5.18

Soils and Global Change in the Carbon Cycle over Geological Time

G. J. Retallack

University of Oregon, Eugene, OR, USA

5.18.1 INTRODUCTION

Soils play an important role in the carbon cycle as the nutrition of photosynthesized biomass. Nitrogen fixed by microbes from air is a limiting nutrient for ecosystems within the first flush of ecological succession of new ground, and sulfur can limit some components of wetland ecosystems. But in the long term, the limiting soil nutrient is phosphorus extracted by weathering from minerals such as apatite (Vitousek *et al.*, 1997a; Chadwick *et al.*, 1999). Life has an especially voracious appetite for common alkali (Na^+ and K^+) and alkaline-earth (Ca^{2+} and Mg^{2+}) cations, supplied by hydrolytic weathering, which is in turn amplified by biological acidification (Schwartz-mann and Volk, 1991; see Chapter 5.06). These mineral nutrients fuel photosynthetic fixation and chemical reduction of atmospheric CO_2 into plants and plantlike microbes, which are at the base of the food chain. Plants and photosynthetic microbes are consumed and oxidized by animals, fungi, and other respiring microbes, which release CO_2, methane, and water vapor into the air. These greenhouse gases absorb solar radiation more effectively than atmospheric oxygen and nitrogen, and are important regulators of planetary temperature and albedo (Kasting, 1992). Variations in solar insolation (Kasting, 1992), mountainous topography (Raymo and Ruddiman, 1992),

and ocean currents (Ramstein *et al.*, 1997) also play a role in climate, but this review focuses on the carbon cycle. The carbon cycle is discussed in detail in Volume 8 of this treatise.

The greenhouse model for global paleoclimate has proven remarkably robust (Retallack, 2002), despite new challenges (Veizer *et al.*, 2000). The balance of producers and consumers is one of a number of controls on atmospheric greenhouse gas balance, because CO_2 is added to the air from fumaroles, volcanic eruptions, and other forms of mantle degassing (Holland, 1984). Carbon dioxide is also consumed by burial as carbonate and organic matter within limestones and other sedimentary rocks; organic matter burial is an important long-term control on CO_2 levels in the atmosphere (Berner and Kothavala, 2001). The magnitudes of carbon pools and fluxes involved provide a perspective on the importance of soils compared with other carbon reservoirs (Figure 1).

Before industrialization, there was only 600 Gt (1 Gt $= 10^{15}$ g) of carbon in CO_2 and methane in the atmosphere, which is about the same amount as in all terrestrial biomass, but less than half of the reservoir of soil organic carbon. The ocean contained only $\sim$3 Gt of biomass carbon. The deep ocean and sediments comprised the largest reservoir of bicarbonate and organic matter, but that carbon has been kept out of circulation from the atmosphere for geologically significant periods of time (Schidlowski and Aharon, 1992). Humans have

tapped underground reservoirs of fossil fuels, and our other perturbations of the carbon cycle have also been significant (Vitousek *et al.*, 1997b; see Chapter 8.10).

Atmospheric increase of carbon in CO_2 to 750 Gt C by deforestation and fossil fuel burning has driven ongoing global warming, but is not quite balanced by changes in the other carbon reservoirs, leading to a search for a "missing sink" of some 1.8 ± 1.3 Gt C, probably in terrestrial organisms, soils, and sediments of the northern hemisphere (Keeling *et al.*, 1982; Siegenthaler and Sarmiento, 1993; Stallard, 1998). Soil organic matter is a big, rapidly cycling reservoir, likely to include much of this missing sink.

During the geological past, the sizes of, and fluxes between, these reservoirs have varied enormously as the world has alternated between greenhouse times of high carbon content of the atmosphere, and icehouse times of low carbon content of the atmosphere. Oscillations in the atmospheric content of greenhouse gases can be measured, estimated, or modeled on all timescales from annual to eonal (Figure 2). The actively cycling surficial carbon reservoirs are biomass, surface oceans, air, and soils, so it is no surprise that the fossil record of life on Earth shows strong linkage to global climate change (Berner, 1997; Algeo and Scheckler, 1998; Retallack, 2000a). There is an additional line of evidence for past climatic and atmospheric history in the form of fossil soils, or paleosols, now known
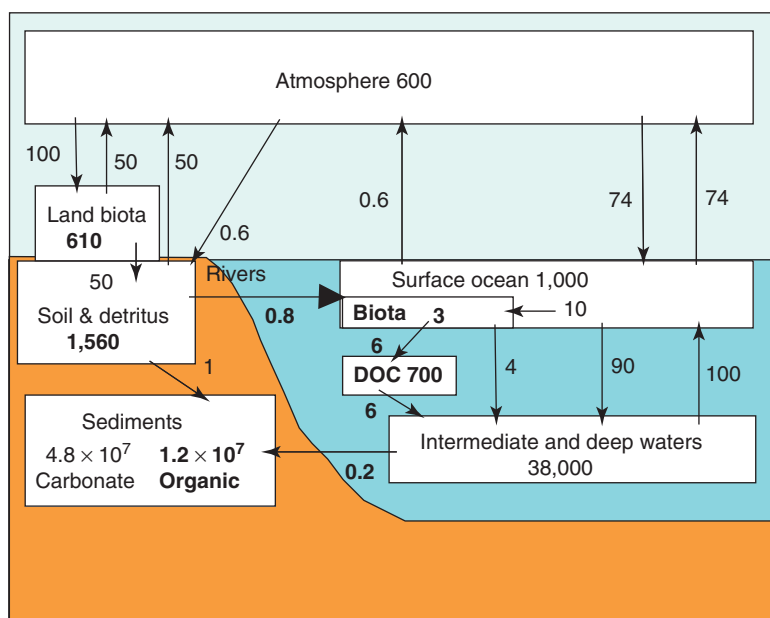

Figure 1 Pools and fluxes of reduced carbon (bold) and oxidized carbon (regular) in Gt in the preindustrial carbon cycle. Sources: Schidlowski and Aharon (1992), Siegenthaler and Sarmiento (1993), and Stallard (1998).
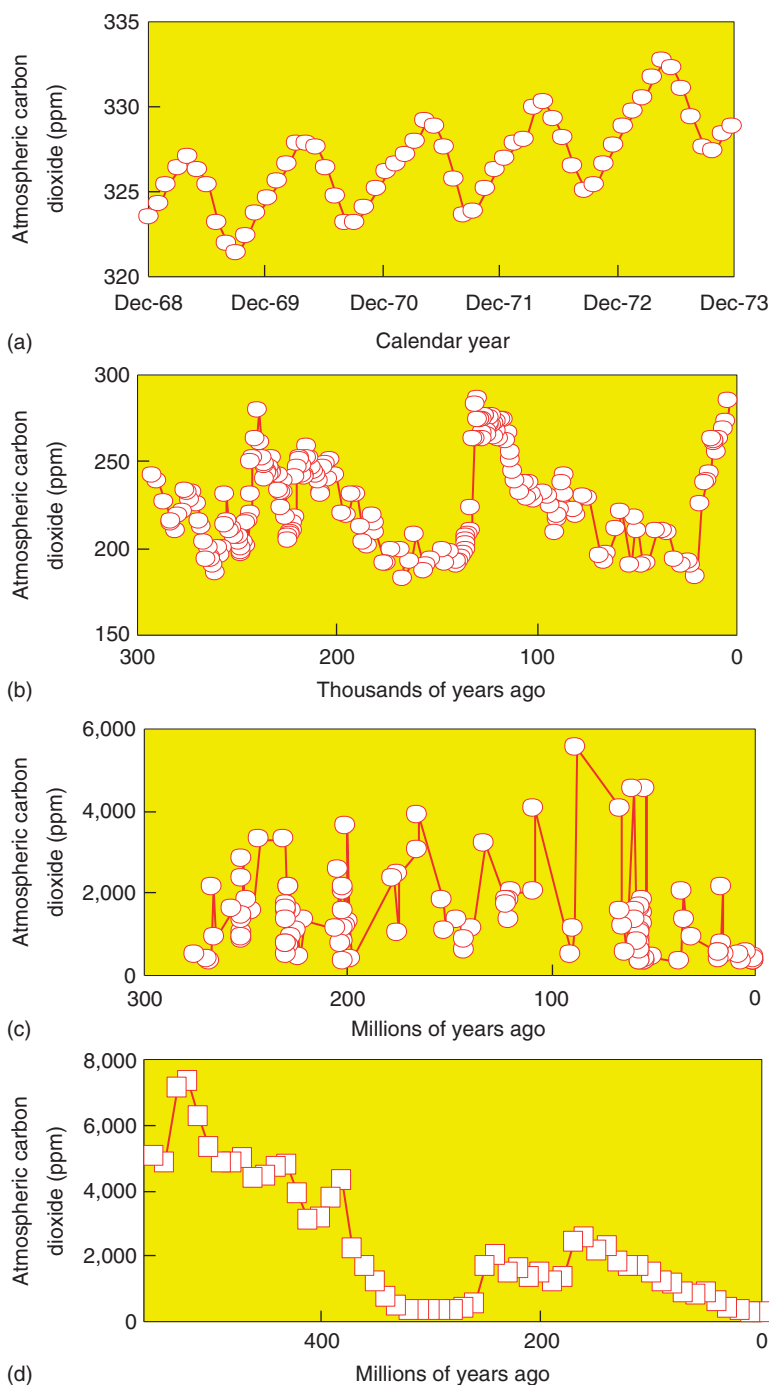
Figure 2 Variation in atmospheric CO$_2$ composition on a variety of timescales ranging from annual to eonal (a) Reproduced from Keeling *et al.* (1982). (b) Reproduced by permission of Nature Publishing Group from Petit *et al.* (1999). (c) Reproduced from Retallack (2001d). (d) Reproduced by permission of American Journal of Science from Berner and Kothavala (2001).

to be abundant throughout the geological record (Retallack, 1997a, 2001a). This chapter addresses evidence from fossil soils for global climate change in the past, and attempts to assess the role of soils in carbon cycle fluctuations through the long history of our planet.

5.18.2 APPROACHES TO THE STUDY OF PALEOSOLS

Many approaches to the study of paleosols are unlike those of soil science, and more like soil geochemistry prior to the earlier part of the

twentieth century (Thaer, 1857; Marbut, 1935). Such measures of soil fertility as cation-exchange capacity and base saturation that are used for characterizing surface soils (Buol et al., 1997) are inappropriate for the study of paleosols because of profound modification of the cation-exchange complex during burial and lithification of paleosols (Retallack, 1991). Many paleosols are now lithified and amenable to study using petrographic thin sections, X-ray diffraction, electron microprobe, and bulk chemical analysis (Holland, 1984; Ohmoto, 1996; Retallack, 1997a).

5.18.2.1 Molecular Weathering Ratios

Soil formation (see Chapter 5.01) is not only a biological and physical alteration of rocks, but a slow chemical transformation following a few kinds of reactions that seldom reach chemical equilibrium. In many soils, the most important of these reactions is hydrolysis: the incongruent dissolution of minerals such as feldspars to yield clays and alkali and alkaline-earth cations in solution. A useful proxy for the progress of this reaction in soils and paleosols is the molar ratio of alumina (representing clay) over the sum of lime, magnesia, soda, and potash (representing major cationic nutrients lost into soil solution). A large database of North American soils (Sheldon et al., 2002) has shown that this ratio is usually less than 2 for fertile soils (Alfisols and Mollisols of Soil Survey Staff, 1999), but more than 2 in less-fertile soils (Ultisols). In soils that have been deeply weathered in humid tropical regions for geologically significant periods of time (Oxisols of Soil Survey Staff, 1999), the molar ratio of alumina over bases can reach 100 or more, indicating that the slow progress of hydrolysis has almost gone to completion.

Application of this approach to a Precambrian (1,000 Ma) paleosol from Scotland (Figure 3) showed the expected decrease of hydrolytic weathering down from the surface, and an overall degree of hydrolytic alteration that is modest compared with deeply weathered modern soils (Figure 4). Effects of hydrolysis of this Precambrian paleosol can also be seen in petrographic thin sections and electron microprobe analyses, which document conversion of feldspar into clay (Retallack and Mindszenty, 1994).

Other molar weathering ratios can be devised to reflect leaching (Ba/Sr), oxidation (FeO/Fe_2O_3), calcification ($CaO + MgO/Al_2O_3$), and salinization (Na_2O/K_2O). Two of these ratios reflect differential solubility of chemically comparable elements, but the calcification ratio quantifies the accumulation of pedogenic calcite and dolomite, and the ratio of iron of different valence gives reactant and product of iron oxidation reactions. In the Precambrian paleosol illustrated (Figure 4), these molar ratios indicate that the profile was oxidized and well drained, but little leached, calcified, or salinized. Advantages of using molar weathering ratios are their simplicity and precision, free of assumptions concerning parent material composition and changes in volume during weathering and burial compaction. Smooth depth functions of molar weathering ratios

Figure 3 Sheigra paleosol (bleached and reduced zone ~1 m thick to right) under Torridonian (1,000 Ma) alluvial fan deposits, and Staca paleosol at same unfonconformity but on amphibolite (left-hand side) near the hamlet of Sheigra, northwest Scotland. Photo courtesy of G. E. Williams; geological age revised by Williams and Schmidt (1997).
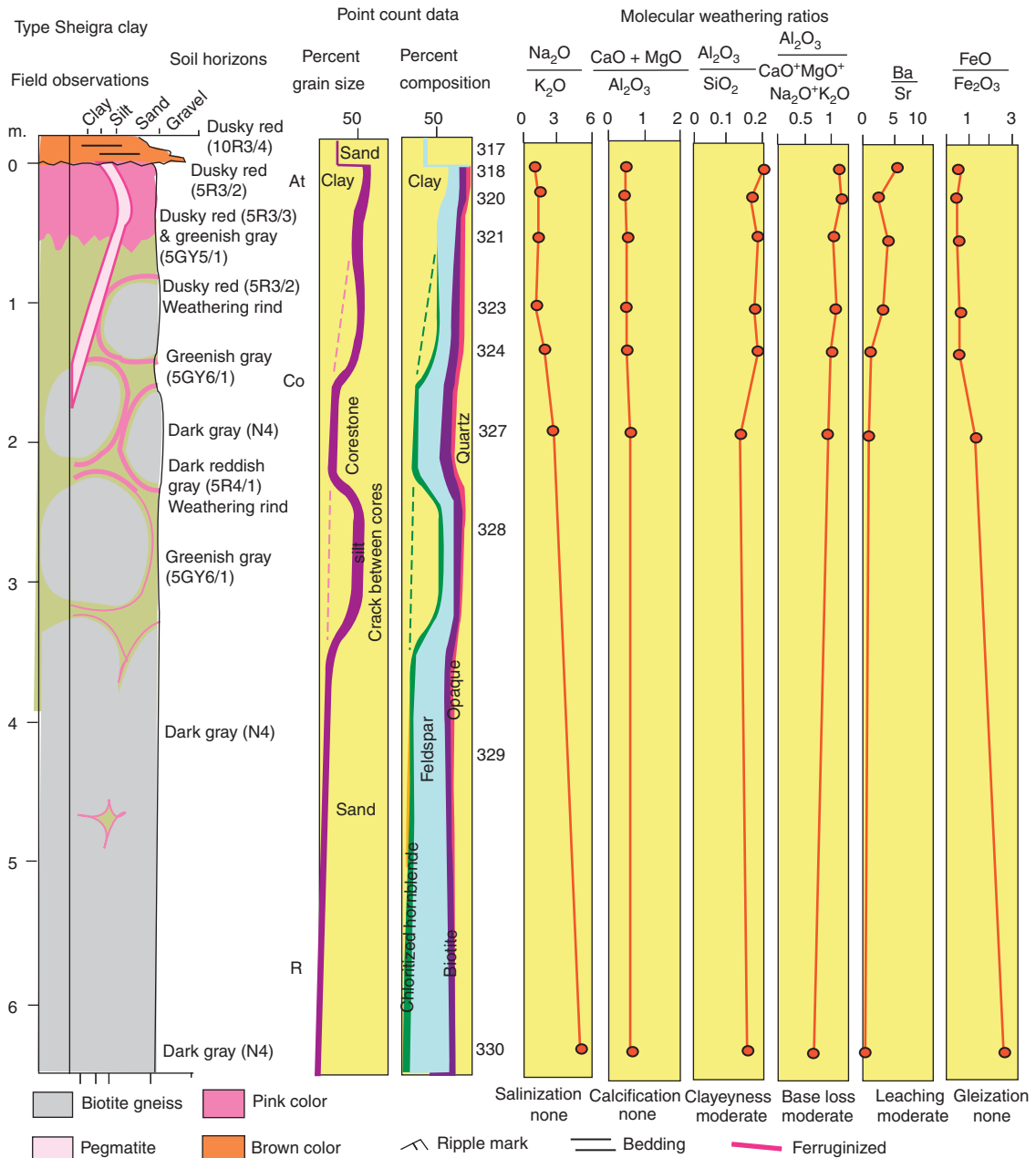
Figure 4 Columnar section (measured in field), petrographic composition (from point counting), and molecular weathering ratios (from major element chemical analyses) of the Sheigra paleosol. Reproduced by permission of Society for Sedimentary Geology from Retallack and Mindszenty (1994).

