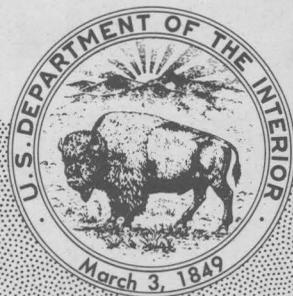


827  
GEOLOGICAL SURVEY CIRCULAR 822



# Paleoclimate and Mineral Deposits



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Edited by Thomas M. Cronin, William F. Cannon,  
and Richard Z. Poore

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G E O L O G I C A L   S U R V E Y   C I R C U L A R   8 2 2

**United States Department of the Interior**

JAMES G. WATT, *Secretary*



**Geological Survey**

Dallas L. Peck, *Director*

**Library of Congress Cataloging in Publication Data**

Main entry under title

Paleoclimate and mineral deposits

(Geological Survey Circular; 822)

Bibliography: p. 49

1. Paleoclimatology—United States. 2. Mines and mineral resources—United States. I. Cronin, Thomas I<sup>a</sup>.

II. Cannon, William F. III. Poore, Richard Z. IV. Series

QE75.C5 no. 822 [QC884] 557.3s [553.1] 83-600159

*Free on application to Distribution Branch, Text Products Section,  
U. S. Geological Survey, 604 South Pickett Street, Alexandria, VA 22304*

## PREFACE

Earth climate obviously plays an important role in our daily lives through its effects on agriculture, floods, droughts, energy use, and other areas. Further, predicting or forecasting future climatic trends has properly been given high priority in national research programs because of the expected increase of global temperatures over the next 100 years owing to increasing atmospheric CO<sub>2</sub>. Perhaps as important, however, is the increasing realization by geologists that past climates have played a primary role in the genesis of economic and strategic fuel and nonfuel minerals. Imbrie (1982) refers to the application of our knowledge of the geologic record of the Earth's climate as "hindcasting." More specifically, predicting the occurrence and distribution of a particular mineral on a global or local scale can be significantly enhanced if geologists understand the particular environmental conditions under which that mineral forms and is preserved and how the distribution of these environments has changed through time. In many marine and continental sedimentary deposits, climatic conditions had a major effect on the physical, chemical, and biological conditions during deposition and diagenesis. In some cases, global conditions at a specific time in Earth history caused the widespread formation of a mineral; a good example is the formation, during middle to Late Cretaceous time, of major oilfields and gasfields that were caused by warm global climates and relatively high sea levels. Conversely, local conditions superimposed on broader climatic trends, such as the formation of major phosphate deposits at regions of upwelling of cool nutrient-rich water along continental margins, also can be important.

Several major advances have brought paleoclimatology to the forefront as a major discipline that unites many previously disjunct areas of geoscience. Among these advances, the success of the Deep Sea Drilling Project in determining the history of the modern ocean basins (Society of Economic Paleontologists and Mineralogists Special Publication No. 32) has given geologists a relatively continuous view of the last 150 m.y. The availability of accurate paleogeographic maps for the Phanerozoic (Ziegler and others, 1979; Scotese, 1979) has provided boundary conditions for paleoclimate reconstructions. The publication of the global "sea-level" curve (Vail and others, 1977) has provided a model for eustatic sea-level events and a framework for examining specific climatic events. Research on Quaternary climates done primarily by the National Science Foundation's CLIMAP Program over the last 10 years has established the key role played by deterministic causes of climatic change, such as the correlation of Milankovitch astronomical cycles with Pleistocene glacial-interglacial cycles.

These new sources of data and resulting concepts about Earth history have given geologists a new perspective from which to study the genesis of economically important commodities such as oil, natural gas, coal, phosphate, metals, bauxites, manganese, sulfides, iron, uranium, and others. Understanding the processes and boundary conditions of the formation and preservation of these commodities is a prerequisite for developing predictive models to guide future exploration. A recent report by the National Academy of Sciences (Berger and Crowell, 1982) notes that our ability to locate new deposits of several important minerals will be improved by increased understanding of climates throughout Earth history.

The U.S. Geological Survey (USGS) is actively involved with paleoclimatic research and, consequently, with linking patterns of past climatic change to mineral deposits. Because paleoclimatology involves almost the entire spectrum of the geosciences, a 2-day workshop (September 23-24, 1982) was convened to bring together geochemists, sedimentologists, paleontologists, hydrologists, marine geologists, mineralogists, and other specialists to provide a forum for interchange of data and ideas. This circular contains expanded abstracts of presentations made during the workshop. The wide variety of topics addressed demonstrates the breadth of expertise, interest, and ongoing research concerning climates and mineralization that exists in the USGS.

The common thread uniting all of the papers presented below is that paleoclimatology is a multidisciplinary field that requires coordination and interchange of ideas and data among scientists. Further, it is clear that the deeper we investigate a sedimentary mineral, the more relevant the paleoenvironmental conditions during deposition and diagenesis become to understanding its formation. As a corollary, we must seek improved sedimentary, geochemical, and paleontologic tools to identify paleoenvironments, and we must test these tools in the field.

Assessing the Nation's mineral and energy resources is a primary and congressionally mandated function of the USGS. We anticipate that future research and advances in understanding paleoclimates and the effects of climate on the origin and distribution of resource-bearing sedimentary rocks will aid the USGS in fulfilling its mission to produce a better inventory of the Nation's known and potential mineral resources.

Thomas M. Cronin  
William F. Cannon  
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*Editors*



