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James R. Ehleringer Thure E. Cerling
M. Denise Dearing
Editors

A History of Atmospheric CO_2 and Its Effects on Plants, Animals, and Ecosystems

With 151 Illustrations

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James R. Ehleringer
M. Denise Dearing
Department of Biology
University of Utah
Salt Lake City, UT 84112
USA

Thure E. Cerling
Department of Geology and Geophysics
and
Department of Biology
University of Utah
Salt Lake City, UT 84112
USA

Cover illustration: Illustrated are the changes in the atmospheric carbon dioxide concentrations over three time periods. The left plate shows long-term decreases in atmospheric carbon dioxide levels over the last 550 million years and the role of the biota in significantly decreasing carbon dioxide levels when plants invaded land. The middle plate shows the variations in carbon dioxide levels over the last 400,000 years. The right plate shows the imprint of humans over the last half century, increasing carbon dioxide levels significantly well above interglacial levels. Data are based on graphics in Chapters 1, 2, 4, and 5.

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Preface

Our planet's atmosphere is thought to have changed gradually and over a very wide range of CO_2 concentrations throughout history. From ancient atmospheric gases trapped in ice bubbles, we have strong evidence indicating that atmospheric CO_2 values reached minimum concentrations of approximately 180 parts per million during the Last Glacial Maximum, which was only 15,000 years ago. At the other extreme, calculations suggest that some 500+ million years ago the atmospheric CO_2 concentrations may have been about 4000 to 5000 parts per million. The available evidence suggests that the decline in atmospheric CO_2 over time has been neither steady nor constant, but rather that there have been periods in Earth's history when CO_2 concentrations have decreased and other periods in which CO_2 levels were elevated. The changes in atmospheric CO_2 concentrations over geological time periods are the result of biological, chemical, and geological processes. Biogeochemical processes play a significant role in removing organic matter from the active carbon cycle at Earth's surface and in forming carbonates that are ultimately transported to the continental plates, where they become subducted away from Earth's surface layers.

Atmospheric CO_2 concentrations rose rapidly as Earth transitioned out of the last Ice Age, and the atmosphere has changed dramatically since the dawn of the Industrial Age with especially large increases over the past five decades. Both terrestrial and aquatic plant life significantly influence the sequestration of atmospheric CO_2 into organic matter. There is now substantial evidence to show that these terrestrial and marine photosynthetic organisms currently play a major

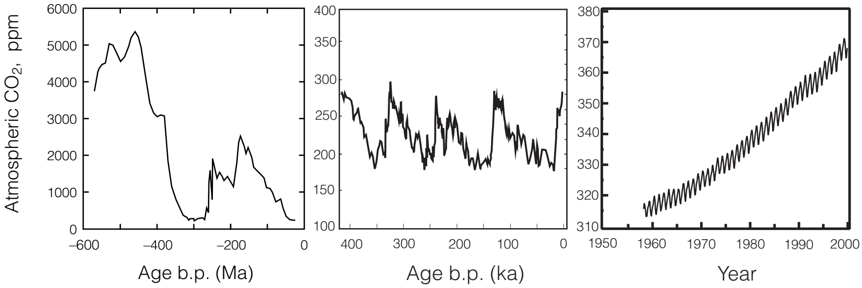

Illustration. Illustrated are the changes in the atmospheric carbon dioxide concentrations over three time periods. The left plate shows long-term decreases in atmospheric carbon dioxide levels over the last 550 million years and the role of the biota in significantly decreasing carbon dioxide levels when plants invaded land. The middle plate shows the variations in carbon dioxide levels over the last 400,000 years. The right plate shows the imprint of humans over the last half century, increasing carbon dioxide levels significantly well above interglacial levels. Data are based on graphics in Chapters 1, 2, 4, and 5.

role in reducing the rate of atmospheric CO_2 increase. It is thought that, in turn, and over much longer time periods, atmospheric CO_2 concentrations greatly affected both the evolution and the functioning of biota.

In this volume, we explore interactions among atmospheric CO_2, ecosystem processes, and the evolution and functioning of biological organisms. The motivation for this volume originated from a Packard Foundation award to the University of Utah to promote basic interdisciplinary research involving geochemistry, paleontology, and biology and interactions among atmospheric CO_2, plants, and animals. More specifically, this volume is the result of a symposium that expanded on the original interdisciplinary research by bringing together a diverse scientific audience to address these interactions from an even broader perspective. Too often by working in separate disciplines, we fail to realize our common ground and overlapping interests. In this volume, we try to capture some of the excitement revolving around the known changes in atmospheric CO_2, how these changes in our atmosphere have influenced biological processes across our planet, and in turn how biological processes have produced feedback to the atmosphere and thereby have influenced the rate of change in atmospheric CO_2.

The first section of this volume focuses both on understanding processes that have influenced atmospheric CO_2 and on quantitatively documenting the known variations in atmospheric CO_2 over the past several hundred million years. The chapters include coarse-scale calculations of the possible ranges of atmospheric CO_2 based on geological proxies as well as fine-scale, high-precision measurements based on ice cores over the past four hundred thousand years. We complete this documentation with direct observations over the past five decades from the longest continuously running atmospheric measurement program to date.

In the second section, we examine how changes in atmospheric CO_2 have influenced the evolution and expansion of not only terrestrial plants but also animals, including humans. Here we see that there is strong physiological, ecological, and evolutionary evidence suggesting that changes in atmospheric CO_2 have had both direct and indirect effects on the kinds of plant taxa that dominate Earth's surface. Certainly, atmospheric CO_2 concentrations influence primary productivity, but apparently they also influence the abundance of different types of plants. In turn, these changes in the food supply are likely to have influenced the evolution of herbivorous animal systems. Paleontological studies provide convincing evidence of the changes in mammalian taxa, with stable isotope analyses providing information about the dietary preferences of different mammalian herbivore lineages.

The third and fourth sections of this volume explore the functioning of historical and modern ecosystems and, in particular, how the structure and functioning of current ecosystems are expected to change under future elevated atmospheric CO_2 concentrations. In these sections, we focus on understanding carbon sequestration patterns of terrestrial ecosystems and how they are influenced by interactions with other aspects of the climate and physical environment. Terrestrial ecosystems cannot be fully grasped without an understanding of the animal herbivores that selectively graze on different vegetation components. Elevated atmospheric CO_2 concentrations are expected to impact herbivorous animal systems indirectly through the effect of changes in food quality on herbivory. The work presented in these sections points to the need for bringing together plant, animal, and climate studies if we are to try, ultimately, to predict the consequences of changes in atmospheric CO_2 on the functioning of future terrestrial landscapes.