(Figure 4) are characteristic of soils and paleosols, whereas parent material heterogeneity is revealed by erratic swings in weathering ratios. Whole-rock chemical analyses are commonly used to calculate molar weathering ratios, and thus conflate weathered parts of the soil with unweathered interiors of soil grains. This problem can be circumvented by calculating molar weathering ratios from electron microprobe spot analyses of weathered and unweathered grains within paleosol samples, which can illustrate reaction paths (Bestland and Retallack, 1993).

5.18.2.2 Strain and Mass-Transfer Analysis

A full accounting of volume and chemical changes during weathering and burial can be made by assuming that one component of a paleosol has remained stable from the parent material. This method requires measurement

of bulk density and identification of a parent material. Alumina, titania, and zirconium are commonly used as stable constituents, with zirconium favored because its mobility can be checked by microscopic examination of pitting of grains of zircon, which is the main soil mineral containing zirconium (Brimhall *et al.*, 1991). The assumption of geochemical stability allows one to calculate volume losses or gains (i.e., strain) of samples from a parent composition and material losses or gains (i.e., mass transfer) of individual chemical elements from a soil or paleosol (see Chapter 5.01). This formulation of strain is especially useful for paleosols, because some component of strain is due to burial compaction, which can be expressed visually (Figure 5).

The Precambrian paleosol illustrated as an example of this approach shows moderate weathering and volume loss with weathering and burial compaction. Most elements were lost from the profile, except potassium, and in one (but not another adjacent) paleosol, iron (Figure 5). This represents a thorough geochemical accounting of changes relative to zirconium during soil development and burial of this paleosol, but is not at variance with the simpler molar weathering ratio approach,

which includes a partial normalization to alumina.

Limitations on calculating strain and mass transfer come mainly from the identification and characterization of the parent material of soils and paleosols. The actual materials from which they weathered no longer exist (Jenny, 1941). The nature of parent materials can be reconstructed by studying the rock or sediment lower within soil or paleosol profiles. Parent material reconstruction can be checked chemically and petrographically for degree of weathering in igneous or metamorphic rocks below a soil (Figures 3 and 4), but is not so easily assessed in sediments or colluvium below a soil. It is difficult to rule out soil formation from a thin sedimentary or colluvial cap to an igneous rock, although large influxes of new material from wind, floods, or landslide will be revealed by positive strain values.

Kinetic modeling approaches (Merino *et al.*, 1993) can be applied to isovolumetric weathering if conservation of volume is supported by textural evidence (Delvigne, 1998). Computer-aided thermodynamic modeling of ancient weathering has also proven useful, especially for Precambrian paleosols (Schmitt, 1999).
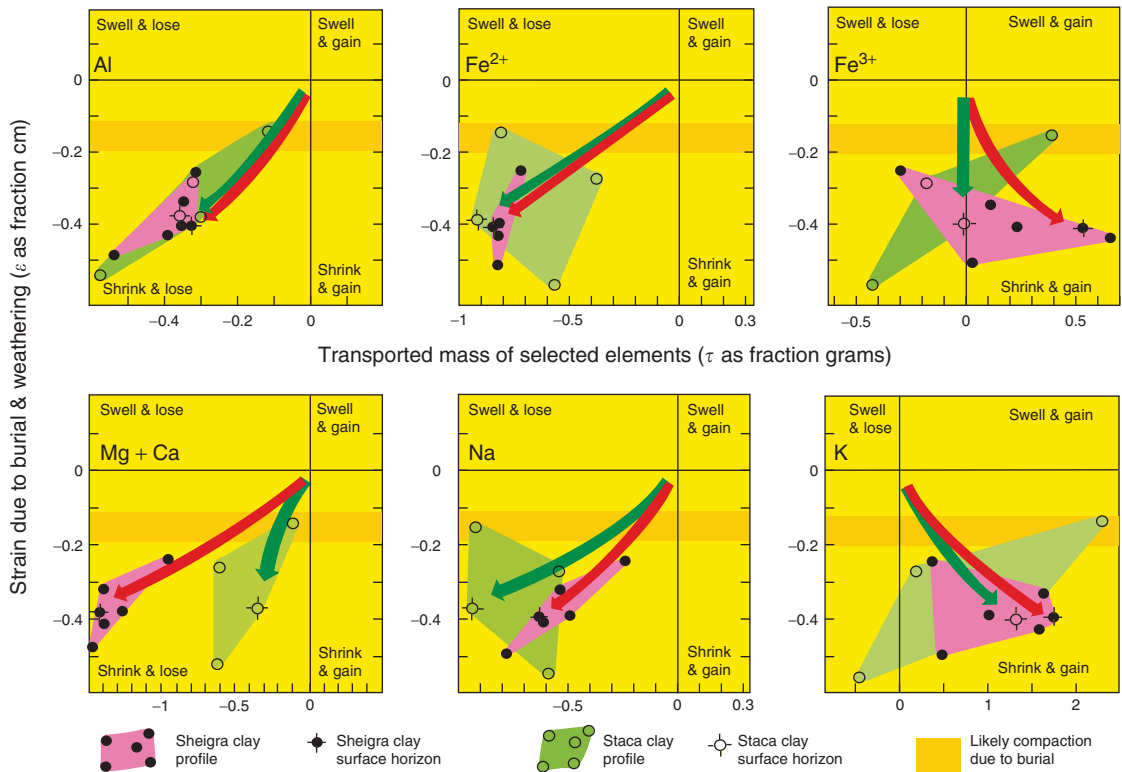

Figure 5 Mass transfer and strain of the Sheigra paleosol. The stippled bars are a range of values for likely strain due to burial compaction, as opposed to pedogenic strain. Reproduced by permission of Society for Sedimentary Geology from Retallack and Mindszenty (1994).

5.18.2.3 Analyses of Stable Isotopes of Carbon and Oxygen

Three isotopes of carbon are commonly assayed by mass spectrometer: the common isotope ^{12}C, the rare isotope ^{13}C, and the radiogenic isotope ^{14}C. Radiocarbon is formed in the atmosphere, incorporated within plants and animals, and then fossilized as a constituent of carbonates and organic carbon. The progressive radioactive decay of radiocarbon is used for isotopic dating, but unfortunately its abundance decreases to undetectable amounts after $\sim 10^5$ years. In contrast, the stable isotopes ^{12}C and ^{13}C are found in rocks and paleosols of all geological ages. Their relative abundance is commonly reported on a scale of per mil that reflects their ratios normalized to a standard, a fossil belemnite from the Peedee formation of North Carolina (PDB), or the mean value of modern ocean water (SMOW). These carbon isotopic values (δ^{13}C) are affected by a variety of physical, chemical, and biological processes. The key photosynthetic enzyme of plants, Rubisco, selects the light isotope (^{12}C) preferentially to the heavy isotope (^{13}C), so that plant organic matter is isotopically much lighter (δ^{13}C more negative) than the atmospheric or oceanic CO_2 from which it was derived.

Some plants employ a photosynthetic pathway creating at first a three-carbon phosphoglyceric acid (C_3 or Calvin–Benson photosynthesis). These plants fractionate isotopes more intensely, and so have more negative δ^{13}C values (−33‰ to −22‰ PDB) than plants that use a photosynthetic pathway creating at first a four-carbon malic and aspartic acid (C_4 or Hatch–Slack photosynthesis:−16‰ to −9‰ PDB). Crassulacean acid metabolism (CAM) is yet another photosynthetic pathway, which creates organic matter of intermediate isotopic composition (−35‰ to −11‰ PDB). Methanogenic microbes are more extreme in their fractionation of the light isotope (δ^{13}C down to −110‰ and typically −60‰ PDB; Jahren *et al.*, 2001). Today most C_4 plants are tropical grasses, and most CAM plants are submerged aquatic plants and desert succulents. Most other kinds of plants use the C_3 photosynthetic pathway. There is the potential to recognize these various metabolic pathways from the isotopic composition of organic carbon in paleosols and fossil plants, and in the fossils of animals that ate the plants (Cerling *et al.*, 1997; MacFadden *et al.*, 1999; Krull and Retallack, 2000).

The isotopic composition of carbon in carbonate in paleosols can also be used as a CO_2 paleobarometer (Cerling, 1991). Under high atmospheric CO_2 levels, isotopically heavy CO_2 intrudes into soil pores, and can be fixed there by the precipitation of pedogenic carbonate. In contrast, under low atmospheric CO_2 levels, CO_2 of soil air is isotopically light, because it is respired with relatively minor isotopic fractionation from isotopically light soil plant material, and may, therefore, generate isotopically light pedogenic carbonate. It is also prudent to measure the isotopic composition of organic carbon in the same paleosol, as a guide to the isotopic composition of CO_2 in the ancient atmosphere, because this can vary substantially (Mora *et al.*, 1996; Jahren *et al.*, 2001). A Phanerozoic atmospheric CO_2 curve constructed from a compilation of such data (Ekart *et al.*, 1999) is consistent with independent evidence of CO_2 levels from the stomatal index of fossil leaves during all but a few episodes of catastrophic methane–clathrate outbursts (Retallack, 2001b, 2002).

The attenuation of atmospheric isotopic values within paleosol profiles can also be used to estimate former soil respiration (Yapp and Poths, 1994), sometimes with surprising results, such as the near-modern soil respiration rates inferred from the dramatic attenuation of isotopic values (δ^{13}C) in a Late Ordovician paleosol (Figure 6). In this case, carbonate occluded within pedogenic goethite was analyzed, rather than pedogenic carbonate itself, because this might have been contaminated by overlying marine rocks.

Oxygen isotopes, ^{16}O and ^{18}O, are usually reported in per mil (δ^{18}O) relative to the same standards used for carbon isotopes (PDB and SMOW). Oxygen isotopes are also fractionated differently by C_3 and C_4 plants because they contribute to the mass of CO_2 taken in for photosynthesis (Farquhar *et al.*, 1993). Oxygen isotopic values are also determined by the composition of water in soil, coming in as rain, and later flowing out as groundwater through buried paleosols (Amundson *et al.*, 1998). Temperature, degree of evaporation, and salinity strongly affect the isotopic composition of oxygen in surface water, and can potentially be inferred from the isotopic composition of oxygen in paleosol carbonates (Mora *et al.*, 1998), paleosol clays (Bird and Chivas, 1993), and fossils in paleosols (Jahren and Sternberg, 2002).

5.18.3 RECORD OF PAST SOIL AND GLOBAL CHANGE

Paleosols have long been recognized in the geological record (Hutton, 1795; Webster, 1826; Buckland, 1837), but their great abundance in terrestrial sedimentary sequences was not
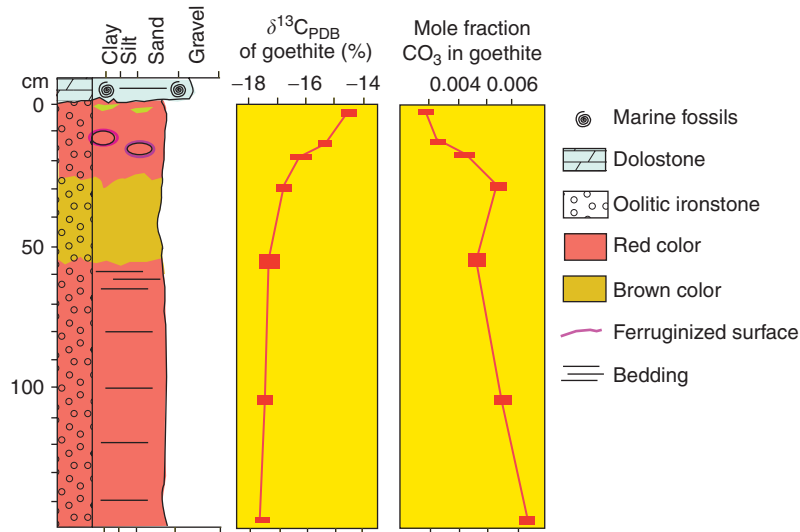
Figure 6 Isotopic composition of carbon in carbonate and mole fraction CO_3 in goethite of a Late Ordovician paleosol from Iron Knob, Wisconsin, showing surprisingly high soil respiration from shallow distance of adjustment of soil to atmospheric values. Reproduced by permission of Paleontological Society from Retallack (2000a).

appreciated until the 1970s (Allen, 1974; Retallack, 1976). Many variegated red beds, such as the Oligocene Big Badlands of South Dakota, are volumetrically dominated by paleosols (Retallack, 1983). Almost all coal seams are paleosols (Histosols), and these are not the only paleosols in thick coal measure sequences (Retallack, 1994a). Thousands of paleosols of all geological ages have been described since the early 1980s, and there is now the prospect of using them to interpret long-term patterns of environmental and biotic change.

5.18.3.1   Origins of Soil

Soil, like love and home, is difficult to define precisely. If one follows some soil scientists in defining soil as a medium of plant growth (Buol *et al.*, 1997), then the formation of soils began either at the Silurian advent of vascular land plants (Gray, 1993), or at the Cambrian advent of nonvascular land plants (Strother, 2000), or at the Late Precambrian advent of eukaryotic soil algae or algal phycobionts of lichens (Retallack, 1994b; Steiner and Reitner, 2001). A geological view of soils, however, would include rocks and soils altered by hydrolytic weathering, which has been well documented at least as far back as the Archean (2,800 Ma; Rye and Holland, 1998). Hydrolytic weathering has also been proposed for rocks as old as 3,500 Ma (Buick *et al.*, 1995), and meteorites as old as 4,566 Ma (Retallack, 2001a). The author prefers to follow the US National

Aeronautical and Space Administration (NASA) in using the widely understood word soil for nonsedimentary modified surfaces of the Moon and the Mars.

Whether there was or is life on Mars remains uncertain (McSween, 1997). There is no discernible life in lunar or martian soils at the time of this writing, but that may change with future human discoveries and colonization of space. If the Moon and the Mars are considered to have soils, then soil formation goes back to the first alterations of planetismal and planetary surfaces which occurred in place, as opposed to those transported to form sediments, which are distinct and antithetic to soil formation. Thus defined, both soils and sediments are very ancient.

Hydrolytic alteration of mafic minerals (pyroxene and olivine) to clays (iron-rich smectite), oxides (magnetite), carbonates (gypsum, calcite), and salts (kieserite) has been documented in carbonaceous chondritic meteorites (Bunch and Chang, 1980; Volume 1 of this treatise). Carbonaceous chondrites also show opaque weathering rinds around mafic grains, crosscutting veins filled with carbonate, clay skins, and distinctive clayey birefringence fabrics (sepic plasmic fabric; Retallack, 2001a). Carbonate veins have been dated radiometrically at no more than 50 Ma younger than enclosing clayey meteorites dated at 4,566 Ma (Birck and Allègre, 1988; Endress *et al.*, 1996). Carbonaceous chondrites are similar to the surface of some asteroids (Veverka *et al.*, 1997). One interpretation of carbonaceous chondrites is as fragments of paleosols from asteroid-sized

planetesimals formed early during the formation of the solar system. As primeval soils of the solar system, they were similar in their smectites, salts, and carbonates to the soils of Mars, which are probably paleosols relict from a time of free water at the martian surface until at least 2,500 Ma (Retallack, 2001a).

A second interpretation of carbonaceous chondrites is as primary condensates of the solar nebula. By this view, their hydrolytic alteration is due to melting in cometary nuclei during close passes with the Sun, or due to transient heating events by shock waves or collisions (McSween, 1999). Other carbonaceous chondrites show metamorphic alteration with minerals similar to those in Earth formed during deep burial under elevated temperatures and pressures (Brearley, 1999). Like soils and paleosols on Earth and Mars, carbonaceous chondrites demonstrate the great antiquity of hydrolytic weathering in dilute acidic solutions, presumably of carbonic acid derived from water vapor and CO_2. These remain the principal gases released from volcanoes, and soils remain important buffers for this environmental acid.

5.18.3.2 Archean–Paleoproterozoic Greenhouse Paleosols

Despite predictions that Precambrian paleosols would be thin, rocky, and dominated by physical weathering (Schumm, 1956), hundreds of Precambrian paleosols now described have been found to be thick, clayey, deeply weathered, and in some cases with possible traces of life, so that chemical and biological weathering can be traced back almost to the beginning of the suitably preserved sedimentary rock record on Earth (Rye and Holland, 2000). The oldest known profile interpreted to be a paleosol shows alteration to depths of 50 m on granites unconformably underlying the 3,500 Ma sedimentary succession of the Warrawoona Group in northwestern Western Australia (Buick et al., 1995). Corundum ores in the 3,500 Ma Aldan Schists of Siberia have been interpreted as metamorphosed, deeply weathered bauxites (Serdyuchenko, 1968).