## CONTENTS

	Page
Preface-----	III
Continental aluminous weathering sequences and their climatic implications in the United States, by Harry A. Tourtelot-----	1
Effect of sea-level fluctuations on porosity and mineralogic changes in coastal aquifers, by William Back and Bruce B. Hanshaw-----	6
Pliocene and Pleistocene calcitic veins as indicators of paleohydrologic, paleo-climatologic, and neotectonic events, southern Great Basin: An initial appraisal, by Isaac J. Winograd, Barney Szabo, Tyler B. Copen, and Gene C. Doty-----	8
The oxygen minimum zone of continental margins, by Thomas M. Cronin-----	10
Cenozoic paleoceanography, by Richard Z. Poore-----	13
The U.S. Atlantic Continental Margin: Eustasy, paleoceanography, and mineral deposits, by John S. Schlee-----	16
Building a biostratigraphic framework around an anoxic-kenoxic event, by Joseph E. Hazel-----	18
Inorganic geochemistry of deep-sea black shales, by Walter E. Dean-----	19
Some climatic and oceanographic controls on the time and place of mineralization, by W. F. Cannon-----	24
Influences of ocean anoxic events on manganese deposition and ophiolite-hosted sulfide preservation, by Eric R. Force, W. F. Cannon, Randolph A. Koski, Keith T. Passmore, and Bruce R. Doe-----	26
Late Cretaceous and Paleogene nonmarine climates in North America, by Jack A. Wolfe-----	30
Volcanic manganese deposits in the Western Cordillera: Lithologic associations and paleoceanographic settings and economic deposits associated with biogenic siliceous rocks, by James R. Hein and Randolph A. Koski-----	32
Organic carbon, sulfur, and iron relationships as an aid to understanding depositional environments and syngenetic metals in recent and ancient sediments, by Joel S. Leventhal-----	34
Paleozoic atmospheric circulation and oceanic upwelling, by Judith Totman Parrish-----	37
Paleoclimatic controls on the occurrence and quality of coal, by C. B. Cecil, R. W. Stanton, S. G. Neuzil, F. T. Dulong, and L. F. Ruppert-----	40

Carbon dioxide, geochemical modeling, and paleoenvironmental reconstructions, by Eric T. Sundquist-----	43
Isotopic research, climate, and the genesis of mineral deposits, by Bruce R. Doe-----	44
References-----	49

## ILLUSTRATIONS

	Page
FIGURE 1. Map showing selected aluminous weathering sequences in the United States-----	2
2. Graph showing inferred temperatures for Tertiary time-----	4
3. Diagram showing interface between freshwater and seawater flow systems that forms zone of dispersion-----	6
4. Graph showing upward concavity of activity coefficient $\gamma_i$ as a function of ionic strength-----	6
5-7. Diagrams showing:	
5. Diagenetic processes known to occur in mixing zone-----	7
6. Hypothesis that some manganese ores may be deposited in zone of dispersion-----	7
7. Characteristics of oxygen minimum zones-----	11
8. Chart showing Tertiary sea levels and climatic trends-----	15
9. Graph showing observed range and geometric mean of concentrations of major-element oxides and trace elements in samples of red and green claystone and black shale from DSDP Hole 530A-----	20
10. Plots showing carbonate-free concentrations of certain elements versus depth in samples of black shale from DSDP Site 530A-----	21
11. Diagrams showing how certain processes may contribute to accumulation and redeposition of sediments containing various amounts of organic carbon-----	23
12-13. Graphs showing:	
12. Relative rates of accumulation of marine sedimentary deposits of manganese, iron, and phosphate on a worldwide scale-----	24
13. Tons of iron in known deposits of marine sedimentary type as a function of time in comparison with accumulations of crude oil in source rocks as a function of time-----	25
14. Profile showing dissolved manganese and depositional model for anoxic event-----	26
15. Eh-pH diagram showing oxidation path of anoxic water mass-----	27

16. Stratigraphic column showing composite shallow marine manganese deposit-----	27
17. Chart showing age correspondence of ocean anoxic events, shallow marine manganese deposits, and ophiolitic sulfides-----	28
18. Diagram comparing axial ridge vents during and after anoxic events-----	28
19. Stratigraphic record of waning anoxic event at Cyprus-----	29
20. Graph showing relationship of carbon to sulfur in Black Sea marine sediments deposited below oxygenated water and H <sub>2</sub> S-containing water-----	35
21. Diagram showing geochemical relationships in oxic, anoxic, and euxinic sedimentary environments-----	36
22. Map showing atmospheric circulation in the Late Cambrian northern winter-----	39
23. Inferred paleoclimate changes and generalized stratigraphic column from the Upper Mississippian to the Lower Permian central Appalachian Basin-----	42
24. Chart showing distribution pattern for $\delta^{34}\text{S}$ values of H <sub>2</sub> S and sulfide minerals when sulfate $\delta^{34}\text{S}=+20$ percent is reduced by various mechanisms-----	45
25. Map of North America showing contours of approximate average $\delta\text{D}$ values of meteoric water-----	46
26. Graph showing behavior of $\delta\text{D}$ and $\delta^{18}\text{O}$ in meteoric water-----	47
27. Plot of $\delta\text{D}$ of fluid inclusions versus calculated $\delta^{18}\text{O}$ values of hydrothermal fluids for various epithermal ore deposits-----	48



## PALEOCLIMATE AND MINERAL DEPOSITS

### CONTINENTAL ALUMINOUS WEATHERING SEQUENCES AND THEIR CLIMATIC IMPLICATIONS IN THE UNITED STATES

By Harry A. Tourtelot

#### Introduction

Weathering sequences in the geologic record are characterized by accumulations of minerals that form chiefly by weathering processes. Weathering processes result in the mechanical disintegration of rocks and the chemical alteration of minerals at and near the surface of the Earth. Weathering goes on all the time, and the relative intensities and effectiveness of mechanical and chemical processes are controlled in large part by climate as well as other variables. Both mechanical and chemical weathering lead to the primary formation of mineral resources and soils. Patterson (1981) provides an excellent review of weathering processes and some resulting mineral deposits. Bauxite, coal, and evaporites are regarded in themselves as being indicators of warm climates (Frakes, 1979; Habicht, 1979). This paper is concerned with aluminous mineral resources, the circumstances of their origin in relation to climate, and their implications for some other mineral resources.

#### Weathering sequences

About 20 high-alumina clay deposits, which the present author calls weathering sequences, are discussed by Patterson (1967, p. 131-151) as possible aluminum resources. Six of these sequences as well as a residuum and two paleosols not included by Patterson (1967) as potential aluminum resources will be described briefly in order of geologic age. General locations are shown in figure 1.

#### Cheltenham clays of Pennsylvanian age

The refractory clays of Missouri, grouped under the name "Cheltenham," are interpreted by Keller (1968) (see also Keller and others, 1954) to represent the influx of kaolinite-rich weathering products into the early Pennsylvanian depositional system. Some of these products were trapped in sinkholes on the northern flank of the Ozark Dome, and some were concentrated in strata of Pennsylvanian age flanking the Ozarks on the north. The clays in the sinkholes

highest on the dome underwent further weathering in Pennsylvanian time to the extent that pure kaolinite, along with much diaspore and boehmite, was formed. Clays in somewhat topographically lower sinkholes were not as intensely altered after deposition, and clays in beds in equivalent sedimentary sequences still lower were hardly altered at all. These Missouri clays are contemporaneous with other refractory clays of Early Pennsylvanian age in Kentucky (Patterson and Hosterman, 1962), in Pennsylvania (Bolger and Weitz, 1952; Foose, 1944), and elsewhere in the eastern midcontinent region (Keller, 1975).

