinite is inferred to have been part of the pre-metamorphic mineral assemblage (Retallack and Krinsley, 1993; Rye and Holland, 2000a,b). Calculated $p\text{CO}_2$ levels are higher than for the recalculated SIS paleobarometer of Rye et al. (1995), and close to present day values (Fig. 1). Furthermore, the berthierine at Waterval Onder is not a pure end member, thus it would have an activity of less than one, further lowering the calculated $p\text{CO}_2$ level. The choice of Al-mineral is relatively unimportant as calculations based on gibbsite instead of kaolinite (not shown) also result in $p\text{CO}_2$ values below present day conditions.

Equilibrium modeling using greenalite or berthierine SIS paleobarometers suggests one of two conclusions, either Precambrian $p\text{CO}_2$ levels were comparable to present atmospheric values, or the whole approach is unreliable. Given the “faint young Sun” paradox (Kasting, 1993), such low levels are difficult to reconcile with the need for a much stronger than present Precambrian greenhouse. Furthermore, by simplifying atmospheric composition down to a single chemical reaction there is a risk of over-interpreting the absence of evidence of a single mineral phase, in this case siderite.

4. Other equilibrium models

In addition to the widely cited approach of Rye et al. (1995), two other recent studies have attempted to estimate atmospheric $p\text{CO}_2$ using equilibrium relationships and the Rye et al. (1995) study as a “jumping off point”. Ohmoto et al. (2004) inverted the logic of Rye et al. (1995) and proposed that massive siderite beds in BIFs prior to $\sim$1.8 Ga imply that atmospheric $p\text{CO}_2$ must have greatly exceeded 100 PAL. They further suggest that atmospheric $p\text{CO}_2$ may have been high enough that no additional greenhouse gas was necessary because the inhibition on siderite formation was elevated $p\text{O}_2$ values in the atmosphere and soil rather than insufficient $p\text{CO}_2$ (Ohmoto et al., 2004). There are a few problems with both the approach and the conclusions. First, Ohmoto et al. (2004) assert that siderite stability requires $p\text{O}_2 = 10^{-6.13}$, a value well below any existing estimate for the Precambrian, but as Sleep (2004) correctly points out, even at the naturally maintained $p\text{O}_2$ minima ($p\text{O}_2 = 10^{-17}$) reaction kinetics dictate that oxidation processes are unlikely to inhibit siderite formation. Furthermore, even at the present day $p\text{O}_2$ value of 0.21, siderite formation in near-modern soils is not restricted (e.g., Achyuthan, 2003) to poorly aerated settings as Ohmoto et al. (2004) asserted. Thus, even if $p\text{O}_2$ levels were higher than most researchers believe (Ohmoto et al., 2004 believe), siderite should form at the Earth’s surface if $p\text{CO}_2$ is significantly elevated. Second, BIFs can only provide weak guidance for Earth surface (and hence atmospheric) conditions because they form in at least moderately deep water (i.e., below storm wave base) and should have enhanced $p\text{CO}_2$ relative to the surface as a result of the decomposition of organic matter (Kasting, 2004).

A second thermodynamic approach set a lower limit for atmospheric $p\text{CO}_2$ by considering equilibrium relationships for rinds on sub-aerially deposited pebbles from the 3.2 Ga Moody Conglomerate (Hessler et al., 2004). Hessler et al. (2004) considered three possible equilibrium relationships that might apply to the formation of the carbonate rinds, which, in contrast to the other SIS paleobarometers, involve no iron silicate rather than no siderite. Their calculated minimum $p\text{CO}_2$ of $2.51 \times 10^{-3}$ bar (or 0.8 PAL) requires an unusual geologic setting in which iron silicates are very unstable at the Earth’s surface, whereas if iron silicates were stable the estimated $p\text{CO}_2$ minimum is significantly higher, though still insufficient to account for the “faint young Sun”. Without more investigation into Archean weathering conditions it is not clear which of their two scenarios is most likely. It is also unclear how common siderite coated pebbles (sans iron silicates) are in the geologic record, and thus how often they may provide a $p\text{CO}_2$ constraint. However, where appropriate, the Hessler et al. (2004) thermodynamic model appears to provide a useful constraint. Thermodynamic models in general oversimplify the problem of estimating Precambrian $p\text{CO}_2$ levels, and with slightly different starting assumptions (e.g., SIS paleobarometers of Rye et al. (1995), Ohmoto et al. (2004), and this paper) or thermodynamic data (e.g., this paper), vastly different conclusions may be drawn. Extreme caution is thus advocated in their application, because even the mostly widely cited one (Rye et al., 1995) has a number of fundamental flaws, and other approaches (Hessler et al., 2004) may have only limited use if they apply to relatively rare sedimentary occurrences.