The Jerico Dam paleosol of South Africa (3,000 Ma; Grandstaff et al., 1986), the Pronto paleosol of Canada (2,450 Ma; Mossman and Farrow, 1992), the Hokkalampi paleosol of Finland (2,200 Ma; Marmo, 1992), a variety of paleosols associated with the Hekpoort Basalt of South Africa (2,100 Ma; Yang and Holland, 2003), and the Sheigra paleosol of Scotland (1,000 Ma; Figures 3 and 4) have been

subjected to exceptionally detailed geochemical and petrographic analyses. Along with many other Precambrian paleosols reviewed by Rye and Holland (1998), these paleosols reveal the antiquity and thoroughness of hydrolytic weathering during the Precambrian. Even then, rock and sediment were under relentless acid attack, which leached base cations (especially Ca^{2+}, Mg^{2+}, and Na^+), and left thick, clayey soil.

It is likely that at least back to 3,500 Ma, the principal environmental acid driving this hydrolytic reaction was carbonic acid dissolved in rain and groundwater (Holland, 1984), as is the case in soils today (Nahon, 1991). Much soil CO_2 may also have come from respiring organisms, which also could have contributed organic acids. Nitric and sulfuric acid may have been locally important in soils developed on particular parent materials, but nitrogen and sulfur salts are so far unreported in Precambrian paleosols, unlike modern soils of mine dumps (Borden, 2001), and hypothesized modern soils on Mars (Bell, 1996; Farquhar et al., 2002) and Venus (Barsukov et al., 1982; Basilevsky et al., 1985).

This view of the likely acids involved in forming Precambrian soils on Earth is supported by the isotopic composition of carbon, nitrogen, and sulfur in sedimentary organic matter, carbonates, sulfates, and sulfides, which are surprisingly similar to their modern counterparts back to 3,500 Ma, and unlike meteoritic or mantle values (Schidlowski et al., 1983; Des Marais, 1997; Canfield and Teske, 1996).

Evidence for life in Precambrian soils comes from isotopic studies of organic carbon within paleosols. Microlaminated chips in the 2,765 Ma Mt. Roe paleosol of Western Australia have extremely depleted carbon isotopic compositions ($\delta^{13}C_{org}$ −40‰). Isotopic fractionation of carbon to this degree is only known in methanogens and methanotrophs (Rye and Holland, 2000). These chips could be fragments of pond scum rather than a true soil microbiota. Organic matter in the 2,560 Ma Schagen paleosols of South Africa is not nearly as depleted (−16‰ to −14‰ $\delta^{13}C_{org}$) as organic matter in overlying marine sediments (−35‰ to −30‰ $\delta^{13}C_{org}$). Interpretation of the carbon in this paleosol as the signature of a hypersaline microbial soil community is compatible with shallow dolocretes and other features of the paleosols (Watanabe et al., 2000).

Normal isotopic values for soil organic matter (−25‰ to −27‰ $\delta^{13}C_{org}$) have been reported from Precambrian paleosols as well (Mossman and Farrow, 1992; Retallack and Mindszenty, 1994). Virtually all Precambrian paleosols have a very low content of organic

carbon comparable with that of well-drained paleosols of the Phanerozoic. If life had been present in the Early Precambrian paleosols, they would have become carbonaceous in the absence of a decomposing microbiota of actinobacteria and of fungi and metazoans during the later Precambrian. Isotopic evidence thus suggests that methanogenic, hypersaline, normal, and decompositional microbes were present in Precambrian paleosols. Other evidence for life in Precambrian paleosols includes microfossils (1,300 Ma; Horodyski and Knauth, 1994), microbial trace fossils (2,200 Ma; Retallack and Krinsley, 1993), chemofossils (2,900 Ma; Prashnowsky and Schidlowski, 1967), plausible megafossils (2,900 Ma; Hallbauer *et al.*, 1977; Retallack, 1994b), and the impressive thickness and soil structure of Precambrian paleosols (3,500 Ma; Retallack, 1986, 2001a; Buick *et al.*, 1995; Gutzmer and Beukes, 1998; Beukes *et al.*, 2002). Life and its byproducts such as polysaccharides may have been soil binders, like molasses applied to a cornfield (Foster, 1981), protecting soils from physical weathering so that biochemical weathering could proceed.

The likely existence of microbial mats at the soil surface considerably complicates the use of paleosols as indicators of ancient atmospheres (Ohmoto, 1996). Tropical rainforest soils now have soil CO_2 levels up to 110 times that of the atmosphere, because of high levels of soil respiration by termites and microbes of an abundant supply of soil organic matter that forms in a living membrane separating the subsoil from the atmosphere (Brook *et al.*, 1983; Colin *et al.*, 1992). Nevertheless, modeling by Pinto and Holland (1988) makes it unlikely that microbial scums of the Precambrian were as productive and effective membranes as rainforests.

The observation that Precambrian paleosols were chemically weathered to an extent comparable with rainforest soils today probably indicates much higher levels of CO_2 in the atmosphere at that time (Holland, 1984). The extent of this greenhouse is poorly constrained, but the apparent lack of siderite in paleosols such as the Hekpoort and Mt. Roe paleosols has been used by Rye *et al.* (1995) to argue that CO_2 concentrations could not have been more than ca. 100 times present levels before the rise of oxygen at ca. 2,100 Ma.

Siderite is common in Phanerozoic wetland paleosols (Ludvigsen *et al.*, 1998) in which respired soil CO_2 exceeded this level. Thus, the estimate of Rye *et al.* (1995) of no more than 100 times present levels of soil CO_2 also is a cap on soil respiration and biological productivity during the Precambrian (Sheldon *et al.*, 2001). The contribution of CH_4 to the atmospheric greenhouse effect was probably also much higher than at present, because it was necessary to maintain planetary temperatures above that of the freezing of water at the time of a faint young Sun (Kasting, 1992; Pavlov *et al.*, 2000).

5.18.3.3 Proterozoic Icehouse Paleosols

The oldest known periglacial paleosols are from the 2,300 to 2,400 Ma Ramsay Lake Formation of Ontario, Canada (Young and Long, 1976; Schmidt and Williams, 1999). They have prominent ice wedges, which are strongly tapering cracks filled originally with ice, but now with massive or horizontally layered sand and claystone breccia. Modern ice wedges form in climates with a mean annual temperature of −4 to −8 °C, coldest month temperatures of −25 to −40 °C, warmest month temperatures of 10–20 °C, and a mean annual precipitation of 50–500 mm (Williams, 1986; Bockheim, 1995). Periglacial paleosols of the Late Precambrian (600–1,000 Ma) in Scotland, Norway, and South Australia include sand wedges (Figure 7), which indicate an even drier and more frigid climate: a mean annual temperature of −12 to −20 °C, a mean cold-month temperature of −35 °C, a mean warm-month temperature of 4 °C, and mean annual precipitation of 100 mm (Williams, 1986). Some of the Late Precambrian glaciations were remarkable in extending to very low latitudes, as indicated by the paleomagnetic inclination of glaciogene sediments, and have been dubbed Snowball Earth events (Kirschvink, 1992; Hoffman *et al.*, 1998; Schmidt and Williams, 1999). Between and before these Precambrian episodes of periglacial paleosols and associated glaciogene sediments there is no evidence of frigid conditions, so that the alternation of global icehouse and greenhouse paleoclimates is ancient indeed.

These climatic fluctuations could be attributed to changes in solar luminosity, volcanic degassing, or ocean current reorganization with continental drift (Barley *et al.*, 1997; Dalziel, 1997), but paleosols reveal that these ice ages were also times of change in the atmosphere and life on land. Highly ferruginized pisolitic lateritic paleosols first appear in the geological record at 2,200–1,920 Ma in South Africa (Gutzmer and Beukes, 1998; Beukes *et al.*, 2002). The lateritic paleosols are part of a complex erosional landscape with a variety of paleosols of significantly different geological ages, including mildly oxidized (Retallack, 1986; Maynard, 1992) and chemically reduced

Figure 7 Near-vertical sandstone wedge remaining from fill of ice wedge penetrating the Cattle Grid Breccia (680 Ma), in the Mt. Gunson Mine, South Australia. Photo courtesy of G. E. Williams.

paleosols (Rye and Holland, 1998). Opinions differ on the nature and timing of this apparent oxygenation event. Holland (1984), Holland and Beukes (1990), and Yang and Holland (2003) proposed an abrupt rise from less than 0.1% (v/v) to more than 3% O_2 at $\sim 2,100$ Ma.

In contrast, Ohmoto (1996, 1997) and Beukes et al. (2002) argue that the Great Oxidation Event interpretation does not take into account the reducing power of biological activity within Precambrian paleosols, and that O_2 levels were close to present levels from 3,000 to 1,800 Ma. An intermediate view of rising, but fluctuating atmospheric oxidation also is compatible with available paleosol data (Retallack, 2001a), and with limited evidence from mass-independent fractionation of sulfur isotopes (Farquhar et al., 2002).

Oxidation of the atmosphere and soils could have come from lichens, possibly actinolichens, considering the small diameter of their filaments, reported from the 2,900 Ma Carbon Leader of South Africa (Hallbauer et al., 1977). Their organic geochemical and isotopic composition gives clear evidence of a photosynthetic component (Prashnowsky and Schidlowski, 1967). The potent greenhouse gas CH_4 was produced by methanogens, detected isotopically in a paleosol dated at 2,765 Ma (Rye and Holland, 2000). Later, plausibly lichenlike and carbon-sequestering organisms are represented by enigmatic, small (1×0.5 mm), encrusted, and ellipsoidal objects in the 2,200 Ma Waterval Onder and correlative paleosols (Retallack and Krinsley, 1993; Gutzmer and Beukes, 1998). A later swing to greenhouse conditions could be inferred from molecular sequence data for a Mid- to Late Precambrian (1,458–966 Ma) origin of ascomycete fungi, after the origin of

algae and before the origin of metazoans (Heckman et al., 2001). This question is also discussed in Chapter 5.06. There has long been a debate about plausible permineralized ascomycetes in the 770 Ma Skillogallee Dolomite of South Australia (Retallack, 1994b). Late Precambrian (600 Ma) enigmatic fossils, widely called "Twitya disks" after their original northwest Canadian discovery site, are probably microbial colonies (Grazdhankin, 2001), and some have been found in ferruginized paleosols (Retallack and Storaasli, 1999). Latest Precambrian (550–540 Ma) interglacial and postglacial circular fossils, widely interpreted as cnidarian medusae, have also been reinterpreted as lichenized microbial colonies and are found in paleosols (Retallack, 1994b; Grazdhankin, 2001; Steiner and Reitner, 2001). The appearance of lichens with their deeply reaching rhizines in a world of cyanobacterial mats could have greatly increased the rate of biochemical weathering, carbon sequestration, oxygenation of the atmosphere, and global cooling (Schwartzmann and Volk, 1991).

5.18.3.4 Cambro-Ordovician Greenhouse Paleosols

The most obvious way in which Ordovician paleosols differ from those of the Precambrian is in the local abundance of animal burrows. Because burrows are known in Late Precambrian marine rocks, the main problem in establishing the presence of animals on land during the Ordovician was to prove that the burrows were formed at the same time as the paleosols, and not during inundation before or

after soil formation. This evidence came in part from petrographic studies of soil carbonate in the paleosols, which is cut by some burrows and cuts across other burrows (Figure 8). This carbonate is a largely micritic mixture of calcite and dolomite, as is common in pedogenic carbonates (Retallack, 1985). Compelling evidence also came from the isotopic composition of carbon in this carbonate, which was isotopically too light to have formed in aquatic or marine environments (Retallack, 2001c). Comparable burrows and tracks of millipedelike creatures have now been reported in several Ordovician paleosol sequences (Johnson et al., 1994; Trewin and McNamara, 1995; Retallack, 2000a), but these were probably only a small part of the overall soil respiration of Ordovician paleosols. Glomalean fungi discovered in Ordovician marine rocks of Wisconsin (Redecker et al., 2000) were also part of an active

community of microbial soil respirers. Burrows are not obvious in the Late Ordovician Iron Knob paleosol of Wisconsin, but the short distance of attenuation to atmospheric values of CO_2 mole fraction and $\delta^{13}C$ values of carbon in goethite of that paleosol (Figure 6) indicate soil respiration rates comparable to those of modern savanna grassland soils (Yapp and Poths, 1994). This is remarkable, because there are no clear root traces in Ordovician paleosols, and palynological evidence indicates no more than a cover of liverwort-like plants to feed such soil respiration (Strother et al., 1996; Strother, 2000). Primary carbon fixation by these thin thalli with short root hairs could not have created a quantity of biomass or humus comparable to that of modern grasslands. Furthermore, organic-lean, red Ordovician paleosols contain only sparse reduction spots and soil carbonate nodules (Retallack, 1985; Driese and
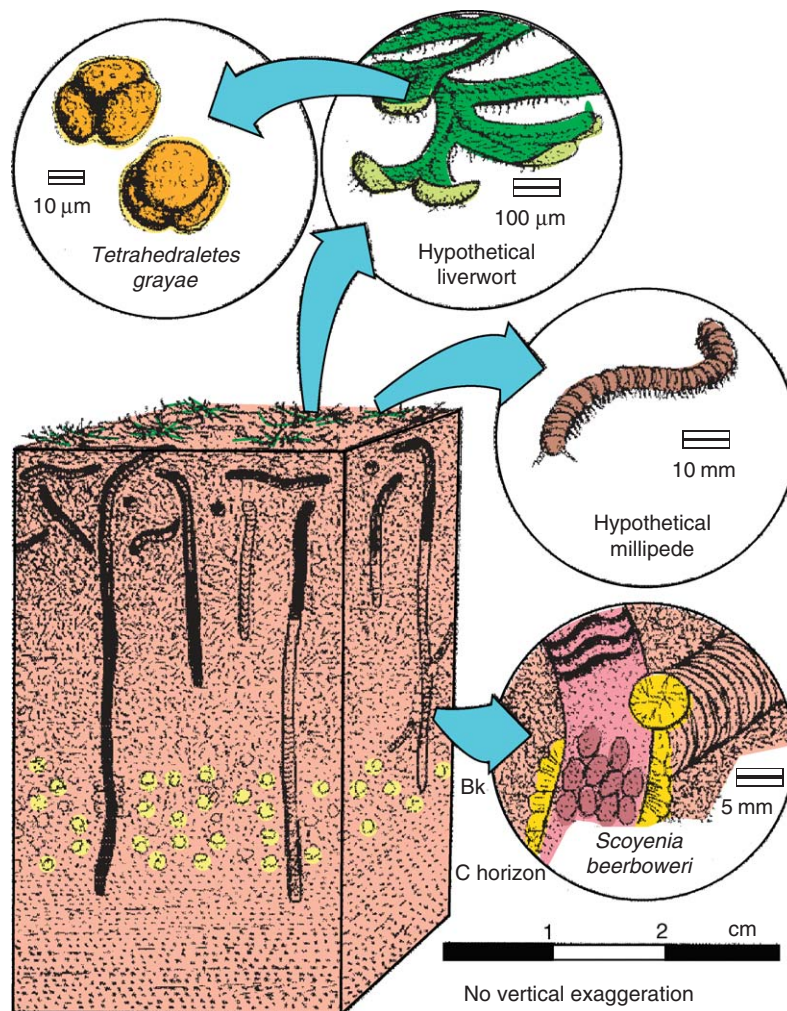

Figure 8 Reconstructed ecosystem of the Late Ordovician Potters Mills paleosol from central Pennsylvania. Reproduced by permission of Palaeontological Association from Retallack (2000a).

Foreman, 1992), indicating modest carbon storage in soil organic matter and carbonate compared, e.g., with modern savanna grassland soils (de Wit, 1978). The Ordovician paleosols studied so far show unusually high soil respiration, considering their probable low levels of primary productivity. They also formed at a time estimated from sedimentary mass balance models as the steamiest greenhouse period of all Phanerozoic time, with ∼16 times the present atmospheric levels of CO_2 (Berner and Kothavala, 2001). The carbon budget of known Ordovician paleosols would have contributed to this greenhouse.

5.18.3.5 Terminal Ordovician Icehouse Paleosols

Periglacial paleosols, unknown in Cambrian and Early to Middle Ordovician rocks, are found again in latest Ordovician (Hirnantian) rocks. Periglacial paleosols are best documented in South Africa, where patterned ground and sand wedges are common in red beds of the Pakhuis Formation (Daily and Cooper, 1976). The ice sheets extended over much of Africa (Ghienne, 2003).The causes of this ice age are especially enigmatic, because volcanic activity increased through the Ordovician and the continents were dispersed (Bluth and Kump, 1991), thus working against cold Late Ordovician poles. Mass balance models make the Ordovician ice age seem particularly enigmatic, because they predict atmospheric CO_2 levels 16 times PAL (Berner and Kothavala, 2001). This may be an artifact of the 10 Ma spacing of data points in the model, blurring the <10 Ma duration of the ice age that is indicated by carbon isotopic data (Brenchley *et al.*, 1994). Studies of carbonate isotopic compositions from paleosols within the glacial interval are needed to reexamine this question. Also needed is an examination of paleosols within this interval for evidence of fossil mosses, which would have been more deeply rooted than liverworts and so have accelerated weathering and carbon sequestration. Rare Late Ordovician mosslike megafossils (Snigirevskaya *et al.*, 1992) and spores (Nøhr-Hansen and Koppelhus, 1988) support indications from cladistic analysis (Kenrick and Crane, 1997) for a latest Ordovician origin of mosses.