#### Sequences of Cretaceous age

In Colorado, kaolinitic clays in the Dakota Formation were eroded from a weathered hinterland and incorporated in fluvio-deltaic sediments in basal Cretaceous strata in the Pueblo-Canyon City area (Waage, 1953) and in the Golden area (Waage, 1961). In the Golden area, volcanic ash beds in marine strata equivalent to the fluvio-deltaic rocks consist of smectite and can be traced into the fluvio-deltaic sequence where the ash beds consist of kaolinite (Waage, 1961, p. 25). Postdepositional processes thus may be responsible for the formation of some of the kaolinite in the thick nonvolcanic clay beds.

At nearly the same time, a kaolinite-rich residuum was being formed on Precambrian and some Paleozoic rocks in the western part of the central craton in Minnesota (Austin, 1970; Parham, 1970), in North Dakota (Moore, 1979), and in South Dakota (Ludvigson and others, 1981). At some places, kaolinite was eroded from the residuum and concentrated in sedimentary rocks of Cretaceous age where further weathering in Cretaceous time formed minor amounts of gibbsite and boehmite (Parham, 1970, p. 56-60).

#### Sequences of Cretaceous-Eocene age

*Cretaceous to middle Eocene.*—A weathering sequence in central Georgia and western South Carolina is implied by derived deposits of Late

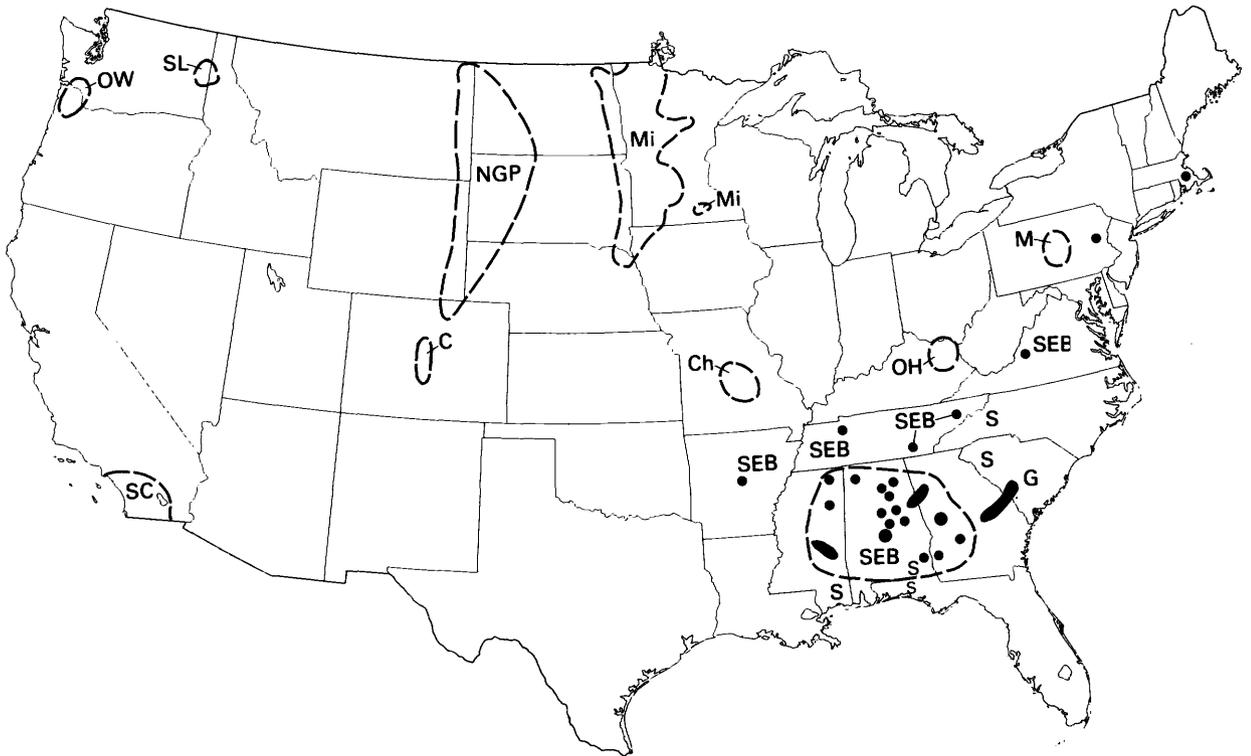


FIGURE 1.—Selected aluminous weathering sequences in the United States. Ch, Cheltenham clays, contemporaneous with similar clays in Kentucky (OH, Olive Hill) and Pennsylvania (M, Mercer clays). C, Colorado clays. Mi, Minnesota residuum. G, Georgia-South Carolina kaolin district. SEB, Southeastern bauxite deposits and related occurrences of kaolin, together symbolized by dark patterns, attributed to the same weathering sequence. SC, Southern California paleosol. NGP, Northern Great Plains paleosol. SL, Spokane-Latah clays. OW, Oregon-Washington ferruginous bauxite. S, saprolite or soil that contains gibbsite.

Cretaceous and middle Eocene ages. It has provided the largest kaolin resources in the country. These strata have long been regarded as being entirely of Cretaceous age (Lang and others, 1965, p. J4), and the complexity of their depositional history is shown by Tschudy and Patterson (1975) as well as others (Hurst, 1979). The kaolinite was eroded from a weathered hinterland developed on pre-Cretaceous rocks generally to the northwest of the present outcrop of Cretaceous and younger strata. Some of the resulting deposits are in nonmarine strata of Cretaceous age, and others are in nonmarine strata of middle Eocene age. A marine sequence separates the two nonmarine sequences and records both Paleocene and Eocene time, but the record is very compressed and different from that of other parts of the Gulf Coastal Plain. Local surface weathering in Cretaceous time produced minor amounts of gibbsite in some of the kaolin deposits of Cretaceous age. Postdepositional alteration of the centers of kaolinite lenses of middle Eocene age has produced pisolitic clay that contains small amounts of gibbsite and that grades in all directions into the kaolin (Hurst, 1979).