This volume is an effort to bridge disciplines, bringing together the different interests in atmospheric science, geochemistry, biology, paleontology, and ecology. It is difficult to understand historical changes in atmospheric CO_2 without appreciating the role of plants in modifying soil chemistry and photosynthesis as a carbon-sequestering process. Our understanding of the future atmosphere, and therefore our future climate system, will hinge on having knowledge of the carbon-sequestering capacities of future vegetation, especially in light of changes in the thermal environment and the nutrients required for sustained plant growth.

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James R. Ehleringer
Thure E. Cerling
M. Denise Dearing

Contents

Contributors

Bacastow, Robert B.	Scripps Institution of Oceanography, University of California, San Diego, CA 92093-0244, USA
Barnola, Jean-Marc	CNRS Laboratoire de Glaciologie et Géophysique de l'Environnement (LGGE), Grenoble, France
Beerling, David J.	Department of Animal and Plant Sciences, University of Sheffield, Sheffield S10 2TN, UK
Berner, Robert A.	Department of Geology and Geophysics, Yale University, New Haven, CT 06520, USA
Bhattacharya, S.K.	Physical Research Laboratory, Navarangpura, Ahmedabad 380 009, India
Blunier, Thomas	Climate and Environmental Physics, Physics Institute, University of Bern, Switzerland

Braswell, Bobby H.	Morse Hall, University of New Hampshire, 39 College Road, Durham, NH 03824-3525, USA
Cerling, Thure E.	Department of Geology and Geophysics and Department of Biology, University of Utah, 257 South 1400 East, Salt Lake City, UT 84112, USA
Chamberlain, C. Page	Department of Geological and Environmental Sciences, Stanford University, Stanford, CA 94305, USA
Chapman, David S.	Room 719, Department of Geology and Geophysics, University of Utah, 135 S 1460 E, Salt Lake City, UT 84112-0111, USA
Churkina, Galina	Max Planck Institute for Biogeochemistry, Carl-Zeiss-Promenade 10, 07745 Jena, Germany
Dearing, M. Denise	Department of Biology, University of Utah, 257 South 1400 East, Salt Lake City, UT 84112, USA
Ehleringer, James R.	Department of Biology, University of Utah, 257 South 1400 East, Salt Lake City, UT 84112, USA
Enting, Ian	CSIRO Atmospheric Research, Private Bag 1, Aspendale, Victoria 3195, Australia
Etheridge, David	CSIRO Atmospheric Research, Private Bag 1, Aspendale, Victoria 3195, Australia
Francey, Roger	CSIRO Atmospheric Research, Private Bag 1, Aspendale, Victoria 3195, Australia
Freeman, Katherine H.	Department of Geosciences, Pennsylvania State University, University Park, PA 16802, USA

Ghosh, Parthasarathi	Geological Studies Unit, Indian Statistical Institute, 203, B.T. Road, Calcutta 700 035, India
Ghosh, Prosenjit	Physical Research Laboratory, Navarangpura, Ahmedabad 380 009, India
Harris, John M.	George C. Page Museum of La Brea Discoveries, 5801 Wilshire Boulevard, Los Angeles, CA 90036, USA
Harris, Robert N.	Room 719, Department of Geology and Geophysics, University of Utah, 135 South 1460 East, Salt Lake City, UT 84112, USA
Heimann, Martin	Max Planck Institute for Biogeochemistry, Jena, Germany
Huxman, Travis E.	Ecology and Evolutionary Biology, University of Arizona, Tucson, AZ 85721-0088, USA
Joyce, Linda A.	Rocky Mountain Research Station, USDA Forest Service, Fort Collins, CO 80526, USA
Keeling, Charles D.	Scripps Institution of Oceanography, University of California, San Diego, CA 92093-0244, USA
Leafloor, James O.	Canadian Wildlife Service, Winnipeg R3C 4W2, Canada
Leakey, Meave G.	The National Museums of Kenya, P.O. Box 40658, Nairobi, Kenya
Lindroth, Richard L.	237 Russell Laboratories, Department of Entomology, University of Wisconsin, Madison, WI 53706, USA
Lund, Christopher P.	Carnegie Institution of Washington, Institute for Global Ecology, 260 Panama Street, Stanford, CA 94305, USA

Lupia, R.	Sam Noble Oklahoma Museum of Natural History and School of Geology and Geophysics, University of Oklahoma, 2401 Chautauqua Avenue, Norman, OK 73072, USA
MacFadden, Bruce J.	Florida Museum of Natural History, P.O. Box 112710, Gainesville, FL 32611, USA
McElwain, Jennifer C.	Department of Geology, Field Museum of Natural History, 1400 South Lake Shore Drive, Chicago, IL 60605, USA
McMurtrie, Ross E.	School of Biological, Earth and Environmental Sciences, University of New South Wales, Sydney 2052, Australia
McWilliams, Scott R.	Department Natural Resources Science, University of Rhode Island, 105 Coastal Institute in Kingston, Kingston, RI 02881, USA
Medlyn, Belinda E.	School of Biological Earth and Environmental Sciences, University of New South Wales, Sydney, New South Wales 2052, Australia
Meijer, Harro A.	Centre for Isotope Research, University of Groningen, Groningen, Netherlands
Monnin, Eric	Climate and Environmental Physics, Physics Institute, University of Bern, Switzerland
Norby, Richard J.	Environmental Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA
Pagani, Mark	Department of Earth and Planetary Sciences, Yale University, New Haven, CT 06520, USA