5.18.3.6 Siluro-Devonian Greenhouse Paleosols

Root traces of vascular land plants appear in Silurian paleosols, but until the Early Devonian, root traces are small and shallow within the profiles (Figure 9b). The earliest known vascular land plants of the Middle and Late Silurian lacked true roots. Instead, they had stems that ran along the surface and just beneath the surface of the soil as runners and rhizomes furnished with thin unicellular root hairs (Kenrick and Crane, 1997). Plant bioturbation in soils only extended down to a few centimeters, but burrows of millipedes reached more deeply, and in some soils were more abundant than plant traces (Retallack, 1985). In addition to detritivorous and perhaps also herbivorous millipedes (Retallack, 2001c), Late Silurian soil faunas included predatory centipedes and spiderlike trigonotarbids (Jeram *et al.*, 1990). Fungal hyphae and spores in Silurian and Devonian rocks indicate proliferation of chytrids and other fungi (Sherwood-Pike and Gray, 1985; Taylor and Taylor, 2000).

Early Devonian paleosols have abundant traces of true roots, including woody tap roots of a variety of land plants (Elick *et al.*, 1998). Root traces reached tens of centimeters down into paleosols, extending greatly the depth of the active rhizosphere and its associated mucigel of microbes. Among the numerous roots of Early and Middle Devonian paleosols, the burrows of soil fauna are less prominent (Figure 9b). Devonian soils also have higher clay content and are more deeply weathered of bases than Silurian or Ordovician soils (Figure 9a). They have isotopically lighter pedogenic carbon, closer to the isotopic composition of coexisting organic carbon, than Silurian and Ordovician paleosols (Mora *et al.*, 1996; Mora and Driese, 1999). Within the parameters of the pedogenic carbonate palaeobarometer of Cerling (1991), these data indicate declining atmospheric levels of CO_2 from the Silurian into the Devonian (Figure 9c). Consumption of atmospheric CO_2 by increased hydrolytic weathering, and burial of carbon in limestone and organic matter during the Silurian and Devonian has been widely interpreted as an instance of atmospheric global change induced by the evolution of life (Retallack, 1997b; Berner, 1997; Algeo and Scheckler, 1998).

5.18.3.7 Late Devonian to Permian Icehouse Paleosols

Periglacial paleosols and glaciogene sedimentary facies unknown in Silurian and Early to Middle Devonian appear in the latest Devonian, and remain locally common in Carboniferous and Permian rocks, especially within the Gondwana supercontinent, then positioned near the south pole (Figure 10; Krull,
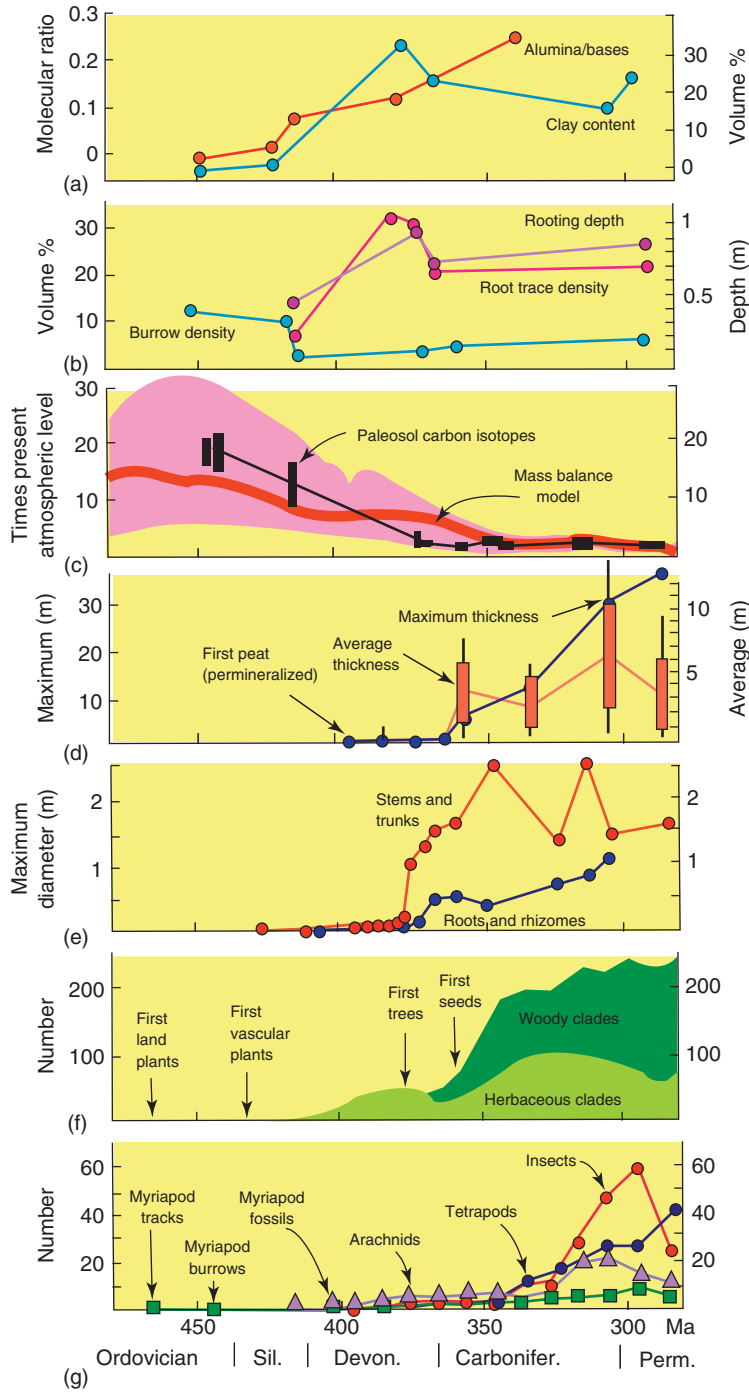
Figure 9 Early Paleozoic changes in (a) soil differentiation as indicated by clay content (vol.%) and alumina/bases (molar ratio) of the most weathered horizon of calcareous red paleosols; (b) soil bioturbation as indicated by proportion of transect in paleosols occupied by roots or burrows (percent) and by measured rooting depth (m); (c) atmospheric CO_2 levels (PAL) calculated from a sedimentary mass balance model; (d) maximum coal seam thickness and average thickness of at least 10 consecutive seams (m); (e) diameter of fossil plant stems and roots (m); (f) diversity of fossil land plants (number of species); (g) diversity of soil animals (number of families). Reproduced by permission of American Association for the Advancement of Science from Retallack (1997c).

1999). However, unlike periglacial paleosols of the Ordovician and Precambrian, these Late Paleozoic profiles include root traces of what must have been frost-hardy woody

plants. The earliest documented examples of tundra (polar shrubland) vegetation have been found in paleosols with freeze–thaw banding and thufur mounds in Carboniferous glacigene

Figure 10 Deep clastic dike in a coal of the Weller Coal Measures of the Allan Hills, Antarctica, interpreted as infill of periglacial polygonal patterned ground (E. S. Krull for scale).

sedimentary rocks near Lochinvar in southeastern Australia (Retallack, 1999a). Taiga (polar forest) paleosols with discontinuous permafrost deformation are found in Early Permian red beds near Kiama, also in southeastern Australia (Retallack, 1999b).

Milankovitch-scale temporal variation in climate and sea level has long been recognized in cyclothemic sedimentation in North American paleotropical Carboniferous marginal marine sequences, and this in turn has been related to ice-volume fluctuations on the south polar Gondwana supercontinent (Rasbury *et al.*, 1998; Miller and West, 1998). Full glacial coal seams (Histosols) alternating with interglacial marine rocks are a clear indication of these changes. Environmental alternations of full-glacial, dry, calcareous, swelling-clay soils (Vertisols), and interglacial, wet, decalcified, forest soils (Alfisols) indicate a terrestrial contribution to multimillenial-scale change in atmospheric greenhouse gases and paleoclimate (Retallack, 1995).

By Middle Devonian time, the evolution of increasingly larger plants culminated in trees with trunks up to 1.5 m in diameter, which leave obvious large root traces in paleosols (Driese *et al.*, 1997), as well as abundant permineralized stumps and logs (Meyer-Berthaud *et al.*, 1999). Middle Devonian paleosols are also the oldest known with clay-enriched subsurface horizons (argillic horizons of Soil Survey Staff, 1999). The clay in modern forest soils is partly formed by weathering in place, and is partly washed down root holes, which taper strongly downward in forest trees. Evidence of both neoformation and illuviation of clay can be seen in thin sections of Devonian forested paleosols (Retallack, 1997b).

Latest Devonian paleosols also include coals from the oldest woody peats. Thin peats of herbaceous plant remains such as the Rhynie Chert of Scotland (Rice *et al.*, 1995) and the Barzass coal of Siberia (Krassilov, 1981) are found in Early Devonian rocks, but by the latest Devonian (Algeo and Scheckler, 1998) and into the Carboniferous, woody coals became widespread and thick (Figure 9d). Carbon consumption by accelerated weathering in forest soils and carbon burial in coals are widely acknowledged as the likely cause for mass balance estimates of Late Paleozoic high atmospheric oxygen levels (perhaps 35 vol.%) and near-modern CO_2 levels (Berner *et al.*, 2000). Low Permian atmospheric CO_2 levels are also confirmed by stomatal index studies (Retallack, 2001b). These atmospheric trends and coeval changes in oceanic Mg/Ca ratio could be attributed to changes in volcanic and hydrothermal activity, particularly at mid-ocean ridges (Stanley and Hardie, 1999). However, the abundance of Early Paleozoic pedogenic dolomite, but Late Paleozoic and Neogene pedogenic calcite (Retallack, 1985, 1993), suggests a role for soils in these changes in oceanic ionic chemistry, as well as in changing atmospheric CO_2 levels.

5.18.3.8 Triassic–Jurassic Greenhouse Paleosols

Greenhouse paleoclimates right from the very beginning of the Mesozoic have been revealed by discovery of deeply weathered paleosols in earliest Triassic rocks of Antarctica (Figure 11), which even at that time was at
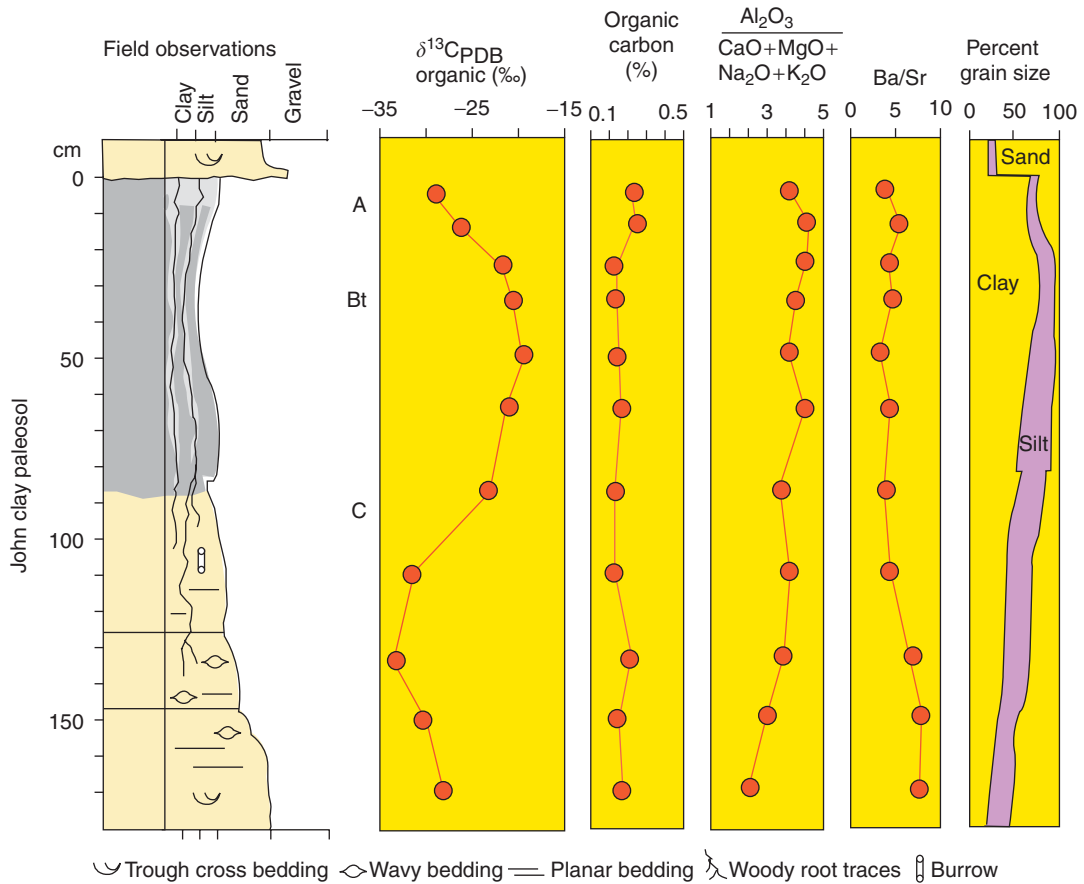
Figure 11 Geochemical (isotopic, major, and trace element) and petrographic (point count) data for a deeply weathered paleosol which formed at a latitude of 70° S in the Allan Hills of Antarctica during the Early Triassic. This is the John paleosol, an Ultisol (Sombrihumult), as indicated especially by its high ratios of alumina to bases and barium to strontium, and its strong subsurface enrichment in clay. Extremely light carbon isotopic values deep in the profile imply a role for methanogenic methane in this postapocalyptic greenhouse. Reproduced by permission of Geological Society of America from Krull and Retallack (2000).

paleolatitudes of 65–77° S (Retallack and Krull, 1999). Comparable modern soils are Ultisols (Soil Survey Staff, 1999) and Acrisols (FAO, 1988), which are not found either north of 48° N latitude or south of 40° S, and are rare outside subtropical regions. Greenhouse conditions at this time are also indicated by stomatal index studies of fossil seed ferns (Retallack, 2001b) and the isotopic composition of carbon and oxygen in marine and nonmarine carbonate and organic matter (Holser and Schönlaub, 1991).

The timing and magnitude of this greenhouse and isotopic excursion immediately at and after the greatest mass extinction of all time has suggested a catastrophic release of methane from permafrost or marine clathrate deposits (Krull and Retallack, 2000; Krull et al., 2000). There is no other source of carbon that is sufficiently large and isotopically depleted to create the observed negative carbon isotopic anomaly.

Release mechanisms for methane could have included meteorite impacts, Siberian Traps volcanism, or continental shelf collapse, which also have been invoked as causes for extinctions at this time (Hallam and Wignall, 1997). Really large life crises were also times of transient global greenhouses indicated by stomatal index data (Retallack, 2001b) at the earliest Jurassic (Pliensbachian), Early Jurassic (Toarcian), Mid-Jurassic (Bathonian), Early Cretaceous (Aptian), Mid-Cretaceous (Cenomanian–Turonian), earliest Paleocene (Danian), and earliest Eocene (Ypresian). During the Early Mesozoic, atmospheric CO_2 minima also were high (at least twice that of the present), and this general and long-term greenhouse calls for a different and noncatastrophic explanation. Paleosols and permineralized wood of forest ecosystems at high latitudes provide evidence for this long-term greenhouse during which no periglacial paleosols are recorded (Ollier and Pain, 1996;

Retallack, 2001a). The Triassic appearance of large sauropod dinosaurs such as *Massospondylus* and *Plateosaurus*, together with footprints and other dinoturbation (Lockley, 1991), and of a variety of termite and ant nests in paleosols (Hasiotis and Dubiel, 1995), would have effectively increased the destruction of woody tissues in and on soils (Olsen, 1993). The effect of such evolutionary innovation may have been to decrease carbon sequestration by lignin in swamps, forests, and their soils.