5. An alternative approach using mass balance

One common method of assessing gains and losses of different elements in soils and paleosols is through
constitutive mass balance (e.g., Brimhall and Dietrich, 1987; Chadwick et al., 1990; Brimhall et al., 1991). Mass balance can be reduced to two concepts, strain (ε) of an “immobile” element and transport (τ) of a second element with respect to the immobile element. The open system mass-transport function for element j in the weathered sample (w) is defined as follows:

\[ \tau_{j,w} = \left( \frac{\rho_j C_{j,w}}{\rho_j C_{j,p}} \right) [\varepsilon_{i,w} + 1] - 1. \]  

(3)

where \( \rho_j \) is the density of the weathered material, \( C_j \) the chemical concentration (weight percentage) of element j in the weathered material, \( \rho_p \) the density of the parent material, and \( C_{j,p} \) is the chemical concentration (weight percentage) of element j in the parent material. If \( \varepsilon_{i,w} = 0 \) (i.e., element j was immobile), then \( \tau_{j,w} \) can be solved for as follows:

\[ \varepsilon_{i,w} = \left( \frac{\rho_j C_{j,p}}{\rho_j C_{j,w}} \right) - 1. \]  

(4)

where \( \varepsilon_{i,w} \) is the strain on immobile element i in the weathered sample.

During silicate weathering, total CO2 consumption can be approximated by the following reactions:

\[ \text{MgO + 2CO}_2 + \text{H}_2\text{O} \rightarrow \text{Mg}^{2+} + 2\text{HCO}_3^- \]  

(5)

\[ \text{CaO + 2CO}_2 + \text{H}_2\text{O} \rightarrow \text{Ca}^{2+} + 2\text{HCO}_3^- \]  

(6)

\[ \text{Na}_2\text{O} + 2\text{CO}_2 + \text{H}_2\text{O} \rightarrow 2\text{Na}^+ + 2\text{HCO}_3^- \]  

(7)

\[ \text{K}_2\text{O} + 2\text{CO}_2 + \text{H}_2\text{O} \rightarrow 2\text{K}^+ + 2\text{HCO}_3^- \]  

(8)

where for example, each mole of base cation (e.g., Mg(OH)2) liberated requires two moles of CO2 (e.g., Holland and Zbinden, 1988). Although other elements are weathered, the parent rock concentration of the bases in reactions 5–8 are at least 1–2 orders of magnitude larger than any other mobile element. Because K may be remobilized metasomatically and accumulated in paleosols after burial (e.g., Palmer et al., 1989), it has to be dealt with differently than Ca, Mg, and Na (see below).

Mass transfer values (Eq. (3)) for individual cations can be transformed into mass fluxes as follows:

\[ m_{j,\text{flux}}(\text{g/cm}^2) = \rho_j C_{j,P} \int_{Z=0}^{Z=Z_{i,s}} \tau_{j,w}(Z) dZ \]  

(9)

where Z is the depth in the soil profile and \( Z_{i,s} \) is the total depth of the profile (e.g., Chadwick et al., 1990). Because many Precambrian paleosols have been deeply buried and compacted (e.g., Retallack, 1986; Holland and Zbinden, 1988), it is necessary to decompact the profiles to their original thickness rather than using their present thickness. Sheldon and Retallack (2001) derived the following equation for calculating the compaction (C) of soils and paleosols due to burial:

\[ C = \frac{-S_i}{\left( \frac{\rho_i}{\rho_m} \right) - 1}. \]  

(10)

where \( S_i \) is initial solidity, \( F_1 \) initial porosity, D the depth of burial in km, and k is an empirically derived constant. Each of the variables has been determined for different soil orders, and using the constants for a Vertisol (Retallack, 1986; Retallack and Krinsley, 1993) the calculated compaction of the ∼2.2 Ga old Watervalloord paleosol was 72% of the profile’s original thickness, while direct measurement of folded veins gave 67–73% compaction (Sheldon and Retallack, 2001), suggesting that Eq. (10) gives suitable estimates for the compaction of even deeply buried Precambrian paleosols.