Piper, Stephen C.	Scripps Institution of Oceanography, University of California, San Diego, CA 92093-0244, USA
Rayner, Peter	CSIRO Atmospheric Research, Private Bag 1, Aspendale, Victoria 3195, Australia
Sage, Rowan F.	Department of Botany, University of Toronto, 25 Willcocks Street, Toronto, Ontario M5S 3B2, Canada
Schimel, David	National Center for Atmospheric Research, 1850 Table Mesa Drive, Boulder, CO 80305, USA
Shaw, M. Rebecca	Carnegie Institution of Washington, Institute for Global Ecology, 260 Panama Street, Stanford, CA 94305, USA
Trenbath, James	Max Planck Institute for Biogeochemistry, Carl-Zeiss-Promenade 10, 07745 Jena, Germany
Trudinger, Cathy	CSIRO Atmospheric Research, Private Bag 1, Aspendale, Victoria 3195, Australia
van der Merwe, Nikolaas J.	Archaeology Department, University of Cape Town, Rondebosch 7701, South Africa
Wahlen, Martin	Scripps Institution of Oceanography, University of California, San Diego, CA 92093-0244, USA
Waldbauer, Jacob R.	Department of Geological and Environmental Sciences, Stanford University, Stanford, CA 94305, USA
Ward, Joy K.	Department of Biology, University of Utah, 257 South 1400 East, Salt Lake City, UT 84112, USA

Whorf, Timothy P.	Scripps Institution of Oceanography, University of California, San Diego, CA 92093-0244, USA
Willis, K.J.	School of Geography and the Environment, University of Oxford, Mansfield Road, Oxford OX1 3PS, UK
Wullschleger, Stan D.	Environmental Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6422, USA

1. The Rise of Trees and How They Changed Paleozoic Atmospheric CO_2, Climate, and Geology

Robert A. Berner

1.1 Introduction

Large vascular plants with deep, extensive root systems arose and spread over the continents starting about 380 million years ago during the Devonian Period. Previously there were only bryophytes, algae, and small vascular plants restricted to the edges of water courses (Gensel and Edwards 2001). Large plants are important because their vast root systems produce a larger interface between the geosphere and the biosphere than do the more primitive species, where the plant/mineral interface is greatly reduced. This large interface allows plants to take up nutrients more rapidly, to grow bigger and faster (Algeo and Scheckler 1998), and to accelerate mineral weathering (Berner 1998). In addition, the larger plants, upon death, supply a much greater mass of organic matter for burial in sediments. Because of these effects, the rise of large vascular plants brought about a dramatic change in the level of atmospheric CO_2, the climate, and the formation of carbon-rich deposits (coal) during the late Paleozoic.

1.2 Plants, Weathering, and CO_2

The level of CO_2 is controlled, on a long-term, multimillion-year timescale, by two carbon cycles: the silicate-carbonate cycle and the organic matter cycle. The silicate-carbonate cycle can be represented succinctly by the following reactions (stated in words by Ebelmen 1845 but symbolized by Urey 1952):

$$CO_2 + CaSiO_3 \rightarrow CaCO_3 + SiO_2 \tag{1.1}$$

$$CO_2 + Mg\ SiO_3 \rightarrow MgCO_3 + SiO_2 \tag{1.2}$$

The arrows, from left to right, refer to all Ca-Mg silicate weathering (the silicate formulae are generalized) plus sedimentation of marine carbonates. These two weathering reactions summarize many intermediate steps, including photosynthetic fixation of CO_2, root/mycorrhizal respiration, organic litter decomposition in soils, the reaction of carbonic and organic acids with primary silicate minerals thereby liberating cations to solution, the conversion of CO_2 to HCO_3^- in soil and ground water, the flow of riverine Ca^{++}, Mg^{++}, and HCO_3^- to the sea, and the precipitation of Ca-Mg carbonates in bottom sediments. (The reactions, from right–to–left, represent thermal decomposition of carbonates at depth resulting in degassing of CO_2 to the atmosphere and oceans by diagenesis, metamorphism, and volcanism.)

Plants accelerate the rate of weathering and liberation of Ca^{++}, Mg^{++}, and HCO_3^- to solution in the following ways:

1. Rootlets (+ symbiotic microflora) with high surface area secrete organic acids/chelates, which attack primary minerals in order to gain nutrients (in this case Ca and Mg).
2. Organic litter decomposes to carbonic and organic acids providing additional acid for mineral dissolution.
3. Plants recirculate water via transpiration and thereby increase water/mineral contact time.
4. Plants anchor clay-rich soil against erosion allowing retention of water and continued dissolution of primary minerals between rainfall events.

Based on present-day field studies of the quantitative effects of plants on weathering rate (Drever and Zobrist 1992; Arthur and Fahey 1993; Bormann et al. 1998; Moulton, West, and Berner 2000), these effects combine to accelerate silicate weathering rates by a factor of approximately 2 to 10. When the field results are applied to global carbon cycle modeling, the calculated effect on atmospheric CO_2, due to the rise of trees during the Paleozoic Era, turns out to be dramatic (Fig. 1.1).

1.3 Plants, the Organic Cycle, and CO_2

The organic cycle can be represented succinctly by the following reaction (stated in words by Ebelmen 1845):

$$CO_2 + H_2O \rightarrow CH_2O + O_2 \tag{1.3}$$

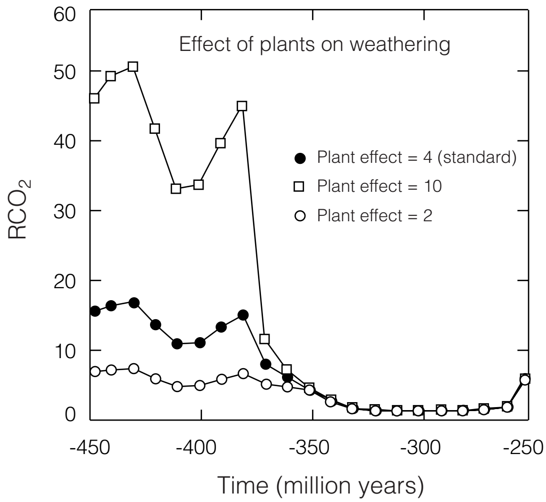

Figure 1.1. Plot of RCO_2 versus time based on GEOCARB III modeling (Berner and Kothavala 2001). The three curves illustrate sensitivity to the quantitative effect of the rise of large land plants on weathering rate. RCO_2 is the ratio of mass of carbon dioxide in the atmosphere at a past time divided by the present preindustrial mass.