5.18.3.9 Early Cretaceous Icehouse Paleosols

Fossil patterned and hummocky ground reveal permafrost conditions during the Early Cretaceous (Aptian) sediments of southeastern Australia, which at that time was at $66-76°$ S and attached to the Antarctic portion of the Gondwana supercontinent (Rich and Vickers-Rich, 2000). This ice age does not appear to have been as extensive or severe as the Permo-Carboniferous or modern ice ages. This episode of planetary cooling coincides with a dramatic evolutionary radiation of flowering plants (Retallack and Dilcher, 1986; Truswell, 1987; Crane *et al.*, 1995). The key evolutionary innovation of flowering plants was an abbreviated life cycle, in which pollination, fertilization, and germination followed one another in quick succession (Wing and Boucher, 1998). Early angiosperms were largely confined to weakly developed soils (Entisols) of disturbed coastal and streamside habitats, which they colonized and weathered more rapidly than associated conifers and cycadlike plants (Retallack and Dilcher, 1981). Angiosperm leaves were less coriaceous and less well defended with resins and other toxins, and so rotted more rapidly to create a richer soil humus than leaves of conifers and cycadlike plants (Knoll and James, 1987). Erosion control and soil humification from newly evolved angiosperms may have played a role in Early Cretaceous chilling.

5.18.3.10 Cretaceous–Paleogene Greenhouse Paleosols

Another long period of generally warmer planetary climates without evidence of polar ice caps or periglacial paleosols lasted from the Mid-Cretaceous to the latest Eocene. Mid-Cretaceous (Cenomanian) tropical paleosols (Ultisols and Oxisols) are known from South Australia, then at $60°$ S (Firman, 1994), and the United States, then at $45°$ N (Thorp and Reed, 1949; Joeckel, 1987; Mack, 1992). The mid-Cretaceous greenhouse was unusually long and profound, judging from the stomatal index of fossil ginkgo leaves (Retallack, 2001b). Volcanic activity that created the enormous Ontong–Java Plateau has been cited as a cause for this long-term greenhouse (Larson, 1991), but there is another plausible explanation in the co-evolution with angiosperms of ornithopod dinosaurs such as *Iguanodon*, with their impressive dental batteries for processing large amounts of foliage. The feeding and trampling efficiency of these large, newly evolved dinosaurs may have further promoted the spread of early angiosperms with their ability to tolerate higher levels of disturbance than other plants (Bakker, 1985). Newly evolved ornithopod dinosaurs and their trackways are associated with carbonaceous and early successional paleosols (Entisols, Inceptisols, and Histosols), whereas archaic sauropod dinosaurs and their trackways remained associated with less fertile and less carbonaceous paleosols (Aridisols) throughout the Cretaceous (Retallack, 1997c).

Other times of unusually extensive tropical paleosols were the latest Paleocene (55 Ma; Taylor *et al.*, 1992), latest Eocene (35 Ma; Bestland *et al.*, 1996; Retallack *et al.*, 2000), and Middle Miocene (16 Ma; Schwarz, 1997). These events are notable as short-lived (< 0.5 Myr) spikelike warmings in both stable isotopic records from the ocean (Veizer *et al.*, 2000; Zachos *et al.*, 2001) and stomatal index studies (Retallack, 2001b). The latest Paleocene warm spike is associated with such profound carbon isotopic lightening that it can only reasonably be attributed to the methane from isotopically light methane clathrates from ocean floor sediments, permafrost, or volcanic intrusion (Koch, 1998). Short-term physical forcings are thus also recorded in the paleosol record of paleoclimate.

5.18.3.11 Neogene Icehouse Paleosols

Periglacial paleosols appear during Late Miocene time (8 Ma) in Antarctica (Sugden *et al.*, 1995; Retallack *et al.*, 2001), where soil development is so slow that some surface soils may be of comparable antiquity (Campbell and Claridge, 1987). Antarctic soil formation is not only promoted by ground ice deformation, but includes the effects of salt accumulation and eolian mass addition in an extremely dry continental frigid climate (Figure 12).

The Late Miocene is best known for the Messinian salinity crisis, when the Mediterranean Sea became a desert (Krijgsman *et al.*, 1999). It was also a significant time for geographic and climatic expansion of grassland
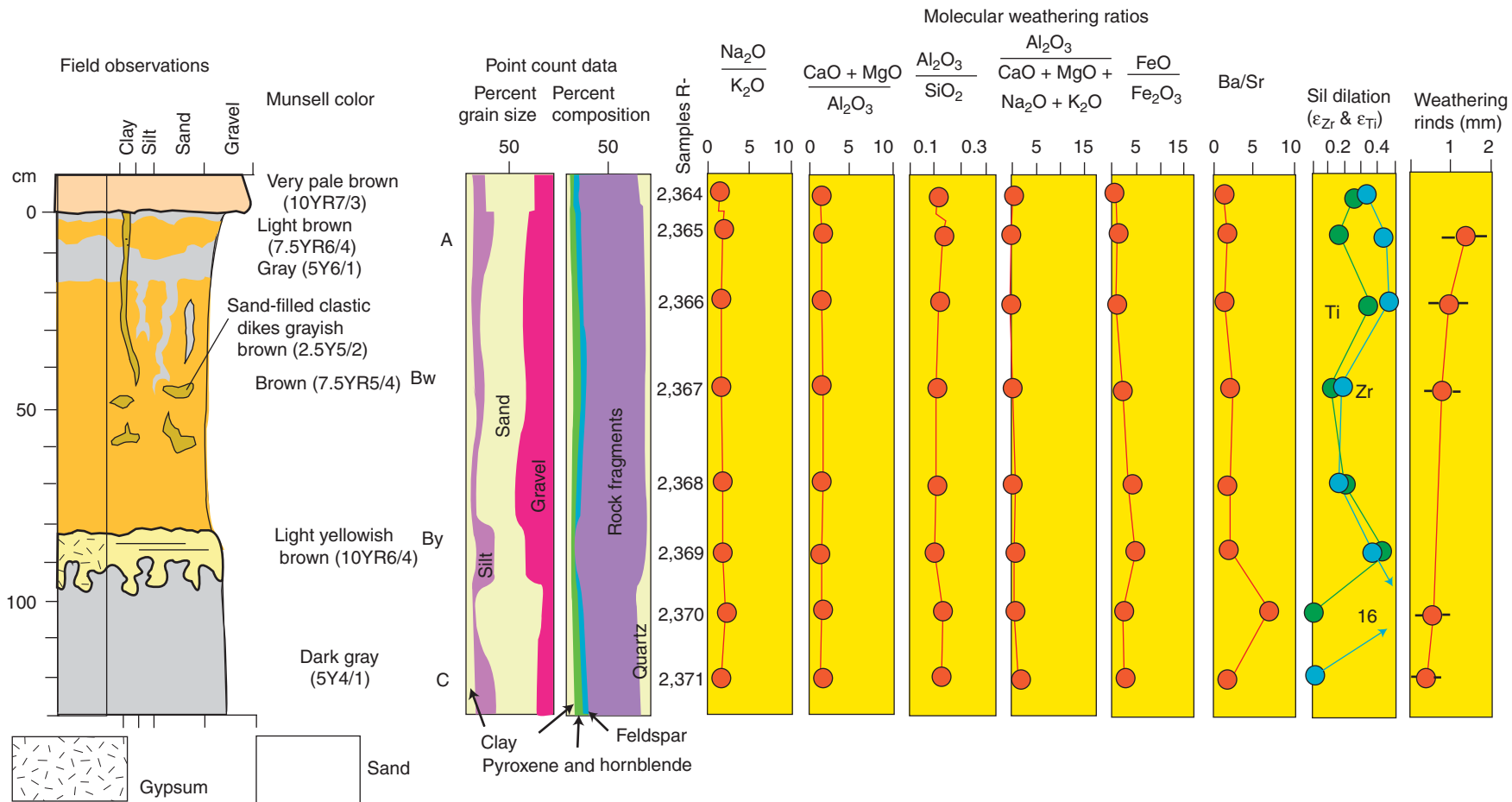
Figure 12 Geochemical data for the Siesta paleosol of Pliocene age (3 Ma) from the Meyer Desert Formation at Oliver Bluffs, central Transantarctic Mountains. Reproduced by permission of Geological Society of London from Retallack *et al.* (2001).

Figure 13 Tall grassland (Mollisol) paleosol with thick, dark brown crumb-textured surface over a deep (79 cm) white nodular calcic horizon, over a thinner short grassland paleosols with carbonate nodules at a depth of 39 cm, in the Late Miocene (7 Ma) Ash Hollow Formation, 13 km north of Ellis, Kansas.

biomes and their characteristic soils: Mollisols of Soil Survey Staff (1999) or Chernozems of FAO (1988). Evidence for this transformation in tropical regions comes from the dramatic change to a less depleted (less negative) carbon isotopic composition ($\delta^{13}C$) of pedogenic carbonate and organic matter, and of the apatite of fossil mammalian tooth enamel attributed to the tropical expansion of C_4 grasses (Cerling *et al.*, 1997; MacFadden, 2000). There is also evidence from adaptations to grazing in fossil mammals (Janis *et al.*, 2002), from traces of grassland invertebrates such as dung beetles (Genise *et al.*, 2000), and from increased abundance of silica bodies (phytoliths) and pollen characteristic of grasses (Strömberg, 2002).

Paleosols also demonstrate Late Miocene expansion of grasslands capable of forming sod of the sort that is unrolled to create lawns and golf courses. The dense growth of fine (< 2 mm diameter) adventitious roots, together with the slime of abundant earthworms, create a characteristic soil structure consisting of fine crumb peds, which can be preserved in paleosols (Figure 13). Grassland soils are also unusually rich in organic matter, intimately admixed with clay, often with as much as 10 wt.% C down to a meter or more, although this organic matter is not always preserved in paleosols. The soft, low-density upper horizons of grassland soils are also rich in mineral nutrients (Ca^{2+}, Mg^{2+}, Na^+, and K^+), and their subsurface horizons commonly include nodules of soil carbonate (usually micritic low magnesium calcite). It has long been known that such pedogenic nodules form at shallow depths within soil profiles in dry climates and deeper within the profile in more humid climates (Jenny, 1941; Retallack, 1994c). Observations of depth to carbonate horizon together with root traces and crumb peds of grassland paleosols can be used to constrain the paleoclimatic range of grasslands (Retallack, 1997d, 2001d).

Observations on hundreds of paleosols in the North American Great Plains, Oregon, Pakistan, and East Africa have revealed a broad schedule of origin and paleoclimatic expansion of bunch and then sod grasslands (Figure 14). The increased organic carbon content, high internal surface area, elevated albedo, and greater water retention capacity of grasslands compared with woodlands of comparable climatic regions would have been a potent force for global cooling as grasslands emerged to occupy almost a quarter of the current land area (Bestland, 2000; Retallack, 2001d). Mountain uplift and ocean currents played a role in Neogene climate change as well (Raymo and Ruddiman, 1992; Ramstein *et al.*, 1997), but there remain problems with the timing and magnitude of carbon sequestration by these physical mechanisms (Retallack, 2001d).

5.18.3.12 Pleistocene Glacial and Interglacial Paleosols

Over the past million years, large ice caps have grown to engulf the present-day location
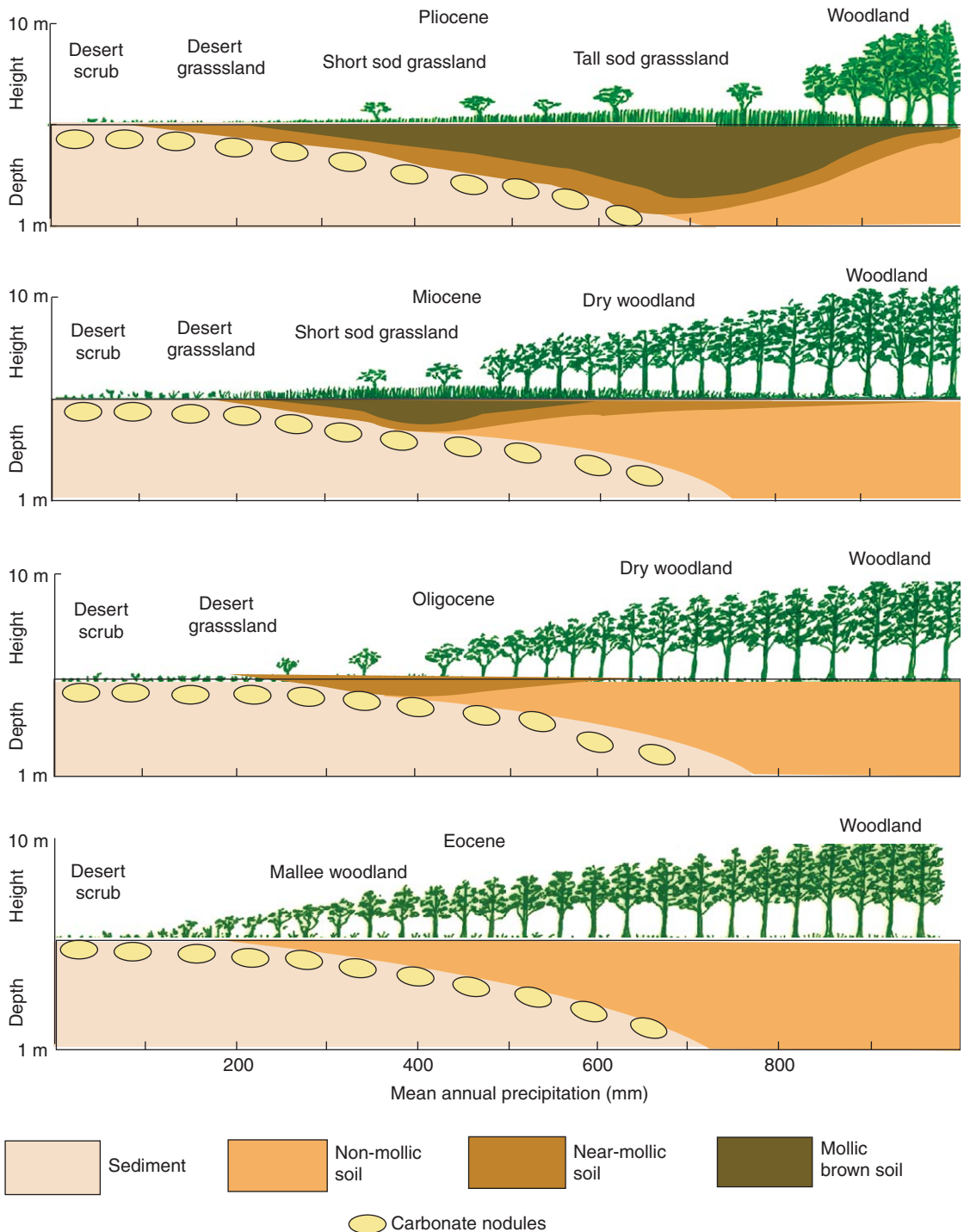
Figure 14 A scenario for climatic and geographic expansion of grasslands and their soils in the Great Plains of North America. Reproduced by permission of Society for Sedimentary Geology from Retallack (1997d).

of Chicago within more than a kilometer of ice during glacial maxima, then retreated to the current ice caps of Greenland and Alaska during interglacial times at Milankovitch scale frequencies of 100 ka. There have also been less

extreme paleoclimatic oscillations on the other Milankovitch frequencies of 42 and 23 ka (Hays et al., 1976; Petit et al., 1999). In Illinois, interglacials are defined by paleosols such as the Sangamon paleosol, which is comparable with

modern forest soils under oak–hickory forest. The 42 and 23 ka interstadials are defined by paleosols such as the Farmdale paleosol, which is comparable with modern boreal forest paleosols under spruce forest (Follmer *et al.*, 1979). Ice, till, loess, and periglacial soils (Gelisols) alternated with forest soils (Alfisols or Inceptisols) through these paleoclimatic fluctuations.

Oscillations between different ecosystems can be inferred from many paleosol sequences, even beyond the ice margin (Figure 15). In the Palouse loess of Washington, for example, grassland soils (Mollisols) with crumb peds and earthworm castings during interglacials and interstadials alternate with sagebrush soils (Aridisols) with cicada burrows and shallow carbonate horizons during glacials and interstadial minima (Busacca, 1989; O'Geen and Busacca, 2001). Vegetation of the paleosols can be inferred from carbon isotopic values typical for CAM saltbush in the sagebrush paleosols, and for C_3 grasses in the grassland paleosols, as well as from the characteristic phytoliths of these plants (Blinnikov *et al.*, 2002). Comparable alternations of ecosystems with paleoclimatic fluctuation are seen in many Quaternary sequences of paleosols (Paepe and van Overloop, 1990; Feng *et al.*, 1994; Wang *et al.*, 1998). Differences in primary production and carbon sequestration of these alternating ecosystem types on a global basis may have played a role in the relative abundance of greenhouse gases during glacial–interglacial paleoclimatic cycles.