After the compaction-corrected mass fluxes are calculated for each individual base cation and converted to moles, the total flux of CO2 required for the observed weathering (M) is given by

\[ M(\text{mol CO}_2/\text{cm}^2\text{ year}) = 2 \sum m_{j,\text{flux}}. \]  

(11)

Soils do not form instantaneously, so to calculate a true flux, M must be divided by time (T). The time-averaged flux (M/T) is a product of two distinct sources of CO2: CO2 in the atmosphere being added by rainfall to the soils (Xrain), and CO2 added by direct diffusion into the soils (Xdiff). Holland and Zbinden (1988) quantified Xrain and Xdiff as follows:

\[ \frac{M}{T}(\text{mol/ cm}^2\text{ year}) = X_{\text{rain}} + X_{\text{diff}} = \rho \text{CO}_2 \left[ \frac{K \text{CO}_2}{10^5} + \left( \frac{D \text{CO}_2}{L} \right) \right] \]  

(12)

where \( \rho \text{CO}_2 \) is the partial pressure of atmospheric CO2 (atm), \( K \text{CO}_2 \) the Henry’s Law constant for CO2 (discussed below), \( r \) rainfall rate (cm/year), \( D \text{CO}_2 \) the diffusion constant for CO2 in air (0.162 cm²/s; CRC Handbook, 1995), \( a \) the ratio of diffusion constant for CO2 in soil divided by the diffusion constant for CO2 in air (discussed below), \( L \) the depth to the water table, and \( k \) is a constant which is the ratio of seconds in a year divided by the number of cm² per mole of gas at standard temperature and pressure (1.43 × 10¹⁰ s cm⁻³ mol⁻¹). Implicit in Eq. (12) is the assumption that the partial pressure of atmospheric CO2 is much larger than the partial pressure of CO2 at the water table (depth = L) and that the CO2 diffusion constant and gradient are constant with depth. There also is no explicit term including any CO2 processes involving a terrestrial biosphere (i.e., it is assumed to...
play a negligible role), a point that will be discussed further below. Eq. (12) can be rearranged to solve for atmospheric $p_{\text{CO}_2}$ as follows:

$$ M = \frac{p_{\text{CO}_2}}{10^5 \left( \frac{\text{K}_2\text{O}}{10^4} + \frac{\text{Na}_2\text{O}}{10^3} \right)} $$

Thus, by quantifying $M$ using direct measurements of paleosol mass balance and estimating $T$ and $L$, it is possible to calculate the partial pressure of atmospheric $\text{CO}_2$ at the time the paleosols formed. One substantial advantage of this approach over the thermodynamic approaches discussed above is that it is not redox sensitive (i.e., atmospheric $p_{\text{O}_2}$ does not matter), removing one of the primary sources of uncertainty in all of the SIS paleobarometers.

### 6. $p_{\text{CO}_2}$ levels 2.2 Ga ago

To test this approach, atmospheric $p_{\text{CO}_2}$ values have been calculated for a variety of model conditions using data for the Hekpoort paleosol from Rye and Holland (2000a), who analyzed three separate cores through the paleosol. Though these “profiles” are time equivalents to the widely studied Waterfall Onder profile (e.g., Retallack, 1986; Retallack and Krinsley, 1993; Rye and Holland, 2000a; Beukes et al., 2002), the completeness of that profile has recently been questioned (Beukes et al., 2002), so it has not been used here. Using the data of Rye and Holland (2000a) also allows the robustness of the method to be examined since results from three separate profiles of the same paleosol can be compared. Basalt-parented paleosols are ideal for this type of calculation because the depth of the water table is essentially the thickness of the soil given the relative porosity of basalt as compared to most soils.