The reaction, from left to right, refers to the burial of organic matter in sediments. This represents a net excess of global photosynthesis over respiration and is a major sink for atmospheric CO_2. (From right to left, the reaction refers to weathering of old organic matter (kerogen) on the continents or thermal decomposition of organic matter upon deep burial combined with the oxidation of reduced gases emitted to the atmosphere and oceans.)

Enhanced burial of organic matter occurred after the rise of large land plants. This is because of the production of a new compound, lignin, which is relatively resistant to biodecomposition. The burial of lignin-derived humic material, and other plant-derived microbiallyresistant substances, in terrestrial and coastal swamps and in the oceans (after transport there via rivers) resulted in not only large increases in the global burial of organic matter (Holland 1978; Berner and Canfield 1989) but also the formation of vast coal deposits of the Carboniferous and Permian periods (Bestougeff 1980). In fact, production and preservation of terrestriallyderived organic debris was so large that it may have dominated over the burial of marine-derived organic matter at this time (Berner and Raiswell 1983; Broecker and Peacock 1999).

1.4 Carbon Cycle Modeling

A carbon cycle model, GEOCARB, has been constructed for calculating weathering rates, carbon burial rates, degassing rates, and levels of atmospheric CO_2

over Phanerozoic time (Berner 1994; Berner and Kothavala 2001). The model quantifies the effects of changes in climate, tectonics, paleogeography, paleohydrology, solar evolution, and plant evolution on the rates of silicate weathering. Sensitivity analysis indicates that for the Paleozoic Era, the most important factor affecting CO_2 was the rise of land plants. Feasible variations in tectonic, paleogeographic, and other factors result in CO_2 variations that are far less divergent than those brought about by plant evolution. Sensitivity of atmospheric CO_2 to the value used for the acceleration of Ca-Mg silicate weathering by plants, based on the results of modern plant-weathering studies mentioned above, is shown in Fig. 1.1. Use of a factor of 4, based on our own modern plant studies in Iceland (Moulton, West, and Berner 2000) results in the plot of CO_2 versus time shown in Fig. 1.2.

The theoretical values of Fig. 1.2 agree well with those obtained for paleo-CO_2 by independent methods (Mora, Driese, and Colarusso 1996; McElwain and Chaloner 1995; Mora and Driese 1999; Cox, Railsback, and Gordon 2001). The figures show that tree-accelerated weathering brought about a large drop in atmospheric CO_2. However, the cause of this drop in CO_2 is often misrepresented as resulting from simply an increased weathering carbon flux. Instead, the acceleration of weathering by plants was balanced by greenhouse-induced decel-

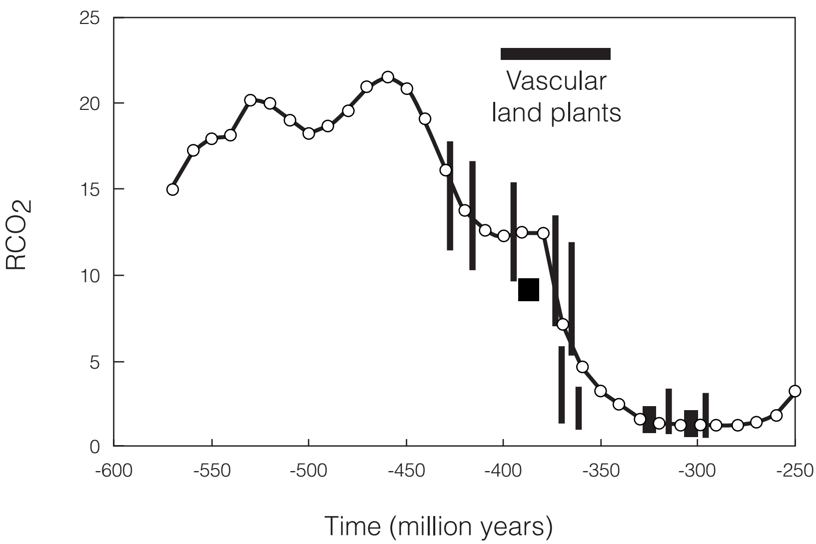

Figure 1.2. Plot of RCO_2 versus time based on GEOCARB III modeling for a fourfold effect (Moulton, West, and Berner 2000) of plants on weathering rate (line connecting dots). The superimposed vertical bars and larger squares represent independent estimates of paleo-CO_2 via the carbonate paleosol method (Mora, Driese, and Colarusso 1996; Mora and Driese 1999; Cox, Railsback, and Gordon 2001), and the stomatal ratio method (McElwain and Chaloner 1995), respectively.

eration of weathering due to falling CO_2, and this resulted in the stabilization of CO_2 at a series of lower levels.

Further drop of CO_2 into the Carboniferous and Permian periods is due to the increased burial of organic matter accompanying the production of bioresistant organic matter by large woody land plants. This is shown in Fig. 1.3 for the result of maintaining the carbon isotopic composition of the oceans and atmosphere constant with time and comparing the result to that based on recorded carbon isotopic data (Berner 1994).

Organic burial rate in GEOCARB modeling is calculated mainly from the carbon isotopic record, with elevated oceanic $^{13}C/^{12}C$ representing faster removal of ^{13}C-impoverished carbon from seawater and the atmosphere due to greater photosynthesis and burial. The additional drop in CO_2 is due to a rise in oceanic $^{13}C/^{12}C$ to high values between 400 and 250 million years ago. (Rapid isotopic equilibration of carbon isotopes between the oceans and the atmosphere is assumed so that burial of plant-derived organic matter on land can affect the $^{13}C/^{12}C$ of the oceans via atmospheric and riverine transport.)