Ice core records show as little as 180 ppmv CO_2 during glacial periods and 280 ppmv during interglacials, in a strongly asymmetric pattern of gradual drawdowns followed by steep rises known as terminations (Figure 2b). Even higher CO_2 levels during interglacials are prevented by high plant productivity of forests in humid, previously glaciated terrains and of grasslands in arid rangelands. This slow weathering and biomass building, together with nutrient leakage to the ocean and carbon burial there, could draw down greenhouse gases and bring on cooling. As ice expands and grasslands are converted into deserts, the carbon sequestration capacity of soils and ecosystems is diminished. Large herds of mammals or populations of humans could disturb these impoverished soils into dustbowl conditions and the massive carbon oxidation events of a glacial termination. Such long-term biological trends, metered by steadily declining and then abruptly renewed soil nutrients, could amplify other drivers of climate, which include large ice caps, ocean currents, mountain building, and orbital configuration (Muller and MacDonald, 2000).

5.18.4 SOILS AND GLOBAL CARBON CYCLE CHANGES

Over geological time there have been dramatic changes in soil, life, and air that are well represented in the fossil record of soils. Paleosols are an underexploited record of past environments in land. This review has emphasized mainly the evidence from paleosols for changes in carbon cycling and greenhouse gases (CO_2, CH_4, and H_2O) in the atmosphere over geological timescales. It is unremarkable that paleosols would change, particularly at high latitudes, as global climates warmed or cooled with changing atmospheric loads of greenhouse gases. It is notable that sequences of paleosols can, under certain circumstances, be high-resolution records of such paleoclimatic change (Figure 15). Parallels between biological activity within soils and greenhouse gas composition have been emphasized in this review as fertile ground for future research (Figure 16). Olsen (1993) has suggested that soil producers such as plants cool the planet, but soil consumers such as animals warm it. This idea, which the author has dubbed the Proserpina principle after the ancient Roman goddess of spring (Retallack, 2000b), is undeniable for the annual spring fall and autumn rise of atmospheric CO_2 with northern hemisphere leaf sprouting and shedding (Figure 2a). This explanation is especially demonstrated by the muted and out-of-phase annual fluctuation of CO_2 in the southern hemisphere (Mooney *et al.*, 1987), where there is less fertile land, more evergreen plants, and different seasons. The question addressed here is whether the Proserpina principle operates on geologically significant timescales, and so far, such a simple idea does not conflict with the history of life and paleoclimate outlined here.

On evolutionary timescales, it is the biochemical evolution of lignin, pyrethrin, caffeine, and other substances that deter herbivory, digestion, and decay, which affect rates of carbon burial in sediments as the principal long-term control on atmospheric CO_2 levels. The role of trees and their soils in Late Paleozoic carbon sequestration, cooling, and glaciation is widely accepted (Berner, 1997; Algeo and Scheckler, 1998; see Chapter 5.06). The role of humans in global warming is also becoming well known (Vitousek *et al.*, 1997b). According to the Proserpina principle, humans may not have been the only organisms to have had significant effects on climate. There remain many other instances of global change less clearly related to changes in life and soils, in part because the numerous paleosols of appropriate age have not yet been studied in detail. Asteroid impacts, volcanic eruptions, and methane outburst events also
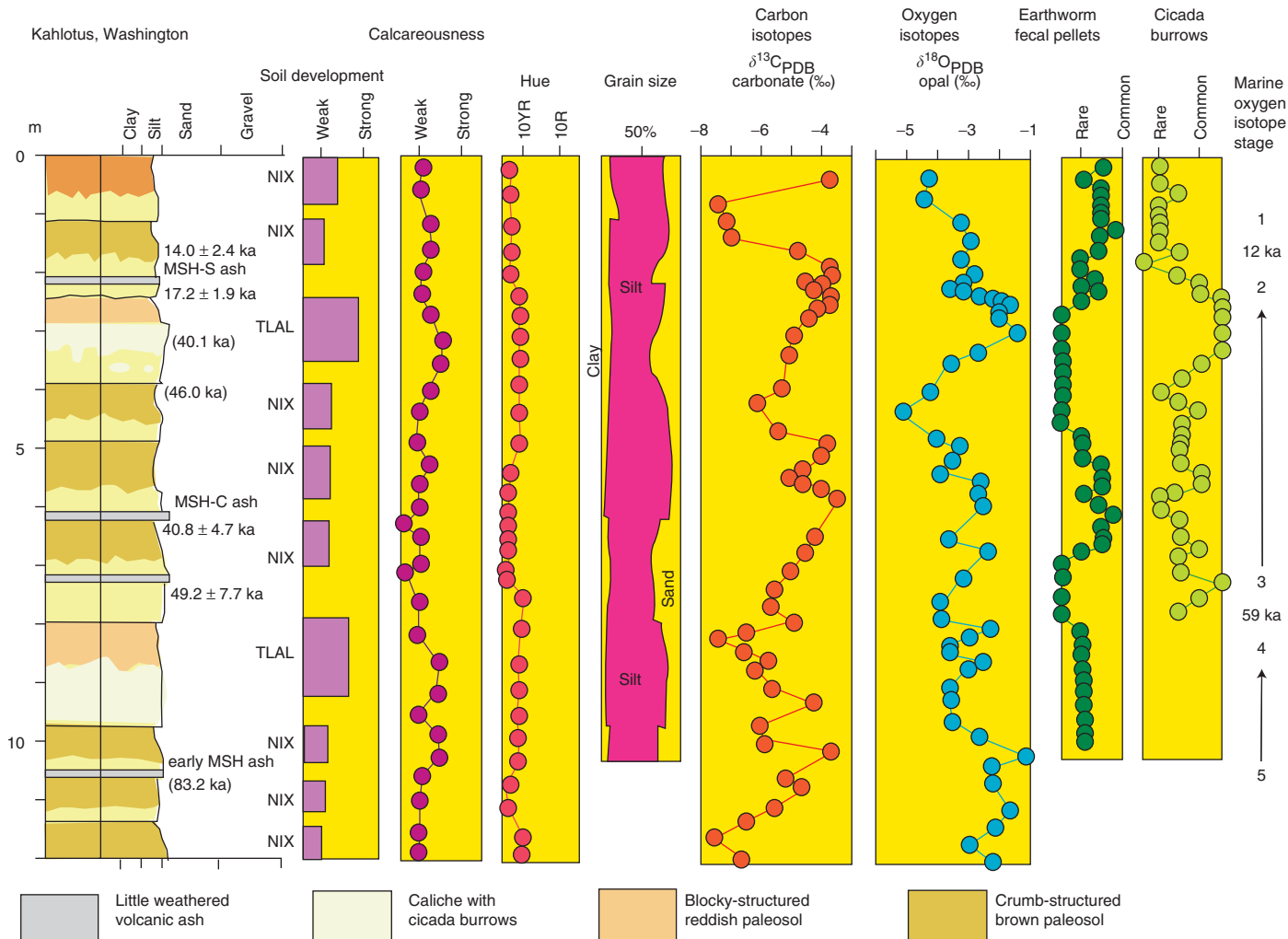
Figure 15 Alternating paleoenvironments of desert CAM shrublands and C₃ grasslands represented by a sequence of Quaternary paleosols (0–100 ka) in the Palouse loess near Kahlotus, Washington, USA; showing (left to right), field section with thermoluminescence dates and paleosol identification (NIX and TLAL are pedotypes for buried Mollisols of grasslands and Aridisols of sagebrush respectively), paleosol position and development (represented by black boxes), paleosol calcareousness (scale based on acid reaction), Munsell hue (measured dry in field), sand–silt–clay proportion, δ¹³C of pedogenic carbonate, δ¹⁸O of opal phytoliths, abundance of earthworm pellets, and abundance of cicada burrows. Source: Retallack (2001c).
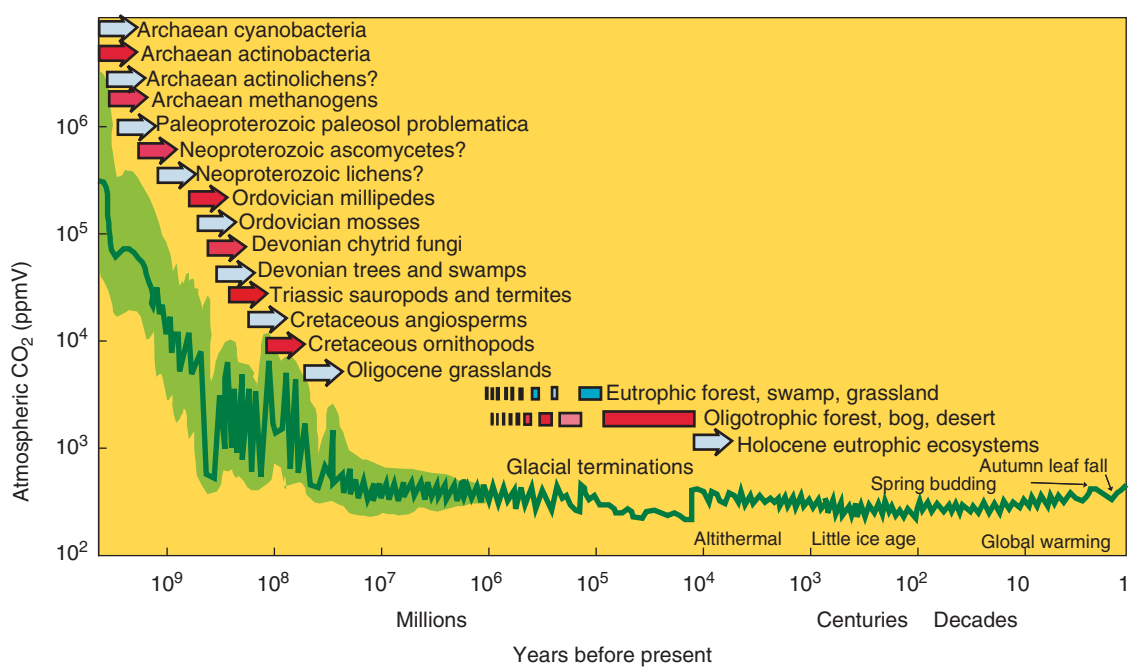
Figure 16 The Proserpina principle relates variation in atmospheric CO_2 concentration with coeval evolutionary and ecological events on a variety of timescales. Carbon sequestering evolutionary innovations and ecological transitions (closed symbols) alternate with carbon oxidizing evolutionary innovations and ecological transitions (open symbols). The CO_2 curve is a composite of those shown in Figure 2 and by Kasting (1992).

affect life and the carbon cycle, producing transient greenhouse events (Retallack, 2001b). Ocean currents and mountain building also are likely to play a role in carbon sequestration (Raymo and Ruddiman, 1992; Ramstein *et al.,* 1997). Soils and their ecosystems play an important role in the carbon cycle today, and the history of that role now decipherable from paleosols appears ripe for modeling and other quantitative comparisons with other likely controls on global paleoclimate change.

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REFERENCES

Algeo T. J. and Scheckler S. E. (1998) Terrestrial–marine teleconnections in the Devonian: links between the evolution of land plants, weathering processes and anoxic events. *Phil. Trans. Roy. Soc. London B* **353**, 113–130.

Allen J. R. L. (1974) Geomorphology of Siluro-Devonian alluvial plains. *Nature* **249**, 644–645.

Amundson R., Stern L., Baisden T., and Wang Y. (1998) The isotopic composition of soil and respired CO_2. *Geoderma* **82**, 83–114.

Bakker R. T. (1985) *The Dinosaur Heresies*. William Morrow, New York.

Barley M. E., Pickard A. L., and Sylvester P. J. (1997) Emplacement of a large igneous province as a possible cause of banded iron formation 2.45 billion years ago. *Nature* **385**, 55–58.

Barsukov V. L., Volkhov V. P., and Khodakovsky I. L. (1982) The crust of Venus: theoretical models of chemical and mineral composition. *J. Geophys. Res. Suppl.* **87A**, 3–9.

Basilevsky A. T., Kuzmin R. O., Nikolaeva O. V., Pronin A. A., Ronca A. B., Avdvesky V. S., Uspensky G. R., Cheremukhina Z. P., Semenchenko V. V., and Ladygin V. M. (1985) The surface of Venus as revealed by the Venera landings. Part II. *Geol. Soc. Am. Bull.* **96**, 137–144.

Bell J. F. (1996) Iron sulfate, carbonate and hydrated minerals on Mars. In *Mineral Spectroscopy: A Tribute to Roger G. Burns* (eds. M. D. Dyar, C. MacCammon, and M. W. Schaeffer). Geochem. Soc. Spec. Publ., vol. 5, pp. 359–380.

Berner R. A. (1997) The rise of plants and their effect on weathering and atmospheric CO_2. *Science* **276**, 543–546.

Berner R. A. and Kothavala Z. (2001) GEOCARBIII: a revised model of atmospheric CO_2 over Phanerozoic time. *Am. J. Sci.* **301**, 182–204.

Berner R. A., Petsch S. T., Lake J. A., Beerling D. J., Popp B. N., Lane R. S., Laws E. A., Westley M. B., Cassor N., Woodward F. I., and Quick W. P. (2000) Isotopic fractionation and atmospheric oxygen: implications for Phanerozoic evolution. *Science* **287**, 1630–1633.

Bestland E. A. (2000) Weathering flux and CO_2 consumption determined from paleosol sequences across the Eocene–Oligocene transition. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **156**, 301–326.

Bestland E. A. and Retallack G. J. (1993) Volcanically influenced calcareous paleosols from the Miocene Kiahera Formation, Rusinga Island, Kenya. *Geol. Soc. London J.* **150**, 293–310.

Bestland E. A., Retallack G. J., Rice A. E., and Mindszenty A. (1996) Late Eocene detrital laterites in central Oregon: mass balance geochemistry, depositional setting and landscape evolution. *Geol. Soc. Am. Bull.* **108**, 285–302.

Beukes N. J., Dorland H., Gutzmer J., Nedachi M., and Ohmoto H. (2002) Tropical laterites, life on land, and the history of atmospheric oxygen in the Paleoproterozoic. *Geology* **30**, 491–494.

Birck J. L. and Allègre C. J. (1988) Manganese–chromium systematics and the development of the early solar system. *Nature* **331**, 571–574.

Bird M. I. and Chivas A. R. (1993) Geomorphic and paleoclimatic implications of an oxygen isotope chronology for Australian deeply weathered profiles. *Austral. J. Earth Sci.* **40**, 345–358.

Blinnikov M., Busacca A., and Whitlock C. (2002) Reconstruction of the late Pleistocene grassland of the Columbia basin, Washington. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **177**, 77–101.

Bluth G. G. S. and Kump L. P. (1991) Phanerozoic paleogeology. *Am. J. Sci.* **291**, 284–308.

Bockheim J. G. (1995) Permafrost distribution in the southern circum-polar region and its relation to the environment: a review and recommendation for further research. *Permafrost Periglac. Process* **6**, 27–45.

Borden R. (2001) Geochemical evolution of sulphide-bearing waste rock soils at the Bingham Canyon Mine, Utah. In *Evolution and Remediation of Acid–Sulphate Systems at Reclaimed Mine Sites* (eds. J. J. Donovan and A. W. Rose). Geological Society of London, pp. 15–21.

Brearley A. J. (1999) Origin of graphitic carbon and pentlandite in matrix olivines in the Allende meteorite. *Science* **285**, 1380–1382.

Brenchley P. J., Marshall J. B., Carden G. A. F., Robertson D. B. R., Long D. E. F., Meidia T., Hints L., and Anderson T. F. (1994) Bathymetric and isotopic evidence for a short-lived Late Ordovician glaciation in a greenhouse period. *Geology* **22**, 293–298.

Brimhall G. H., Chadwick O. A., Lewis C. J., Compston W., Williams I. S., Danti K. J., Dietrich W. E., Power M. E., Hendricks D., and Bratt J. (1991) Deformational mass transport and invasive processes in soil evolution. *Science* **255**, 695–702.

Brook G. A., Folkoff M. E., and Box E. O. (1983) A world model of soil carbon dioxide. *Earth Surf. Process. Landforms* **8**, 79–88.

Buckland W. (1837) *Geology and Mineralogy Considered with Reference to Natural Theology*. W. Pickering, London.

Buick R., Thronetree J. R., McNaughton N. J., Smith J. B., Barley M. E., and Savage M. (1995) Record of emergent continental crust ∼3.5 billion years ago in the Pilbara Craton of Australia. *Nature* **375**, 574–576.

Bunch T. E. and Chang S. (1980) Carbonaceous chondrites. II: Carbonaceous chondrite phyllosilicates and light element geochemistry as indicators of parent body processes and surface conditions. *Geochim. Cosmochim. Acta* **44**, 1543–1577.

Buol S. W., Hole F. D., and McCracken R. W. (1997) *Soil Genesis and Classification*, 4th edn. Iowa State University Press, Ames.

Busacca A. J. (1989) Long Quaternary record in eastern Washington, USA, interpreted from multiple buried paleosols in loess. *Geoderma* **45**, 105–122.

Campbell I. B. and Claridge G. G. C. (1987) *Antarctica: Soils, Weathering Processes and Environment*. Elsevier, Amsterdam.