A comprehensive discussion of the sources of uncertainty in this model can be found in the Data repository, but a summary of the sensitivity of the various parameters can be given as follows (Table 1): (1) changing the Henry’s Law constant over a range of values from 0.031 to 0.045 mol atm$^{-1}$ results in a difference between the highest and lowest $p_{\text{CO}_2}$ values of less than 5%; (2) changing $\alpha$ by ±20% results in $p_{\text{CO}_2}$ variations of ±15%; the estimate of 0.1 from Holland and Zbinden (1988) is used as the “best guess”; (3) including the weathering of $K_2O$ by assuming that it would have the same $T_{\text{geo}}$ values as $Na_2O$, which behaves chemically in a fairly similar manner, the calculated $p_{\text{CO}_2}$ varies by less than 5%; but this parameter has been included for completeness; (4) over the range of semi-arid to sub-tropical mean annual precipitations (50–150 cm/year), the resulting $p_{\text{CO}_2}$ variation is less than 15%, so the present day global mean annual precipitation of ~100 cm/year (Holland and Zbinden, 1988) is used because it is difficult to assess how that value may have varied in the Precambrian.

<table>
<thead>
<tr>
<th>Parameters and sensitivities</th>
<th>Parameter</th>
<th>Range</th>
<th>Resulting $p_{\text{CO}_2}$ variation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_{\text{CO}_2}$</td>
<td>0.031–0.045 (0.034)</td>
<td>5+</td>
<td></td>
</tr>
<tr>
<td>$\alpha$</td>
<td>0.06–0.12 (0.1)</td>
<td>~15</td>
<td></td>
</tr>
<tr>
<td>Include $K_2O$</td>
<td>n.a</td>
<td>5+</td>
<td></td>
</tr>
<tr>
<td>$r$</td>
<td>50–150 (100)</td>
<td>15+</td>
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</tr>
</tbody>
</table>

The parenthetical value is the one used calculations discussed in the text. The other constant values used was $K_{\text{CO}_2} = 0.162$ (CRC Handbook, 1995); $L$ was variable between paleosols and based on the decompacted depth of the profile (BB3 = 1186 cm, BB8 = 1168 cm, BB14 = 819 cm).

The largest difference in the calculated $p_{\text{CO}_2}$ values results from lengthening the formation time from 10,000 to 50,000 years, a range of typical values for thick soils forming on basalt (Sheldon, 2003). Because of the age of the Hekpoort paleosols, it is not possible to distinguish the age of the overlying basalt flow from the flow that underlies the paleosols, so the formation time could have been significantly longer than the range of values examined here (which would decrease calculated $p_{\text{CO}_2}$ values). Data repository figure DR-1. Based on near-modern analogues and the thickness of the profiles (Sheldon, 2003), 50,000±5,000 years is the best guess for the formation time of the Hekpoort paleosols.

Using the “best guess” values for each of the parameters, the resulting $p_{\text{CO}_2}$ values vary between 18 and 31 times present levels (PAL) for the three Hekpoort paleosols. As discussed above, the largest source of uncertainty is formation time of the paleosols, which was probably within a factor of two of the “best guess”. Following Holland and Zbinden, and to be conservative, if the other lesser sources of uncertainty add half again as much uncertainty, $p_{\text{CO}_2}$ 2.2 Ga ago is estimated to have been at least 23±2 PAL. This value is significantly lower than upper limit of 100PAL calculated by Rye et al. (1995), but higher than revised estimates from SIS paleobarometers, and also would be insufficient to account for the reduced insolation of the “faint young Sun” (Kasting, 1993). The likely solution to this $\text{CO}_2$ “greenhouse deficit” is that another greenhouse gas must have been present at higher levels than at present. The best candidate is $\text{CH}_4$ (Pavlov et al., 2000, 2003), a trace gas in the present atmosphere that is a >20 times more

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effective greenhouse gas than CO₂, though this ratio may have been different in a low-O₂ Precambrian atmosphere. Nonetheless, mass balance calculations using paleosols also indicate that atmospheric CO₂ levels were high and that calculations assuming CO₂ levels for the Precambrian just a few times pre-industrial levels (e.g., Pavlov et al., 2000) may overestimate CH₄ levels somewhat.

A final consideration is what role, if any, an emergent biosphere may have played in modulating soil CO₂ levels. The calculations described herein assume that there was no terrestrial biosphere or that it played a negligible role. However, modern soils may have soil pCO₂ values up to 100 times the atmospheric pCO₂ level (Brook et al., 1983) due to in situ production of CO₂ and slow diffusion. Theoretical calculations indicate that even a much smaller biosphere than at present, given the correct soil substrate, could induce modern levels of weathering (Keller and Wood, 1993). Thus, the key question is whether there was a significant terrestrial biosphere to speak of. The answer at present is equivocal.