1.5 Climatic and Geological Consequences

The large decrease in atmospheric CO_2 beginning in the Devonian and continuing into the Carboniferous (see Fig. 1.2) correlates with the initiation of continental glaciation. The Parmo-Carboniferous glaciation was the longest and most extensive glaciation of the entire Phanerozoic (Crowley and North 1991),

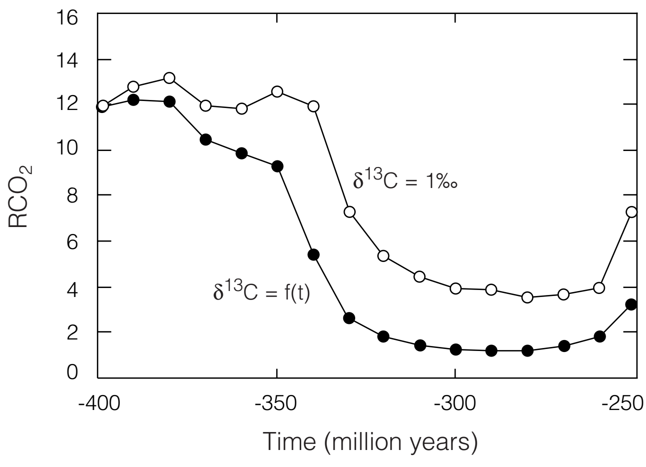

Figure 1.3. Plot of RCO_2 versus time showing the effect of the variation of $^{13}C/^{12}C$ during the Permian and Carboniferous. The lower curve is derived from GEOCARB II modeling (Berner 1994) based on published carbon isotope data. The upper curve represents the effect of holding the value of $\delta^{13}C = 1‰$ for the entire period.

lasting about 80 million years and extending at times from the South Pole to as far north as 30°S. Coincidence of this glaciation with a drop in CO_2 (Crowley and Berner 2001) strongly suggests that CO_2, by way of the atmospheric greenhouse effect, was a major factor in bringing about the glaciation. Although the waxing and waning of the glaciers during this period could have been caused by, for example, variations in Earth's orbit (Crowley and North 1991), the most reasonable explanation is that the lowering of CO_2 to a level sufficient for the year-round accumulation of snow and ice at high latitudes allowed glaciation to be initiated and to occur on a continental scale. This lowering of CO_2 resulted primarily from the rise of large vascular land plants.

The massive burial of plant-derived organic matter also led to the formation of vast coal deposits during the late Paleozoic Era. Permian and Carboniferous coals are much more abundant than coals from any other period (Bestougeff 1980), in spite of the fact that these coals are much older and have been subjected to loss by erosion for a much longer time. This must mean that original production and/or preservation for burial was unusually large. Perhaps preservation was enhanced by a lag in the evolution of lignin-decomposing microorganisms (Robinson 1991). However, the coal abundance also owes something to paleogeography. During the Permian and Carboniferous periods there was one large continent (Pangaea) with vast lowlands under wet climates that were topographically and geomorphically suitable for the growth of swamp plants and the preservation of their debris. Thus, the Permo-Carboniferous increase in organic burial probably was due to both biological and geological factors.

1.6 Summary

The effect on atmospheric CO_2 of the spread of large vascular plants beginning in the Devonian was twofold. First, the uptake of nutrients from rocks resulted in the enhanced weathering of Ca-Mg silicate minerals resulting in the transfer of CO_2 from the atmosphere to marine Ca-Mg carbonates. Second, the rise of trees caused the production of large amounts of microbially resistant organic matter, in the form of lignin, which resulted in increased sedimentary organic burial and further CO_2 removal. These changes in the carbon cycle led to a large drop in atmospheric CO_2, massive long-term glaciation, and the formation of vast coal deposits. Computer models of the long-term carbon cycle, based partly on field studies of the effects of plants on modern weathering, have been employed to calculate atmospheric CO_2 levels over this time period; the resulting values agree with independent estimates.

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2. Atmospheric CO_2 During the Late Paleozoic and Mesozoic: Estimates from Indian Soils

Prosenjit Ghosh, S.K. Bhattacharya, and Parthasarathi Ghosh

2.1 Introduction

Carbon dioxide (CO_2) and water vapor are major greenhouse gases in Earth's atmosphere that control the planet's surface temperature (Houghton and Wood 1989). Variations in CO_2 levels can lead to major changes in climate, surface processes, and biota. For example, over the past two centuries the combustion of fossil fuels has raised the atmospheric CO_2 level from about 275 ppmV (Barnola et al. 1987) to the current level of 365 ppmV (Keeling 1994); this has caused already discernible increases in Earth's near-surface temperature (IPCC 1990). Over a longer timescale, analysis of trapped gases in the polar icecores (Barnola et al. 1987) showed that during the past 150,000 years CO_2 levels have oscillated between approximately 200 and 300 ppmV. Knowledge of past carbon dioxide levels and associated paleoenvironmental and paleoecological changes is useful for predicting future consequences of the current increase in atmospheric CO_2.

While it is possible to directly measure the CO_2 content of the late Pleistocene and Holocene atmosphere, direct estimation of CO_2 levels in the atmosphere is not possible for the pre-Pleistocene epoch.. Several indirect methods (proxy) to estimate the paleo-CO_2 concentration in the atmosphere have been proposed: for example, carbon isotopic analysis of pedogenic carbonates, stomatal index count of fossil leaves, and isotopic composition of marine sedimentary carbon and boron from carbonate fossils (Cerling 1991; McElwain and Chaloner 1996; Ekart et al. 1999; Ghosh, Ghosh, and Bhattacharya 2001; Crowley and Berner 2001). The $\delta^{13}C$ of pedogenic carbonates provide the best $_{p}CO_2$ estimates for the pre-Tertiary (Royer, Berner, and Beerling 2001). The experimental proxies play an important role in putting constraints on the theoretical models of carbon cycle based on mantle evolution (Tajika and Matsui 1992) and biological and tectonic changes in the past (Berner 1994; Berner and Kothavala 2001), which provide estimates of the atmospheric [CO_2] during the Phanerozoic.

How do paleosol carbonates record the past CO_2 level in the atmosphere? These carbonates are precipitated in the root zone of plants when groundwater supersaturated with carbonate ions can release CO_2 by some process. They are common in regions receiving an annual rainfall of less than 800 mm. The addition of CO_2 in the groundwater during plant respiration and subsequent evaporation and transpiration of water from a plant can induce supersaturation and carbonate precipitation. Paleosol carbonates record the isotopic composition of local soil CO_2, which primarily reflects the type of vegetation (fraction of C_3 and C_4 plants) in the ecosystem (Cerling 1984). The soil CO_2 is a mixture of two components: plant respired CO_2 and atmospheric CO_2. It is important to note that $\delta^{13}C$ of atmospheric CO_2 (about-7‰) is very different from that of soil CO_2 (about-25‰). Atmospheric CO_2 penetrates inside the soil by diffusion and mixes with the soil CO_2 leading to its isotopic change. Today, except for ecosystems with very low productivity, such as deserts, the atmospheric contribution to total soil CO_2 is very small because of very low concentration of CO_2 in the modern atmosphere. However, high atmospheric CO_2 can make a significant contribution to total soil CO_2; in times when few or no C_4 plants were present, this contribution could result in significant isotopic shifts in the $\delta^{13}C$ of soil carbonate precipitated in isotopic equilibrium with soil CO_2. Therefore, $\delta^{13}C$ of pedogenic carbonates can act as a proxy indicator for [CO_2] variations in geologic past (Cerling 1991; Ghosh, Bhattacharya, and Jani 1995; Mora, Driese, and Colarusso 1996; Ekart et al. 1999).