Canfield D. E. and Teske A. (1996) Late Proterozoic rise in atmospheric oxygen concentration inferred from phylogenetic and sulphur isotope studies. *Nature* **382**, 127–132.

Cerling T. E. (1991) Carbon dioxide in the atmosphere: evidence from Cenozoic and Mesozoic paleosols. *Am. J. Sci.* **291**, 377–400.

Cerling T. E., Harris J. M., MacFadden B. J., Leakey M. G., Quade J., Eisenmann V. V., and Ehleringer J. F. (1997) Global vegetation change through the Miocene/Pliocene boundary. *Nature* **389**, 153–158.

Chadwick O. A., Derry L. A., Vitousek P. M., Huebert B. J., and Hedin L. O. (1999) Changing sources of nutrients during four million years of ecosystem development. *Nature* **397**, 491–497.

Colin F., Brimhall G. H., Nahon D., Lewis C. J., Baronnet A., and Danti K. (1992) Equatorial rain forest lateritic mantles: a geomembrane filter. *Geology* **20**, 523–526.

Crane P. R., Friis E. M., and Pedersen K. J. (1995) The origin and early diversification of angiosperms. *Nature* **374**, 27–33.

Daily B. and Cooper M. R. (1976) Clastic wedges and patterned ground in the Late Ordovician–Early Silurian tillites of South Africa. *Sedimentology* **23**, 271–283.

Dalziel I. W. D. (1997) Neoproterozoic–Paleozoic geography and tectonics: review, hypothesis, environmental speculation. *Geol. Soc. Am. Bull.* **109**, 16–42.

Delvigne J. E. (1998) Atlas of micromorphology of mineral alteration and weathering. *Canadian Mineralogist* (Special Publication) **3**, 495.

Des Marais D. J. (1997) Isotopic evolution of the biogeochemical carbon cycle during the Proterozoic Eon. *Org. Geochem.* **27**, 185–193.

de Wit H. A. (1978) *Soils and Grassland Types of the Serengeti Plain (Tanzania)*. Medelingen Landbouwhogeschool, Wageningen.

Driese S. G. and Foreman J. L. (1992) Traces and related chemical changes in a Late Ordovician paleosol, Glossifungites ichnofacies, southern Appalachians, USA. *Ichnos* **1**, 207–219.

Driese S. G., Mora C. I., and Elick J. M. (1997) Morphology and taphonomy of root and stump casts of the earliest trees (Middle and Late Devonian), Pennsylvania and New York, USA. *Palaios* **12**, 524–537.

Ekart D. P., Cerling T. E., Montanez I. P., and Tabor N. J. (1999) A 400 million year carbon isotope record of pedogenic carbonate: implications for paleoatmospheric carbon dioxide. *Am. J. Sci.* **299**, 805–827.

Elick J. E., Driese S. E., and Mora C. I. (1998) Very large plant root traces from the Early to Middle Devonian: implications for early terrestrial ecosystems and p CO_2 estimates. *Geology* **26**, 143–146.

Endress M., Zinner E., and Bischoff A. (1996) Early aqueous activity on primitive meteorite parent bodies. *Nature* **379**, 701–704.

FAO (1988) *Soil Map of the World. Vol. 1*. Revised Legend. UNESCO, Rome.

Farquhar G. D., Lloyd J., Taylor J. A., Flanagan L. B., Syvertsen J. P., Hubick K. T., Chin Wong S., and Ehleringer J. R. (1993) Vegetation effects of the isotopic composition of oxygen in atmospheric CO_2. *Nature* **363**, 439–443.

Farquhar J., Wing B. A., McKeegan K. D., Harris J. W., Cartigny P., and Thiemens M. H. (2002) Mass-independent sulfur of inclusions in diamondand sulfur recycling on early Earth. *Science* **298**, 2369–2372.

Feng Z. D., Johnson W. L., Lu L. C., and Ward P. A. (1994) Climatic signals from loess-soil sequences in the central Great Plains, USA. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **110**, 345–358.

Firman J. B. (1994) Paleosols in laterite and silcrete profiles: evidence from the southeast margin of the Australian Precambrian Shield. *Earth Sci. Rev.* **36**, 149–179.

Follmer L. R., McKay E. D., Lineback J. A., and Gross D. L. (1979) Wisconsinan, Sangamonian and Illinoian stratigraphy in central Illinois. *Guidebk Illinois, State Geol. Surv.* **13**, 138.

Foster R. C. (1981) Polysaccharides in soil fabrics. *Science* **214**, 665–667.

Genise J. F., Mángano M. G., Buatois L. A., Laza J. H., and Verde M. (2000) Insect trace fossil associations in paleosols: the *Coprinisphaera* ichnofacies. *Palaios* **15**, 49–64.

Ghienne J. F. (2003) Late Ordovician sedimentary environments, glacial cycles and post-glacial transgression in the Taoudeni Basin, West Africa. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **189**, 117–145.

Grandstaff D. E., Edelman M. J., Foster R. W., Zbinden E., and Kimberley M. M. (1986) Chemistry and mineralogy of Precambrian paleosols at the base of the Dominion and Pongola Groups. *Precamb. Res.* **32**, 91–131.

Gray J. (1993) Major Paleozoic land plant evolutionary bioevents. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **104**, 153–169.

Grazdhankin M. (2001) Microbial origin of some of the Ediacaran fossils. *Abstr. Geol. Soc. Am.* **33**(6), A429.

Gutzmer J. and Beukes N. J. (1998) Earliest laterites and possible evidence for terrestrial vegetation in the early Proterozoic. *Geology* **26**, 263–266.

Hallam A. and Wignall P. (1997) *Mass Extinctions and their Aftermath*. Oxford University Press, New York.

Hallbauer D. K., Jahns H. M., and Beltmann H. A. (1977) Morphological and anatomical observations on some Precambrian plants from the Witwatersrand, South Africa. *Geol. Rundsch.* **66**, 477–491.

Hasiotis S. T. and Dubiel D. L. (1995) Termite (Insecta, Isoptera) nest ichnofossils from the Upper Triassic Chinle Formation, Petrified Forest national Monument, Arizona. *Ichnos* **4**, 111–130.

Hays J. D., Imbrie J., and Shackleton N. J. (1976) Variations in the Earth's orbit: pacemaker of the ice ages. *Science* **194**, 1121–1132.

Heckman D. S., Geiser D. M., Eidell B. R., Stauffer R. L., Kardos N. L., and Hedges S. B. (2001) Molecular evidence for early colonization of land by fungi and plants. *Science* **293**, 1129–1133.

Hoffman P. F., Kaufman A. J., Halverson G. P., and Schrag D. P. (1998) A Neoproterozoic snowball Earth. *Science* **281**, 1342–1346.

Holland H. D. (1984) *The Chemical Evolution of the Atmosphere and Oceans*. Princeton University Press, Princeton.

Holland H. D. and Beukes M. J. (1990) A paleoweathering profile from Griqualand West, South Africa: evidence for a sudden rise in atmospheric oxygen between 2.2 and 1.6 bybp. *Am. J. Sci.* **290**, 1–34.

Holser W. T. and Schönlaub H. P. (1991) The Permian–Triassic boundary in the Carbic Alps of Austria (Gartnerkofel region). *Abh. Geol. Bund. Autriche Wien* **45**, 1–232.

Horodyski R. J. and Knauth L. P. (1994) Life on land in the Precambrian. *Science* **263**, 474–498.

Hutton J. (1795) *Theory of the Earth,* (with proofs and illustrations) . J. W. Creech, Edinburgh.

Jahren A. H. and Sternberg L. S. L. (2002) Eocene meridional weather patterns reflected in the oxygen isotopes of Arctic fossil wood. *GSA Today* **12**(1), 4–9.

Jahren A. H., Arens N. C., Sarmiento G., Guerro J., and Armstrong R. (2001) Terrestrial record of methane hydrate degassing in the Early Cretaceous. *Geology* **29**, 159–162.

Janis C. M., Damuth J., and Theodor J. M. (2002) The origins and evolution of the North American grassland biome: the story from hoofed mammals. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **177**, 183–198.

Jenny H. J. (1941) *Factors in Soil Formation*. McGraw-Hill, New York.

Jeram A. J., Selden P. A., and Edwards D. (1990) Land animals in the Silurian: arachnids and myriapods from Shropshire, England. *Science* **250**, 658–661.

Joeckel R. M. (1987) Paleogeomorphic significance of two paleosols in the Dakota Formation (Cretaceous), southeastern Nebraska. *Contrib. Geol. Univ. Wyoming* **25**, 91–102.

Johnson E. W., Briggs D. E. G., Suthren R. J., Wright J. L., and Tunnicliff J. P. (1994) Non-marine arthropod traces from subaerial Ordovician Borrowdale Volcanic Group, English Lake district. *Geol. Mag.* **131**, 395–406.

Kasting J. F. (1992) Proterozoic climates: the effects of changing atmospheric carbon dioxide concentrations. In *The Proterozoic Biosphere: A Multidisciplinary Study* (eds. J. W. Schopf and C. Klein). Cambridge University Press, Cambridge, pp. 165–168.

Keeling C. D., Bacastow R. B., and Whorf T. P. (1982) Measurement of the concentration of carbon dioxide at Mauna Loa Observatory, Hawaii. In *Carbon Dioxide Review 1982* (ed. W. C. Clark). Oxford University Press, New York, pp. 377–385.

Kenrick P. and Crane P. R. (1997) *Early Evolution of Land Plants*. Smithsonian Institution Press, Washington, DC.

Kirschvink J. (1992) Late Proterozoic low latitude global glaciation. In *The Proterozoic Biosphere: A Multidisciplinary Study* (eds. J. W. Schopf and C. Klein). Cambridge University Press, Cambridge, pp. 51–52.

Knoll M. A. and James W. C. (1987) Effect of the advent and diversification of vascular plants on mineral weathering through geologic time. *Geology* **15**, 1099–1102.

Koch P. L. (1998) Isotopic reconstruction of past continental environments. *Annu. Rev. Earth Planet. Sci.* **26**, 573–613.

Krassilov V. A. (1981) *Orestovia* and the origin of vascular plants. *Lethaia* **14**, 235–250.

Krijgsman W., Hilgen F. J., Ruffi I., Sienro F. J., and Wilson R. S. (1999) Chronology, causes and progression of the Messinian Salinity Crisis. *Nature* **400**, 652–655.

Krull E. S. (1999) Permian palsamires as paleoenvironmental proxies. *Palaios* **14**, 530–544.

Krull E. S. and Retallack G. J. (2000) $\delta^{13}C_{org}$ depth profiles of paleosols across the Permian–Triassic boundary: evidence for methane release. *Geol. Soc. Am. Bull.* **112**, 1459–1472.

Krull E. S., Retallack G. J., Campbell H. J., and Lyon G. L. (2000) $\delta^{13}C_{org}$ chemostratigraphy of the Permian–Triassic boundary in the Maitai Group, New Zealand: evidence for high latitude methane release. *N.Z. J. Geol. Geophys.* **43**, 21–73.

Larson R. L. (1991) Geological consequences of superplumes. *Geology* **19**, 963–966.

Lockley M. (1991) *Tracking Dinosaurs*. Cambridge University Press, Cambridge.

Ludvigsen G. A., González L. A., Metzger R. A., Witzke B. J., Brenner R. L., Murillo A. P., and White T. S. (1998) Meteoric sphaerosiderite lines and their use in paleohydrology and paleoclimatology. *Geology* **26**, 1039–1042.

MacFadden B. J. (2000) Origin and evolution of the grazing guild in Cenozoic New World mammals. In *Evolution of Herbivory in Terrestrial Vertebrates* (ed. H. D. Sues). Cambridge University Press, Cambridge, pp. 223–244.

MacFadden B. J., Solounias N., and Cerling T. E. (1999) Ancient diests, ecology and extinction of 5-million-year-old horses from Florida. *Science* **283**, 824–827.

Mack G. H. (1992) Paleosols as an indicator of climate change at the Early–Late Cretaceous boundary, southwestern New Mexico. *J. Sedim. Petrol.* **62**, 484–494.

Marbut C. F. (1935) *Atlas of American Agriculture*. Part III : *Soils of the United States, US Department of Agriculture Advance Sheets*. Government Printer, Washington, DC, vol. 8.

Marmo J. S. (1992) The lower Proterozoic Hokkalampi paleosol in North Karelia. In *Early Organic Evolution: Implications for Mineral and Energy Resources* (eds. M. Schidlowski, S. Golubic, M. M. Kimberley,

D. M. McKirdy, and P. A. Trudinger). Springer, Berlin, pp. 41–66.

Maynard J. B. (1992) Chemistry of modern soils as a guide to interpreting Precambrian paleosols. *J. Geol.* **100**, 279–289.

McSween H. Y. (1997) Evidence for life in a martian meteorite? *GSA Today* **7**(7), 1–7.

McSween H. Y. (1999) *Meteorites and their Parent Planets*. Cambridge University Press, Cambridge.

Merino E., Nahon D., and Wang Y. F. (1993) Kinetics and mass transfer of pseudomorphic replacement: application to replacement of parent minerals and kaolinite by Al, Fe and Mn oxides during weathering. *Am. J. Sci.* **293**, 135–155.

Meyer-Berthaud B., Scheckler S. E., and Wendt J. (1999) *Archaeopteris* is earliest known tree. *Nature* **398**, 700–701.

Miller K. B. and West R. R. (1998) Identification of sequence boundaries within cyclic strata of the Lower Permian of Kansas, USA: problems and alternatives. *J. Geol.* **106**, 119–132.

Mooney H. A., Vitousek P. M., and Matson P. A. (1987) Exchange of materials between terrestrial ecosystems and the atmosphere. *Science* **238**, 926–932.

Mora C. I. and Driese S. G. (1999) Palaeoenvironment, palaeoclimate and stable carbon isotopes of Palaeozoic redbed palaeosols, Appalachian Basin, USA and Canada. In *Palaeoweathering, Palaeosurfaces and Continental Deposits* (eds. M. Thiry and R. Simon-Coinçon). Int. Assoc. Sedimentology Spec. Publ., vol. 27, pp. 61–84.

Mora C. I., Driese S. G., and Colarusso L. A. (1996) Middle to Late Paleozoic atmospheric CO_2 from soil carbonate and organic matter. *Science* **271**, 1105–1107.

Mora C. I., Sheldon B. T., Elliott N. C., and Driese S. G. (1998) An oxygen isotope study of illite and calcite in three Appalachian vertic paleosols. *J. Sediment. Res. A* **68**, 456–464.

Mossman D. J. and Farrow C. E. G. (1992) Paleosol and ore-forming processes in the Elliot Lake district of Canada. In *Early Organic Evolution: Implications for Energy and Mineral Resources* (eds. M. Schidlowski, S. Golubic, M. M. Kimberley, D. M. McKirdy, and P. A. Trudinger). Springer, Berlin, pp. 67–76.

Muller R. A. and MacDonald G. J. (2000) *Ice Ages and Astronomical Causes: Data, Spectral Analyses and Mechanisms*. Springer, Berlin.

Nahon D. B. (1991) *Introduction to the Petrology of Soils and Chemical Weathering*. Wiley, New York.

Nøhr-Hansen H. and Koppelhus E. B. (1988) Ordovician spores with trilete rays from Washington Land, North Greenland. *Rev. Palaeobot. Palynol.* **56**, 305–311.

O'Geen A. T. and Busacca A. J. (2001) Faunal burrows as indicators of paleovegetation in eastern Washington. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **169**, 23–37.

Ohmoto H. (1996) Evidence in pre-2.2 Ga paleosols for the early evolution of atmospheric oxygen and terrestrial biota. *Geology* **24**, 1135–1138.

Ohmoto H. (1997) Evidence in pre-2.2 Ga paleosols for the early evolution of atmospheric oxygen and terrestrial biota: reply. *Geology* **25**, 857–858.

Ollier C. and Pain C. (1996) *Regolith, Soils and Landforms*. Wiley, Chichester.

Olsen P. E. (1993) The terrestrial plant and herbivore arms race: a major control of Phanerozoic CO_2? *Abstr. Prog. Geol. Soc. Am.* **25**(3), 71.

Paepe R. and van Overloop E. (1990) River and soil cyclicities interfering with sea level changes. In *Greenhouse Effect, Sea Level Change and Drought* (eds. R. Paepe, R. Fairbridge, and S. Jelgersma). Kluwer Academic, Dordrecht, pp. 253–280.

Pavlov A. A., Kasting J. F., Brown L. L., Rage K. A., and Freedman R. (2000) Greenhouse warming by CH_4 in the atmosphere of early Earth and Mars. *J. Geophys. Res.* **105**, 11981–11990.

Petit J. R., Jouzel J., Raynaud D., Barkov N. I., Barnola J. M., Basile I., Bender M., Chapellaz J., Davis M., Pelaygue G., Delmotte M., Kotylakov V. M., Legrand M., Lipankov V. Y., Lorius C., Pepin L., Ritz C., Saltzman E., and Stlevenard M. (1999) Climate and atmospheric history of the past 420,000 years from the Vostok ice core, Antarctica. *Nature* **399**, 429–436.