There is some evidence for Precambrian soil methanogenesis/methanotrophy (Watanabe et al., 2000; Rye and Holland, 2000b), but it is not clear yet if these phenomena were widespread or confined to local niches. Brady et al. (1999) found that basalt weathering intensity is 2–18 times greater under lichens than in abiotic experiments, although confined to a very shallow depth (mm-scale).

Using this somewhat inexact analogue for a Precambrian biosphere as a guide suggests that while there may have been some in situ enhancement of soil CO₂ levels relative to the atmosphere, it was likely only to a shallow depth, and perhaps only a locally important process.

Without additional insight into the Precambrian terrestrial biosphere it is not possible to quantify what part of the calculated atmospheric CO₂ levels were due to biotic enhancement, but given the other sources of uncertainty in the calculations it is unlikely that the results would be fundamentally different.

7. Toward a Precambrian CO₂ curve

A further test of this approach is to analyze other Precambrian paleosols both to see if the values obtained are consistent with one another and also with independent geological evidence. Using data from the Ville Marie (2.5 Ga; Panahi et al., 2000), Drakenstein (2.0 Ga; Wiggering and Beukes, 1990), Flin Flon (1.8 Ga; Holland et al., 1989), Sturgeon Falls (1.1 Ga; Zbinden et al., 1988), and Sheigra (0.98 Ga; Retallack and Mindszenty, 1994) paleosols, a pCO₂ curve for 2.5–1.0 Ga ago can be generated (Fig. 2). Two conclusions can be drawn: (1) atmospheric pCO₂ was fairly constant and elevated from 2.5 to 1.8 Ga ago; (2) at some time between 1.8 and 1.1 Ga ago atmospheric pCO₂ dropped significantly. Without additional data, it is not possible to constrain when this occurred, but this downturn was subsequently reversed at some time in the late Precambrian given that early Paleozoic pCO₂ levels appear to have been comparable to the Paleoproterozoic (Fig. 2; Berner and Kothavala, 2001).

8. Conclusions

Attempts to calculate the Earth’s atmospheric conditions before ∼2.2 Ga ago are fraught with difficulties because the Precambrian rock record is sparse when compared with that of the Phanerozoic. In spite of this, many attempts have been made to estimate the com-
position of the atmosphere because reconstruction of early atmospheric pCO₂ is a crucial component of any discussion of the Earth’s surface temperature history. The “faint young Sun” paradox, and history of life on Earth. Paleosols, which formed in direct contact with atmosphere, have been used in concert with a simple siderite–greenalite thermodynamic model to suggest that atmospheric pCO₂ levels have always been below 60–100 times the present atmosphere (Rye et al., 1995). In addition to theoretical problems with that model, recalculation of pCO₂ levels using revised thermodynamic data gives unrealistically low atmospheric pCO₂. Furthermore, it is almost certainly an oversimplification to calculate atmospheric pCO₂ on the basis of a single equilibrium expression. A new model based upon mass balance gives pCO₂ levels that can be constrained to be at least 23^±3 times present atmospheric levels for 2.2 Ga ago. These pCO₂ levels are still insufficient to make up for a “faint young Sun” (Fig. 2), suggesting that some other greenhouse gas such as methane was present and provided enough additional greenhouse forcing to maintain equable conditions at the Earth’s surface throughout its history. Atmospheric pCO₂ levels appear to have varied little from 2.5 to 1.8 Ga ago, staying above 20 times present levels. At some time between 1.8 and 1.0 Ga ago, pCO₂ dropped down to much lower levels, but the timing and rate of this change cannot be constrained by existing data.

Acknowledgments

Thanks are owed Mark Reed for numerous discussions of this manuscript, and Rob Rye for discussing the Bank Break cores at an early stage of this project. An earlier version of this manuscript benefited from comments by Dick Holland and an anonymous reviewer, and this version benefited from three thoughtful anonymous reviews.

Appendix A. Supplementary data
Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.precamres.2006.02.004.

References