To understand the past [CO_2] variations quantitatively, Berner (1994) proposed the GEOCARB II model based on equations governing the CO_2 outgassing and CO_2 consumption through weathering; he then improved it further in GEOCARB III (Berner and Kothavala 2001). Both of these models predict that in the early Phanerozoic (550 Ma) the [CO_2] was 20 times the present atmospheric level (PAL). Subsequently, the $_{p}CO_2$ declined in the middle and late Paleozoic (450–280 Ma) to reach a minimum value (approximately similar to the PAL) at about 300 million years ago. The period from 300 to 200 million years ago was again characterized by a rapid rise in the [CO_2] when it increased to 5 times the PAL. Next came a gradual decline, down to the PAL, with a small peak in the early Tertiary. Such large changes in [CO_2] during the geologic past must have had significant influences on the climate, biota, and surface processes of Earth (Berner 1991 and 1997; Mora, Driese, and Colarusso 1996).

The motivation for the present study came from the discovery of well-developed and well-preserved paleosols in the Gondwana sediments of central India; these paleosols cover the period of significant CO_2 change mentioned above in well-spaced intervals. The stable isotopic composition of pedogenic carbonates formed in these paleosols was investigated to decipher the CO_2 concentrations and to compare them with those predicted by the Berner-model.

2.2 Description of Paleosols from Central India

The Gondwana sediments and the overlying Deccan trap of the Satpura basin (Fig. 2.1) of central India range in age from the Permo-Carboniferous to the uppermost Cretaceous.

The thickness of the whole sedimentary succession is about 5 km (Fig. 2.2). The sediments comprise alternate layers of coarse clastics (sandstones along with extrabasinal conglomerates) and fine clastics (red mudstone/carbonaceous shale/white mudstone). The basal unit of this succession is a Permo-Carboniferous glaciolacustrine deposit called the Talchir Formation. The formations overlying the Talchir represent several episodes of fluvial, lacustrine, and alluvial deposition (Robinson 1967; Casshyap and Tewari 1988; Casshyap and Qidwai 1971; Casshyap, Tewari, and Khan 1993; Veevers and Tewari 1995; Ghosh 1997). Occurrences of fossil vertebrates (Chatterjee and Roychowdhury 1974; Mukherjee and Sengupta 1998; Bandyopadhyay and Sengupta 1998) and freshwater

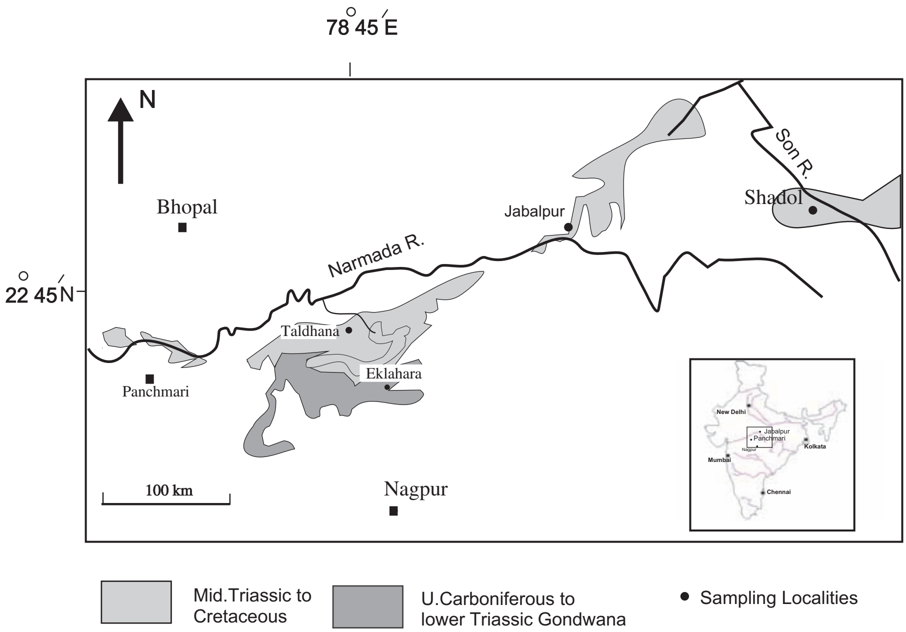


Figure 2.1. Sketch of paleosol locations in the geological map of the Satpura basin and Son Valley basin of the Gondwana supergroup in central India.