*Paleocene-Eocene age.*—A weathering sequence of Paleocene-Eocene age is related to the origin of

bauxite deposits in the southeastern United States (Bridge, 1950; Overstreet, 1964). Kaolinized bedrock in Massachusetts (Kaye, 1967) and clay deposits in central Pennsylvania (Hosterman, 1972) also are attributed to this weathering sequence. These widespread occurrences may constitute an example of a widespread system by which aluminum and perhaps other mineral resources are formed.

Residual bauxite deposits cap partly buried hills of syenite in Arkansas (Gordon and others, 1958, p. 136) and were the source for transported kaolinite and gibbsite in the overlapping strata of late Paleocene and early Eocene age. Residual deposits formed in early Tertiary time may also be represented by kaolinitic and bauxitic weathered strata of presumed Cretaceous age in Alabama (Bergquist and Overstreet, 1965) and in western Georgia (White, 1965).

A weathered hinterland on Paleozoic and older rocks in the Appalachian region is not directly recognizable but is implied by deposits of clay trapped in sinkholes formed in rocks of Paleozoic age and clay incorporated in strata of Eocene age. Sinkhole deposits in Virginia (Warren and others, 1965), Tennessee (Dunlap and others, 1965), Alabama (Cloud, 1966, 1967; Denson and Waage, 1966), and Georgia

(White and Denson, 1966) contain bauxite formed by postdepositional alteration of kaolinite-rich weathering products that accumulated in the sinkholes. Transported clays in strata of Eocene age are found in northeastern Mississippi (Tourtelot, 1964a; Conant, 1965), southeastern Alabama (Warren and Clark, 1965), and southwestern Georgia (Clark, 1965; Zapp and Clark, 1965; Zapp, 1965). Subaerial Eocene weathering of the transported clays formed minor amounts of bauxite in Mississippi, where there may have also been some Eocene weathering of Paleocene clays. Postdepositional alteration by ground water seems to have been responsible for the gibbsitic bauxite that makes up the centers of lenses of kaolinite in the Andersonville district of Georgia (Burst, 1974).

*Regional paleosols of Paleocene and Eocene ages.*—A regional kaolinitic paleosol of probable Paleocene-Eocene age in southern California and adjacent Baja California, Mexico (Peterson and Abbott, 1979), may represent an immature example of a residuum similar to that implied for the hinterland of the southeastern bauxite deposits. A similar paleosol of regional extent in the northern Great Plains (Dunham, 1961; Schultz, 1961; Pettyjohn, 1966) can be dated as Eocene and is the surface on which strata of Oligocene age were deposited unconformably.

#### Washington and Idaho clays of Miocene age

The clays in eastern Washington and adjacent Idaho include both residual (saprolite) and transported clays. The residual clays consist predominantly of halloysite formed by the weathering of basalt and kaolinite formed by the weathering of granodiorite in Miocene time. The transported clays of the Latah Formation consist chiefly of halloysite and kaolinite and were eroded from the residual clays (Hosterman and others, 1960; Hosterman, 1960). The fossils found in the Latah Formation are excellent indicators of the climate during Miocene time.

#### Saprolite in the southeastern United States

Saprolite is a weathered rock that contains secondary minerals formed by the weathering of susceptible minerals in the parent rock and, for the most part, still retains much of the original texture and structure of the parent rock (Patterson, 1967, p. 148). Because it occurs at the present surface, saprolite is thought to have formed in the recent geologic past and perhaps to be forming even at present. Although some saprolite obviously is young (Clarke, 1971), at many places a wide range of ages of weathering is possible, perhaps even as old as Cretaceous (W. R. Griffiths, oral commun., 1982). Gibbsite is a common mineral in saprolite developed on crystalline rocks, in soils developed on saprolite (Clarke, 1972; Cate and McCracken, 1972), and in some soils developed on sedimentary rocks of Neogene age (Clarke, 1971). Enough gibbsite is present at some places for saprolite to have been investigated as a possible source of aluminum (Patterson, 1967, p. 148-151; Beg, 1982).

The presence of gibbsite in saprolite raises questions concerning the relations between climate and mineral resources. If gibbsite and other residual deposits are forming today, as Knechtel (1963) and Hack (1965, p. 66-76) suggest, then the range of climate that controls their formation is broader than what is generally accepted. Conversely, the presence of gibbsite may indicate that some of the saprolite is older than investigators had thought and formed under climates much warmer than today's. Resolution of this problem could have an important bearing on the assessment of aluminum and perhaps other mineral resources in the region and depends in large part on concepts of climatic history.

#### Climatic implications of the geologic record

Lateritic weathering resulting in accumulation of aluminous and ferruginous materials is an obvious feature of present tropical regions. The presence of these materials in the geologic record is taken to indicate similar climates in the past. The various parameters of climate, such as mean annual temperature, annual temperature range, and amount of precipitation and its seasonal distribution, can be quantified for the present. These numbers can be extrapolated into the past (Gordon and others, 1958, p. 143-144), but the significance of such extrapolated numbers is uncertain because so many other factors are involved in the weathering process and its results (Patterson, 1981).

The climate of Pennsylvanian time shows regional variation. The eastern coal regions are interpreted to have had a tropical climate and heavy, seasonally uniform rainfall, whereas the Western Interior coal region had a similar warm climate and seasonally distributed rainfall (Schopf, 1975). This difference is important in a climatological sense, but its effect has not been recognized in the high-aluminum clays of Missouri in comparison with those of Pennsylvania.

The Cretaceous is generally regarded as a time of great warmth (Frakes, 1979, p. 178). The marine record (Pearson, 1978, p. 147-149) suggests distinct warming of the seas from the earliest part of the Cretaceous to mid-Late Cretaceous time and then marked cooling through the rest of the Cretaceous and into the Paleocene. The continental record is much less detailed (Dorf, 1942), but regional differences can be made out. Palynological floras in the Mississippi Embayment and the Rocky Mountain regions are different because they have been separated by the Cretaceous interior seaway and by latitudinal position (Tschudy, 1970). The climates indicated for the two regions are not much different and are within the subtropical-tropical realm. On a smaller scale, some palynological floras contain pollen derived from an upland source that probably was cooler and less humid than the lowlands of the site of deposition (Srivastava, 1967; Jarzen and Norris, 1975).