Pinto J. P. and Holland H. D. (1988) Paleosols and the evolution of the atmosphere. Part II:. In *Paleosols and Weathering through Geologic Time, Spec. Pap. Geol. Soc. Am* (eds. J. Reinhardt and W. Sigleo). Geological Society of America, Boulder, vol. 216, pp. 21–34.

Prashnowsky A. A. and Schidlowski M. (1967) Investigation of a Precambrian thucolite. *Nature* **216**, 560–563.

Ramstein G., Fluteau F., Besse J., and Joussame S. (1997) Effects of orogeny, plate motion and land-sea distribution on European climate change over the past 30 million years. *Nature* **386**, 788–795.

Rasbury E. T., Hanson G. N., Meyers W. J., Goldstein R. H., and Saller A. H. (1998) U–Pb dates of paleosols: constraints on Late Paleozoic cycle durations and boundary ages. *Geology* **26**, 403–406.

Raymo M. E. and Ruddiman W. F. (1992) Tectonic forcing of Late Cenozoic climate. *Nature* **359**, 117–122.

Redecker D., Kodner R., and Graham L. E. (2000) Glomalean fungi from the Ordovician. *Science* **289**, 1920–1921.

Retallack G. J. (1976) Triassic palaeosols in the upper Narrabeen Group of New South Wales: Part I. Features of the palaeosols. *Geol. Soc. Australia J.* **23**, 383–399.

Retallack G. J. (1983) Late Eocene and Oligocene paleosols from Badlands National Park, South Dakota. *Geol. Soc. Am. Spec. Pap.* **193**, 82.

Retallack G. J. (1985) Fossil soils as grounds for interpreting the advent of large plants and animals on land. *Phil. Trans. Roy. Soc. London B* **309**, 105–142.

Retallack G. J. (1986) Reappraisal of a 2,200-Ma-old paleosol from near Waterval Onder, South Africa. *Precamb. Res.* **32**, 195–232.

Retallack G. J. (1991) Untangling the effects of burial alteration and ancient soil formation. *Annu. Rev. Earth Planet. Sci.* **19**, 183–206.

Retallack, G. J. (1993) Late Ordovician paleosols of the Juniata Formation near Potters Mills. In *Paleosols, Paleoclimate and Paleoatmospheric CO_2: Paleozoic Paleosols of Central Pennsylvania* (ed. S. G. Driese). University of Tennessee Department of Geological Sciences Studies in Geology, Knoxville, vol. 22, pp. 33–50.

Retallack G. J. (1994a) A pedotype approach to Latest Cretaceous and Early Paleocene paleosols in eastern Montana. *Geol. Soc. Am. Bull.* **106**, 1377–1397.

Retallack G. J. (1994b) Were the Ediacaran fossils lichens? *Paleobiology* **20**, 523–544.

Retallack G. J. (1994c) The environmental factor approach to the interpretation of paleosols. In *Factors in Soil Formation: A Fiftieth Anniversary Retrospective* (eds. R. Amundson, J. Harden, and M. Singer). Soil. Sci. Soc. Am. Spec. Publ., Soil Society of America, Madison, vol. 33, pp. 31–64.

Retallack G. J. (1995) Pennsylvanian vegetation and soils. In *Predictive Stratigraphic Analysis* (eds. B. Cecil and T. Edgar). US Geol. Surv. Bull., pp. 13–19.

Retallack G. J. (1997a) *A Colour Guide to Paleosols*. Wiley, Chichester.

Retallack G. J. (1997b) Early forest soils and their role in Devonian global change. *Science* **276**, 583–585.

Retallack G. J. (1997c) Dinosaurs and dirt. In *Dinofest* (eds. D. Wolberg and E. Stump). Academy of Natural Sciences, Philadelphia, pp. 345–359.

Retallack G. J. (1997d) Neogene expansion of the North American prairie. *Palaios* **12**, 380–390.

Retallack G. J. (1999a) Carboniferous fossil plants and soils of an early tundra ecosystem. *Palaios* **14**, 324–336.

Retallack G. J. (1999b) Permafrost palaeoclimate of Permian palaeosols in the Gerringong volcanics of New South Wales. *Austral. J. Earth Sci.* **46**, 11–22.

Retallack, G. J. (2000a) Ordovician life on land and Early Paleozoic global change. In *Phanerozoic Terrestrial Ecosystems* (eds. R. A. Gastaldo and W. A. DiMichele) Paleont. Soc. Short Course Notes, Carnegie Museum, Pittsburg, vol. 6, pp. 21–45.

Retallack G. J. (2000b) The Proserpina principle: a role for soil communities in regulating atmospheric composition on time scales ranging from ecological to geological. *Abstr. Geol. Soc. Am.* **32**(7), A486.

Retallack G. J. (2001a) *Soils of the Past*, 2nd edn. Blackwell, Oxford.

Retallack G. J. (2001b) A 300 million year record of atmospheric CO_2 from fossil plant cuticles. *Nature* **411**, 287–290.

Retallack G. J. (2001c) *Scoyenia* burrows from Ordovician paleosols of the Juniata Formation in Pennsylvania. *Palaeontology* **44**, 209–235.

Retallack G. J. (2001d) Cenozoic expansion of grasslands and global cooling. *J. Geol.* **109**, 407–426.

Retallack G. J. (2002) Carbon dioxide and climate over the past 300 Myr. *Phil. Trans. Roy. Soc. London A* **360**, 659–674.

Retallack G. J. and Dilcher D. L. (1981) A coastal hypothesis for the dispersal and rise to dominance of flowering plants. In *Paleobotany, Paleoecology and Evolution* (ed. K. J. Niklas). Praeger, New York, vol. 2, pp. 27–77.

Retallack G. J. and Dilcher D. L. (1986) Cretaceous angiosperm invasion of North America. *Cretaceous Res.* **7**, 227–252.

Retallack G. J. and Krinsley D. H. (1993) Metamorphic alteration of a Precambrian (2.2 Ga) paleosol from South Africa revealed by back-scatter imaging. *Precamb. Res.* **63**, 27–41.

Retallack G. J. and Krull E. S. (1999) Ecosystem shift at the Permian–Triassic boundary in Antarctica. *Austral. J. Earth Sci.* **46**, 785–812.

Retallack G. J. and Mindszenty A. (1994) Well preserved Late Precambrian paleosols from northwest Scotland. *J. Sedim. Res. A* **64**, 264–281.

Retallack G. J. and Storaasli M. (1999) Problematic impressions from the Precambrian of Montana. *Abstr. Geol. Soc. Am.* **31**(7), A362.

Retallack G. J., Bestland E. A., and Fremd T. (2000) Eocene and Oligocene paleosols in central Oregon. *Geol. Soc. Am. Spec. Pap.* **344**, 192.

Retallack G. J., Krull E. S., and Bockheim J. G. (2001) New grounds for reassessing the palaeoclimate of the Sirius Group, Antarctica. *Geol. Soc. London J.* **158**, 925–935.

Rice C. M., Ashcroft W. A., Batten D. J., Boyce A. J., Caulfield J. B. D., Fallick A. E., Hole M. J., Jones E., Pearson M. J., Rogers G., Saxton J. M., Stuart F. M., Trewin N. H., and Turner G. (1995) A Devonian auriferous hot spring system, Rhynie, Scotland. *Geol. Soc. London J.* **152**, 229–250.

Rich T. H. and Vickers-Rich P. T. (2000) *Dinosaurs of Darkness*. University of Indiana Press, Bloomington.

Rye R. and Holland H. D. (1998) Paleosols and the evolution of atmospheric oxygen: a critical review. *Am. J. Sci.* **298**, 621–672.

Rye R. and Holland H. D. (2000) Life associated with a 2.76 Ga ephemeral pond? Evidence from Mount Roe #2 paleosol. *Geology* **28**, 483–486.

Rye R., Kuo P. H., and Holland H. D. (1995) Atmospheric carbon dioxide concentrations before 2.2 billion years ago. *Nature* **378**, 603–605.

Schidlowski M. and Aharon P. (1992) Carbon cycle and carbon isotopic record: geochemical impact of life over 3.8 Ga of Earth history. In *Early Organic Evolution: Implications for Energy and Mineral Resources* (eds. M. Schidlowski, S. Golubic, M. M. Kimberley, D. M.

McKirdy, and P. A. Trudinger). Springer, Berlin, pp. 147–175.

Schidlowski M., Hayes J. M., and Kaplan I. R. (1983) Isotopic inferences of ancient biochemistries: carbon, sulfur, hydrogen and nitrogen. In *Earth's Earliest Biosphere: Its Origin and Evolution* (ed. J. W. Schopf). Princeton University Press, Princeton, pp. 149–186.

Schmidt P. W. and Williams G. E. (1999) Palaeomagnetism of the Palaeoproterozoic hematitic breccia and paleosol at Ville-Marie, Quebec: further evidence for the low palaeolatitude of Huronian glaciation. *Earth Planet. Sci. Lett.* **172**, 273–285.

Schmitt J. M. (1999) Weathering, rainwater and atmospheric chemistry: an example and modeling of granite weathering in present conditions, in a CO_2 rich and in an anoxic palaeoatmosphere. In *Palaeoweathering, Palaeosurfaces and Continental Deposits* (eds. M. Thiry and R. Simon-Coinçon). Int. Assoc. Sedimentology Spec. Publ., Blackwell, Oxford, vol. 27, pp. 21–41.

Schumm S. A. (1956) The role of creep and rainwash on the retreat of badland slopes. *Am. J. Sci.* **254**, 693–706.

Schwartzmann D. W. and Volk T. (1991) Biotic enhancement of weathering and surface temperatures of Earth since the origin of life. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **90**, 357–371.

Schwarz T. (1997) Lateritic paleosols in central Germany and implications for Miocene paleoclimate. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **129**, 37–50.

Serdyuchenko D. P. (1968) Metamorphosed weathering crusts of the Precambrian: their metallogenic and petrographic fabric. In *Precambrian Geology* (ed. B. Hejtman). Proc. 13th Int. Geol. Congr. Prague. Academia, Prague, vol. 4, pp. 37–42.

Sheldon N. D., Retallack G. J., and Reed M. H. (2001) Siderite–iron–silicate equilibria in paleosols as an atmospheric CO_2 paleobarometer or paleoproductivity index? *Abstr. Geol. Soc. Am. Geol. Soc. London Global Meet. Edinburgh*, 42.

Sheldon N. D., Retallack G. J., and Tanaka S. (2002) Geochemical climofunctions from North American soils and application to paleosols across the Eocene–Oligocene boundary in Oregon. *J. Geol.* **110**, 687–696.

Sherwood-Pike M. A. and Gray J. (1985) Silurian fungal remains: probable records of Ascomycetes. *Lethaia* **18**, 1–20.

Siegenthaler U. and Sarmiento J. L. (1993) Atmospheric carbon dioxide and the ocean. *Nature* **365**, 119–125.

Snigirevskaya N. S., Popov L. E., and Zdebsak D. (1992) Novie nakhodki ostatkov drevnishchikh vishchikh rastenii v srednem ordovike yuzhnogo kazachstana (New findings of the oldest higher plant remains in the Middle Ordovician of South Kazakhstan). *Bot. Zh.* **77**(4), 1–8.

Soil Survey Staff (1999) *Keys to Soil Taxonomy*. Pocahontas Press, Blacksburg, Virginia.

Stallard R. F. (1998) Terrestrial sedimentation and the carbon cycle: coupling weathering and erosion to carbon burial. *Global Biogeochem. Cycles* **12**, 231–257.

Stanley S. M. and Hardie L. A. (1999) Hypercalcification: paleontology links plate tectonics and geochemistry to sedimentology. *GSA Today* **9**(2), 1–7.

Steiner M. and Reitner J. (2001) Evidence of organic structures in Ediacara-type fossils and associated microbial mats. *Geology* **29**, 1119–1122.

Strömberg C. A. E. (2002) The origin and spread of grass-dominated ecosystems in the Late Tertiary of North America: preliminary results concerning the evolution of hypsodonty. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **177**, 59–75.

Strother P. (2000) Cryptospores: the origin and evolution of the terrestrial flora. In *Phanerozoic Terrestrial Ecosystems* (eds. R. A. Gastaldo and W. A. DiMichele). Paleont, Soc. Short Course Notes, vol. 6, pp. 3–20.

Strother P. K., Al-Hatri S., and Traverse A. (1996) New evidence for land plants from the lower Middle Ordovician of Saudi Arabia. *Geology* **24**, 55–58.

Sugden D. E., Marchant D. R., Potter N., Souchez R. A., Denton G. H., Swisher C. C., and Tison J. L. (1995) Preservation of Miocene glacier ice in East Antarctica. *Nature* **376**, 412–414.

Taylor F., Eggleton R. A., Holzhauer C. C., Maconachie L. A., Gordon M., Brown M. C., and McQueen K. G. (1992) Cool climate lateritic and bauxitic weathering. *J. Geol.* **100**, 669–677.

Taylor T. N. and Taylor E. L. (2000) The Rhynie Chert ecosystem: a model for understanding fungal interactions. In *Microbial Endophytes* (eds. C. W. Bacon and J. F. White). Dekker, New York, pp. 31–47.

Thaer, A. D. (1857) *The Principles of Practical Agriculture* (translated by W. Shaw and C. W. Johnson). Saxton, New York.

Thorp J. and Reed E. C. (1949) Is there laterite in rocks of the Dakota Group? *Science* **109**, 69.

Trewin N. H. and McNamara K. J. (1995) Arthropods invade the land: trace fossils and palaeoenvironments of the Tumblagooda Sandstone (?Late Silurian) of Kalbarri, Western Australia. *Roy. Soc. Edinburgh, Earth Sci. Trans.* **85**, 117–210.

Truswell E. M. (1987) The initial radiation and rise to dominance of angiosperms. In *Rates of Evolution* (eds. K. S. W. Campbell and M. F. Day). Allen and Unwin, London, pp. 101–128.

Veizer J., Godderis Y., and François L. M. (2000) Evidence for decoupling of atmospheric CO_2 and global climate during the Phanerozoic. *Nature* **408**, 698–701.

Veverka J., Thomas P., Harch A., Clark B., Bell J. F., Carcich B., Joseph J., Chapman C., Merline W., Robinson M., Malin M., McFaddem L. A., Murchie S., Hawkins S. E., Farquahar R., Isenberg N., and Cheng A. (1997) NEAR's flyby of 253 Mathilde: images of a C asteroid. *Science* **278**, 2109–2114.

Vitousek P. M., Chadwick O. A., Crews T. E., Fownes J. H., Hendricks D. M., and Herbert D. (1997a) Soil and ecosystem development across the Hawaiian Islands. *GSA Today* **7**(9), 1–8.

Vitousek P. M., Mooney H. A., Lubchenko J., and Melillo J. M. (1997b) Human domination of Earth's ecosystems. *Science* **277**, 494–499.

Wang H., Liu C. L., and Follmer L. R. (1998) Climatic trend and habitat variation based on oxygen and carbon isotopes in paleosols from Liujiapo, Shaanxi, China. *Quat. Int.* **51/52**, 52–54.

Watanabe Y., Martini J. E. J., and Ohmoto H. (2000) Geochemical evidence for terrestrial ecosystems 2.6 billion years ago. *Nature* **408**, 574–578.

Webster T. (1826) Observations on the Purbeck and Portland Beds. *Geol. Soc. London Trans.* **2**, 37–44.

Williams G. E. (1986) Precambrian permafrost horizons as indicators of paleoclimate. *Precamb. Res.* **32**, 233–242.

Williams G. E. and Schmidt P. W. (1997) Palaeomagnetic dating of the sub-Torridonian weathering profiles, NW Scotland: verification of Neoproterozoic palaeosols. *Geol. Soc. London J.* **154**, 987–997.

Wing S. L. and Boucher L. D. (1998) Ecological aspects of the Cretaceous flowering plant radiation. *Annu. Rev. Earth Planet. Sci.* **26**, 379–421.

Yang W. and Holland H. D. (2003) The Hekpoort paleosol at Strata 1 Gaborone, Botswana: soil formation during the Great Oxidation Event. *Am. J. Sci.* **303**.

Yapp C. J. and Poths H. (1994) Productivity of pre-vascular biota inferred from $Fe(CO_3)OH$ content of goethite. *Nature* **368**, 49–51.

Young G. M. and Long D. G. F. (1976) Ice wedge casts from the Huronian, Ramsay Lake Formation (2300 m.y. old), near Espanola, northern Canada. *Palaeogeogr. Palaeoclimatol. Palaeoecololo.* **19**, 191–200.

Zachos J., Pagani M., Sloan L., Thomas E., and Billups K. (2001) Trends, rhythms and aberrations in global climate 65 Ma to present. *Science* **292**, 689–693.