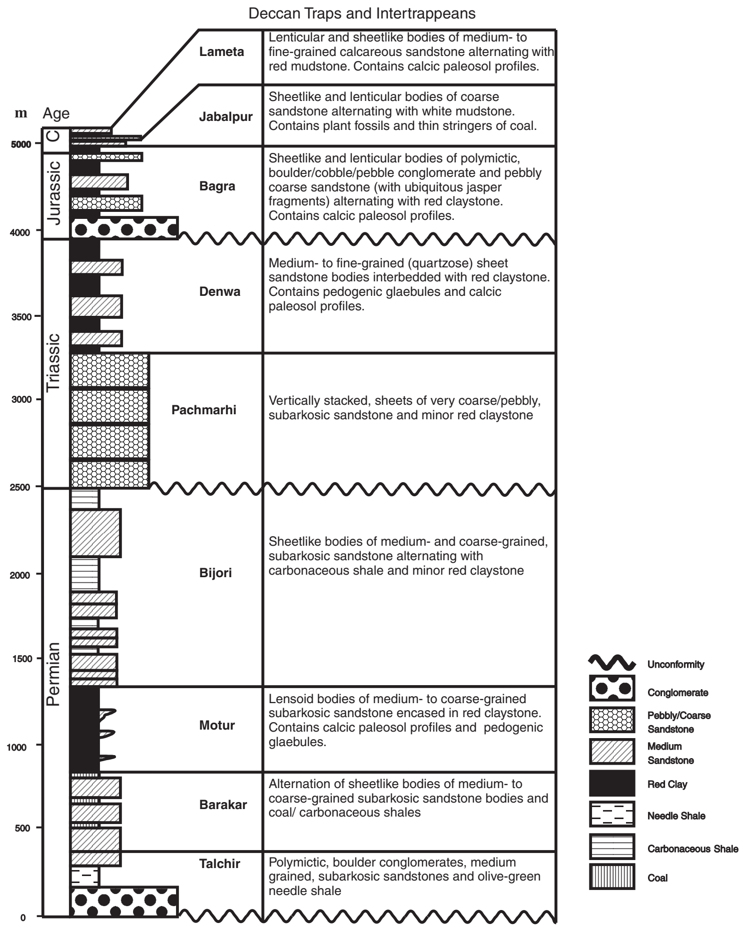


Figure 2.2. Generalized lithostratigraphy of the Gondwana succession of the Satpura basin. (From Ghosh, Ghosh, and Bhattacharrya 2001, with permission from Elsevier Science.)

bivalves, coupled with such evidences of pedogenesis as the presence of rootlet horizons, paleosol profiles, and so forth (Ghosh, Bhattacharya, and Jani 1995, Ghosh, Rudra, and Maulik 1998; Ghosh 1997; Tandon et al. 1995, 1998) give credence to the alluvial origin of these sediments.

In four litho-formations (the Motur, Denwa, Bagra, and Lameta) of the Satpura basin and one ormation (the Tiki) of the Son Valley basin, preserved calcic paleosols have been identified and characterized (Ghosh, Bhattacharya, and Jani 1995; Ghosh 1997, Ghosh, Rudra, and Maulik 1998; Tandon et al. 1995, 1998; Andrews, Tandon, and Dennis 1995). Stable isotopic compositions of the pedogenic carbonates and associated organic matters from the Motur, Bagra, Denwa, and Lameta formations were investigated in an earlier study (Ghosh,

Ghosh, and Bhattacharya 2001). This chapter describes a more refined analysis of the earlier results and presents an additional analysis of soils from the Tiki Formation. A brief description of the five formations is given below.

2.2.1 Motur Formation

The Motur Formation is a 700 m thick succession of fluvial channel sandstone bodies alternating with floodplain complexes made up of red claystone and thin sandy splay deposits. In the middle part of the Motur succession a few calcic paleosols occur within the floodplain deposits. These paleosols are characterised by three to four vertically superposed distinct pedo-horizons forming paleosol profiles (Fig. 2.3A).

Two types of profiles can be recognized. One type is around 50 cm thick, whereas the other is thicker (3–4 m). The thinner variety comprises an uppermost horizon (3–5 cm thick) of coalesced platy globules overlying a 10 to 30 cm thick horizon of closely spaced vertically oriented rhizocretions (Fig. 2.3B).

The rhizocretion horizon grades downward to a horizon with profuse subspherical globules that overlies a gleyed horizon. The uppermost horizon of fused platy globules is similar to the K horizon of modern aridisols whereas the zones of rhizocretions and globules can be compared with the Bk soil horizons (Soil Survey Staff 1975).

The thicker paleosol profiles show a meter-thick upper zone with a number of curved, mutually intersecting inclined surfaces (see Fig. 2.3A), coated with centimeter-thick carbonate layers, within a red claystone host. The underlying horizon is characterized by small, subvertical, dispersed, calcareous rhizocretions. Underneath this horizon is a thin (3–5 cm thick) horizon of subspherical globules overlying a gleyed horizon (~20 cm thick).

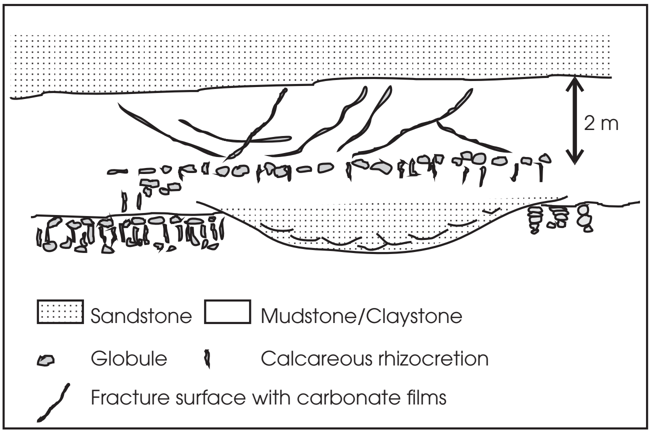


Figure 2.3A. Field sketch of the two vertically superposed calcic paleosol profiles of the Motur Formation, exposed near Eklahara colliery.

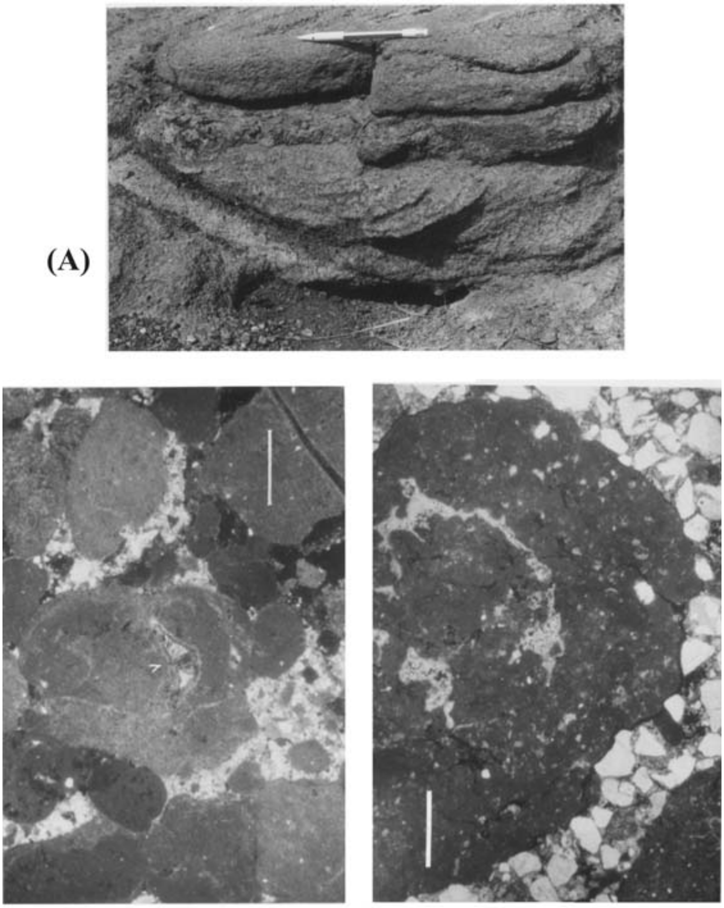
Figure 2.3B. Close-up of globular horizon (Motur Formation, near Eklahara colliery).