The Tertiary record is more detailed than the Cretaceous record and reflects considerable secular and geographic variation. The continental record of climatic variation developed by Wolfe (1978) is particularly useful in considering the relations between

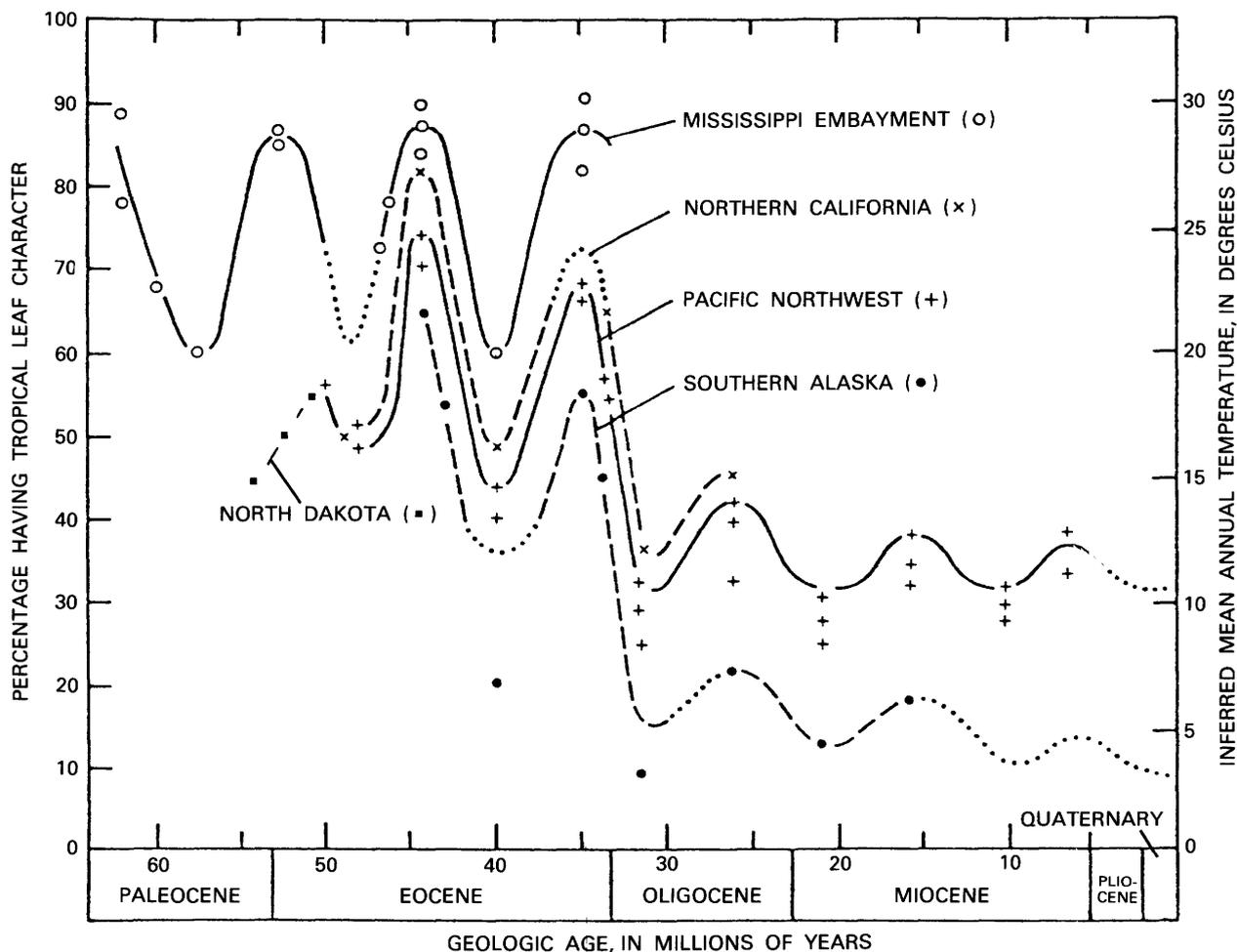


FIGURE 2.--Inferred temperatures for Tertiary time (modified from Wolfe, 1978). Data for North Dakota plotted from Hickey (1977). Dotted lines indicate inferred temperatures.

climate and mineral resources (fig. 2). Mean annual temperature varied from high to low at intervals of about 10 m.y. Expected latitudinal variation also is indicated, as temperatures from the Mississippi Embayment are higher than those from southern Alaska. Estimates of mean annual temperature for a highly kaolinitic transported clay unit of Paleocene age in western North Dakota and for the directly overlying earliest Eocene strata also are plotted on figure 2 (Hickey, 1977, p. 87-88). This plot does not match the other curves very well. The temperatures seem somewhat low in comparison with those estimated for the middle Eocene of northern California and the Pacific Northwest, which are similar in latitude to North Dakota. The climate suggested by these temperatures may have been a relatively local feature developed because of orographic changes taking place in the Paleocene landscape. Because the kaolinite was transported from an unknown hinterland (Freas, 1962; Hickey, 1977), the climatic parameters are not necessarily applicable to

the hinterland in which the kaolinite was formed by weathering.

The highest mean annual temperatures shown on figure 2 range from about 12° to 13°C for the Miocene to about 30°C for the Paleocene and Eocene, but bauxitic mineral resources seemingly could be formed throughout this range. Suitable parent material and other favorable characteristics of the weathering regime, including geologic settings conducive to the preservation of the weathering record, may have an importance equal to that of climate in influencing the present distribution of mineral resources.

Given this broad range of temperatures, it is uncertain whether discrete segments of the temperature variation cycle are closely related to specific occurrences of mineral resources. The correspondence between the times of generally high temperatures during Paleocene and Eocene times and the ages of weathering sequences and related mineral resources is, however, striking.

## Conclusions

Warm, moist climates ranging from perhaps warm temperate to tropical are characteristic for the formation of aluminous and ferriferous lateritic accumulations of economically important mineral resources. The geographic distribution of such climates in the geologic past has been different from that of the present for reasons that still are not entirely clear (Frakes, 1979, p. 24-28). Mineral resources formed by weathering are part of the record of the past distribution of climates but do not necessarily indicate the complete extent of climatic regions. Estimates of the extent of climatic regions may focus attention on areas in which additional mineral resources may be found.

Although climate determines the broad regions in which aluminous and ferriferous mineral resources may occur, other factors also are important in localizing deposits within the region. Some of these factors are listed below, along with examples from the previous discussions:

1. A weathered hinterland in which residual deposits are formed on favorable rocks (Arkansas bauxite) or that serves as a source for transported clays and perhaps transported bauxite.

2. Accumulation of transported clays in favorable sites such as sinkholes (Cheltenham clays; northeast Alabama deposits), lagoonal settings (central Georgia clays of Cretaceous and Eocene ages), or fluvial depositional systems (Colorado clays, Andersonville bauxite).
3. Further surface weathering at the site of deposition of transported clays that may form bauxite or bauxitic material (Georgia clays of Cretaceous and Eocene ages, Minnesota).
4. Further subsurface alteration by ground water of transported clays in favorable hydrologic settings in fluvial systems (Andersonville bauxite).

The trapping of clay in fluvial systems and subsequent postdepositional alteration seem to be particularly important factors. Such fluvial systems could exist in the subsurface in areas of the Gulf and Atlantic Coastal Plains other than those where bauxite and kaolin deposits now are known. Such fluvial systems also could be present in strata of Cretaceous age to the west of the Minnesota residuum and yet be unrecognized because of thick glacial cover. Any deposits in such systems might be so deep as to be unminable at present, but knowledge of their presence—or absence—could be important in the future.

PALEOCLIMATE AND MINERAL DEPOSITS

EFFECT OF SEA-LEVEL FLUCTUATIONS ON POROSITY AND MINERALOGIC CHANGES IN COASTAL AQUIFERS

By William Back and Bruce B. Hanshaw

The ocean is the ultimate base level for ground-water regimes. Climatic changes that affect the relationship between freshwater head and sea level can have pronounced effects on ground-water flow pattern, rate of ground-water discharge, position of the freshwater-saltwater interface in coastal aquifers, and amount of mixing within the zone of dispersion (fig. 3). Because part of the water discharged in coastal areas is brackish owing to mixing of freshwater with ocean water, discharged saltwater must be replenished from the ocean. This discharge generates a flow system within saltwater in the aquifer that is related to, but distinct from, the flow system in freshwater.

The zone of dispersive mixing is a highly reactive chemical system. This reactivity results from differences in significant chemical parameters such as temperature, pH,  $PCO_2$ , and ionic strengths of the two water bodies. For example, the nonlinearity of the activity coefficient  $\gamma_i$  as a function of ionic strength (fig. 4) shows that mixing two waters will yield an activity coefficient less than what the value would be if the relationship were linear.

Because activity equals activity coefficient multiplied by molality, molality must increase and

thereby cause additional solution of the mineral of interest in order to maintain an activity equal to that in either of the original solutions. This effect can be quite pronounced in carbonate aquifers, and it is possible for a water that is in equilibrium with calcite to be mixed with ocean water that is supersaturated with respect to calcite to generate a mixture that is undersaturated with calcite but supersaturated with respect to dolomite (Hanshaw and Back, 1980).

On the basis of these relationships, we developed a mixing-zone model (Hanshaw and Back, 1979) for the formation of dolomite in the zone of dispersion and hypothesized that the boulder zone of Florida that has conventionally been interpreted as a paleokarst feature may be undergoing dissolution and dolomitization at the present time. Badiozamani (1973) named this model the Dorag model and used it effectively to explain the origin of Ordovician dolomite in the midwestern part of the United States. Land and Epstein (1970) independently developed the same hypothesis to explain the dolomitization of Holocene deposits in Jamaica. The petrologic work of Folk and Land (1975) tended to substantiate the mineralogic changes in the mixing zone. Knauth (1979)

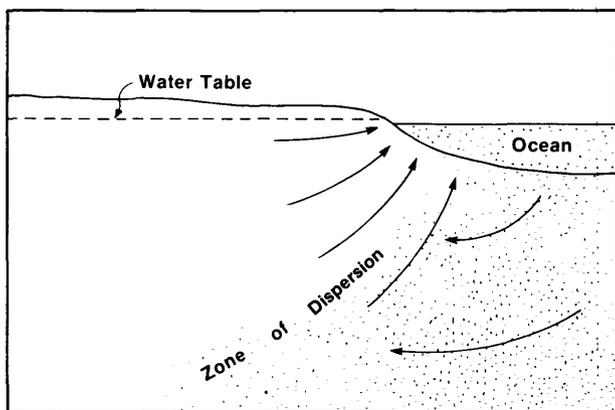


FIGURE 3.—Diagram showing the interface between freshwater and seawater flow systems that forms the zone of dispersion.

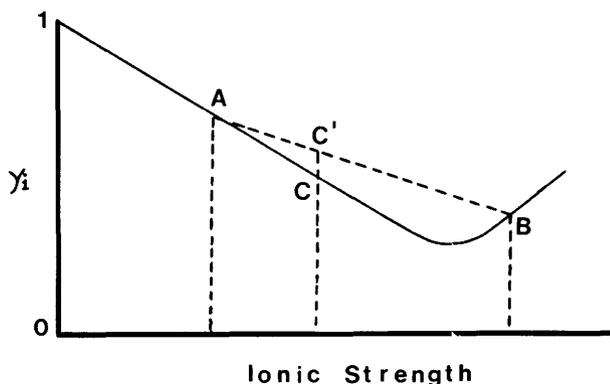


FIGURE 4.—Graph showing the upward concavity of activity coefficient  $\gamma_i$  as a function of ionic strength.

and Land (1977) also developed a mixing-zone model to explain the occurrence of chert lenses and nodules from a biogenic opal precursor in carbonate rocks. Magaritz and others (1980) identified dolomite formed at the freshwater-saltwater interface in Israel. Sea-level fluctuations cause a zone of dispersion to oscillate through the carbonate rocks and thereby permit the rocks to be in the diagenetic environment repeatedly.

We investigated this phenomena in Xel Ha lagoon on the east coast of the Yucatan, where we observed a significant amount of freshwater discharging and mixing with ocean water in the lagoon. We hypothesized that this mixing caused pronounced solution features such as straight-walled and rectilinear channels along well-developed fractures. However, detailed mapping of the chemical character of the water and mass-transfer calculations indicated that outgassing of carbon dioxide from the discharged water was a more rapid chemical reaction than dissolution of limestone, and water therefore became supersaturated at the time of discharge. We then were able to demonstrate that dissolution was occurring within the aquifer before the ground water discharged into the lagoons and submarine springs (Back and others, 1979).

Our recent work in the Yucatan has demonstrated that lagoons such as Xel Ha and crescent-shaped beaches result from underground dissolution, which forms caves that later collapse (Back and others, 1981). In cores drilled for stratigraphic information in the Yucatan, we have seen the development of secondary porosity and the growth of dolomite rims on calcite crystals. Frank (1981) has described spectacular dolomite crystals zoned with calcite. He has concluded that these crystals grow in an environment where subtle changes in the chemistry of the water can cause pronounced differences in the resulting mineralogy. We believe that this type of dolomite would develop in a mixing-zone environment.