The curved inclined surfaces, within the clayey host, in the upper part of these paleosols resemble the zone of pedogenic slickensides (ss horizon) that develop in modern vertisols in response to shrinking and swelling of the soil clay matrix. The underlying horizons of rhizocretions and globules can be compared with modern Bk horizons. The field features of these paleosol profiles are similar to the Appalachian Paleozoic vertic paleosol profiles described by Driese and Mora (1993) and Mora et al. (1998).

A total of 21 samples were collected from the Motur Formation near Eklahara colliery (22°12'N, 78°41'E). Studies on the vertic paleosols have demonstrated that the globules occurring within the vertic horizons are enriched in ^{13}C compared to those occurring below the vertic horizons and compared to the rhizocretions in general (Driese and Mora 1993; Mora, Fastovsky, and Driese 1993). The cracks that develop in the vertic soils in response to the shrinking and swelling of the soil clay matrix possibly allow direct and nondiffusive penetration of the heavier atmospheric CO_2 deeper down the soil; hence, samples from this horizon may provide an incorrectly high estimate of the atmospheric CO_2. The vertic paleosols, therefore, were sampled for rhizocretions and globules from the horizons that occur considerably below the horizon of slickensides and above the gleyed zone. For the thinner paleosols, samples of rhizocretions and globules were collected from the basal part of the horizon of rhizocretions and the underlying horizon of globules. The horizons of platy globules were not sampled; thus, the studies avoided a possible anomalous large contribution of atmospheric CO_2 near the soil-to-atmosphere contact (Cerling 1984, 1991).

2.2.2 Denwa Formation

The Denwa Formation is about 600 m thick at its maximum. The lower half of the formation is characterized by a regular alternation of medium- to fine-grained, thick (3–15 m) fluvial channel sandstone bodies and floodplain deposits. The floodplain deposits comprise red mudstones intercalated with centimeter-to-decimeter thick, fine-grained sandstone layers. In contrast to the lower part of the formation, the upper half is fines-dominated. The red mudstones encase



(A) (B) (C)

Figure 2.4. **(A)** Close-up of a trough cross-stratified channel-fill deposit, made up of pedogenic globules within the upper part of the Denwa Formation. **(B)** Photo-micrograph of pedogenic globules; note the spar-filled cracks within the calcareous matrix of the globules. Scale bar = 0.8 mm. **(C)** Photomicrograph of a globule; note the sharp and rounded outline of the globule and the spar-filled (lighter) circum-granular crack. Scale bar = 1 mm. (**C** from Ghosh, Ghosh, and Bhattacharyya 2001, with permission from Elsevier Science.)

fine-grained (fine sandstones and siltstones) point bar deposits that are 2 to 4 m thick and lenticular channel-fill bodies that are about 1 m thick. Detrital subspherical globules that are the size of pebbles to coarse sand constitute the bulk of these channel-fill bodies. These bodies are internally trough cross-stratified (Fig. 2.4A).

Microscopic observations of the detrital globules reveal that they are composed mostly of micrite and minor microspar with one or two sand-sized detrital quartz grains floating in the carbonate groundmass (Fig. 2.4B).

A number of globules show radial fractures filled with either blocky spars or barite. Spar-filled, circum-granular cracks also have been noted in some of the globules along with such pedogenic features as clotted micrite and corroded detrital quartz grains (Fig. 2.4B,C).

The field occurrence of paleosols in the Denwa Formation is limited, and only the widespread occurrence of detrital globules with pedogenic microfabrics provides indirect evidence of pedogenesis during the later part of the Denwa sedimentation. However, exposed paleosols with two distinct pedohorizons can be studied in a single exposure. The profile is more than 4 m thick. Its upper 2 to 3 m is characterized by a number of inclined and mutually intersecting nearly planer surfaces and dispersed globules the size of small pebbles to coarse sand and pale yellow blotches. Larger inclined features are about 5 m long and 5 to 7 cm thick, whereas the length of the smaller ones is 1 to 2 m and these are less than a centimeter thick. Large inclined features are filled with calcareous very fine sandstone. The surfaces of the smaller inclined surfaces have a polished appearance and are, at places, coated by 1 to 5 cm thick carbonate layers. This horizon passes gradually to an underlying horizon of numerous isolated pebble-sized globules, small (2–7 cm long) calcareous rhizocretions and pale yellow-gray mottles. The larger inclined features of the overlying horizon, however, cut across the lower horizon. The discordant relationship between the horizons and the large inclined features along with their sandy fills suggest that these are possibly desiccation cracks. The smaller inclined features can possibly be equated with the pedogenic slickensides noted in the upper part of the modern day vertisols (Soil Survey Staff 1975). The lower horizon represents the zone of carbonate accumulation at a deeper part of the soil. The macroscopic characters of the Denwa paleosol profiles are also similar to the Appalachian vertic paleosols (Driese and Mora 1993; Mora et al. 1998).

Nineteen samples of soil carbonates were collected from the formation (see Fig. 2.4D). The bulk of the samples comprise detrital pedogenic globules of the channel-fill bodies (between 22°38'N, 78°20'E and 22°35'N, 78°38'E). The rhizocretions and globules from the basal horizon of the paleosol near Taldhana village (22°37'N, 78°32'30"E) also were sampled.

2.2.3 Tiki Formation

The Tiki Formation is a 1200 m thick succession of fluvial channel sandstone bodies alternating with floodplain complexes made up of shale and thin sandy floodplain deposits. Floodplain deposits consist essentially of bright red colored