At Xcaret, a major cave system on the east coast of the Yucatan, scuba tanks permitted us to observe and photograph the differential dissolution of the limestone in the zone of dispersion. Above the water level, the walls of the cave are relatively smooth, but, in the zone of dispersion, tremendous dissolution causes the rock to look like Swiss cheese. This appearance is reported to be very similar to that of reservoir rock of the Golden Lane oilfield in central Mexico and also typical of some reservoir rocks in Saudi Arabia. Not only does this dissolution cause a great increase in porosity, but the collapse of the cave roof also forms a precursor to solution breccia. Such solution features occur in other parts of the world but have not yet been determined to result from ground-water discharge. However, Paul van Beers (oral commun., 1982) of the Free University of Amsterdam suggested that many of the solution features in the Algarve of the southern coast of Portugal may be the result of ground-water mixing and discharge. Therefore, we believe it well documented that the zone of dispersion can increase porosity, is a suitable environment for dolomitization and chertification, and can provide conditions for formation of solution breccias (fig. 5).

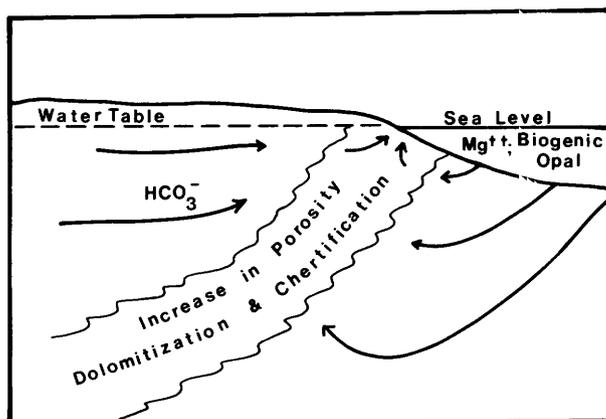


FIGURE 5.—Diagram showing diagenetic processes known to occur in the mixing zone.

By applying these ideas to Cretaceous sediments in Morocco, we can hypothesize that the manganese deposits occurring in Cretaceous dolomites were deposited in a mixing-zone environment (fig. 6). Cannon and Force (1983) show features such as zoned calcite and chert nodules, porosity, chert nodules zoned with pyrolusite, and fillings of pyrolusite in solution breccia. In association with the manganese ore are layers of insoluble residue that presumably resulted from dissolution of the original carbonate material.

The hypothesis is that ground water was discharging near the shore of an anoxic sea in which the manganous ion was mobilized in an organic-rich bottom layer. Ground-water discharge would set up a flow system whereby the saltwater moves into the aquifer, carrying with it the manganous ion that would then be oxidized to pyrolusite by the oxygen in the freshwater. Along with the precipitation of the manganese ore would be the processes of chertification, dolomitization, porosity development, and the concomitant incipient formation of solution breccia.

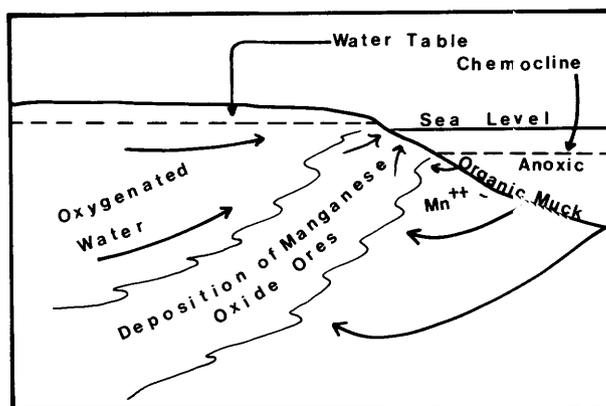


FIGURE 6.—Diagram demonstrating the hypothesis that some manganese ores may be deposited in the zone of dispersion.

## PALEOCLIMATE AND MINERAL DEPOSITS

### PLIOCENE AND PLEISTOCENE CALCITIC VEINS AS INDICATORS OF PALEOHYDROLOGIC, PALEOCLIMATOLOGIC, AND NEOTECTONIC EVENTS, SOUTHERN GREAT BASIN: AN INITIAL APPRAISAL

By Isaac J. Winograd, Barney Szabo, Tyler B. Coplen, and Gene C. Doty

Lakebed stratigraphic sequences currently provide the only major tool for deciphering pre-middle Wisconsin paleoclimatic conditions in the Great Basin. Calcitic veins, exhumed feeders of major fossil springs, represent a second tool potentially capable of providing a continuous record of paleohydrologic and paleoclimatologic events extending back to the middle Pliocene.

The calcitic veins occur in near-vertical fractures in Pliocene and Pleistocene sediments within the Amargosa Desert of Nevada and Death Valley in California. The veins vary from a millimeter to a meter in thickness, locally occur in swarms, and are commonly finely laminated. They can be traced vertically for tens of meters and horizontally over hundreds of meters.

The veins originated as low-temperature (<50°C) precipitates from calcite-saturated artesian ground water rising along tensional (probably extensional) fractures in Pliocene and Pleistocene alluvium, conglomerate, and lakebeds. Evidence for this origin includes (1) occurrence of the veins within a 16-km-long structurally controlled major spring discharge area at Ash Meadows in the Amargosa Desert (Winograd and Doty, 1980) (a regional Paleozoic carbonate-rock aquifer feeds these modern springs via fractures); (2) visible transition of vein to tufa in Furnace Creek Wash adjacent to Death Valley; and (3) a variety of vein morphologies indicative of active flow of water through open fissures. The veins mark the sites of fossil ground-water flow within major modern (Ash Meadows) and exhumed (Furnace Creek Wash) discharge areas of regional flow systems (Winograd and Friedman, 1972; Winograd and Thordarson, 1975; Dudley and Larson, 1976; Winograd and Pearson, 1976) in the southern Great Basin.

Three veins (10B, 13N, and AM-7) have been dated by the uranium-series method. This method is applied in two ways. First, for samples in which the measured  $^{230}\text{Th}/^{234}\text{U}$  activity ratio is less than about 1.1, dates are calculated from the  $^{230}\text{Th}/^{234}\text{U}$  value. Second, for samples in which the  $^{230}\text{Th}/^{234}\text{U}$  value is nearly in radioactive equilibrium, dates are calculated by using the  $^{234}\text{U}/^{238}\text{U}$  activity ratio and the fact that the  $^{234}\text{U}/^{238}\text{U}$  activity ratio of ground water

from the regional artesian carbonate aquifer varies narrowly from 2 to 3. Each vein was divided into groups of laminae representing youngest to oldest portions of the vein as determined from field relations, and each group was analyzed. The veins range in age from 100,000 yr to 1.7 m.y. Extrapolation of growth rates indicates that vein 10B may be as old as 3 m.y. The four oldest laminae of vein 10B maintain a  $^{234}\text{U}/^{238}\text{U}$  activity ratio of 1.0 indicating that closed-system conditions, necessary for reliable dating, prevailed throughout their geologic history.

The veins appear to have three immediate uses: (1) reconstructing the paleohydrology of the Ash Meadows and Furnace Creek Wash areas; (2) building a 3-m.y. record of deuterium (D),  $^{18}\text{O}$ , and  $^{13}\text{C}$  abundance fluctuations in Great Basin winter-spring<sup>1</sup> precipitation; and (3) providing independent evidence bearing on the time and magnitude of uplift of the Sierra Nevada and the Transverse Ranges.

Utilizing the geographic distribution of calcitic veins in the Ash Meadows area, Winograd and Doty (1980) demonstrated, before obtaining uranium-series dates, that late(?) Pleistocene fossil-spring discharge occurred 14 km northeast of the present spring lineament and at altitudes as much as 50 m higher than the altitude of the highest modern spring. Now that the AM-7 vein (collected within the modern spring lineament) is known to have been deposited between 400,000 and 700,000 yr ago, we can unequivocally state that Ash Meadows has been a major discharge area well into the Pleistocene. Mineralogic studies of the lakebeds of the region (Kyser and others, 1981; Khoury and others, 1982) provide additional evidence that such discharge has probably occurred in the same region since the late Pliocene. A byproduct of the continuing paleohydrologic studies will be an estimate of the time of isolation of the pupfish *Cyprinodon diabolis* in Devils Hole, a cavern near the center of the Ash Meadows spring lineament. The time of isolation

<sup>1</sup>Studies in the principal recharge area—the Spring Mountains—indicate an absence of modern recharge from summer precipitation (I. J. Winograd, unpublished data).

of this fish is of major interest to biologists studying rates of evolution. Our work suggests that the *Cyprinodon* may have been isolated for at least 100,000 yr, well in excess of the late Wisconsin isolation time assumed by the biologists.

The D,  $^{18}\text{O}$ , and  $^{13}\text{C}$  record in the dated veins is exciting and perplexing. The 4- to 11-cm-thick veins were sampled at 1mm intervals for  $\delta^{18}\text{O}$ , and  $\delta^{13}\text{C}$  analysis; several millimeter-thick samples were required for analysis of the D content of fluid inclusions. The  $\delta\text{D}$  data are as much as 50 permil heavier than modern (-98 permil relative to Standard Mean Ocean Water) or late Wisconsin (-106 to -103 permil) recharge; most significantly, the values become lighter with decreasing age. We cannot attribute these changes to mineral-water fractionations because there are no major mineral phases in the carbonate aquifer with which hydrogen could have fractionated during flow from recharge areas to discharge areas over the past 2 m.y. At this reconnaissance stage of our study, we cannot unequivocally rule out possible enrichment of the D content of the fluid inclusions by the preferential outward diffusion of  $\text{H}_2\text{O}$  over HDO after uplift of veins 10B and AM-7 above the water table. Nor can we presently evaluate the magnitude and direction of change in D content of several laminae that have been recrystallized. However, such concerns are, in general, not supported by the distribution of  $\delta\text{D}$  values within the veins nor by the very dense nature of the vein calcite.

We believe that the 50-permil depletion of D with decreasing age of these veins reflects major uplift of the Sierra Nevada and the Transverse Ranges during the last 2 m.y. Such uplift would progressively deplete Pacific storms entering the Great Basin from the west and southwest of D. The fluid inclusions in the veins studied preserve this progressive depletion of D in southern Great Basin Pliocene-Pleistocene recharge. Two alternate hypotheses—namely, that during the late Pliocene to mid-Pleistocene, winter precipitation was derived from more southerly (and therefore D enriched) sources than it is at present or that the percentage of recharge derived from summer precipitation (also D enriched) was considerably greater at that time than it is today—deserve consideration. The residence time of water in the regional carbonate aquifer—on the order of 10,000 to 30,000 yr (Winograd and Pearson, 1976)—is a negligible

factor influencing D values in the time frame under consideration in all three hypotheses.

Assuming the validity of the first hypothesis—namely, control of D in precipitation by uplift of the Sierra Nevada and Transverse Ranges—permits an independent estimate of the magnitude of uplift of these ranges since latest Pliocene. The major orographic effects of the Sierra Nevada on the D content of modern precipitation have been well documented by Friedman and Smith (1970) and by Smith and others (1979). Utilizing the D-altitude correlations that they developed, (20-50 permil/1,000 m) and the 50-permil decrease in  $\delta\text{D}$  in the veins, one can postulate a 1,000- to 2,500-m uplift of the Sierra Nevada and Transverse Ranges in the past 2 m.y. These estimates of uplift are within the range postulated by structural geologists for these mountains. Huber (1981) believed that the Sierras have risen about 1,000 m since late Pliocene, whereas Hay (1976) postulated a rise of 1,800 m in the last 4.5 m.y. Gable and Hatton's (1980, plate 4) synthesis of vertical movement data indicates an uplift rate for the Sierras of about 4 to 6 m/10<sup>4</sup> yr or 800 to 1,200 m in the past 2 m.y. Uplift rates capable of raising the Transverse Ranges to their present height (up to 3,500 m) in the last million years have been suggested by Yeats (1981), Lajoie and others (1979), and Morton and others (1982).

In contrast to the  $\delta\text{D}$  data, the  $\delta^{18}\text{O}$  analyses of calcite comprising vein 10B display neither a long duration trend nor a fluctuation over the range of several permil needed to match the changes in the  $\delta\text{D}$  values. An attempt to understand the discrepancy between the  $\delta\text{D}$  and  $\delta^{18}\text{O}$  data in this vein continues. In contrast to the lack of variation of  $\delta^{18}\text{O}$  in vein 10B, the  $\delta^{18}\text{O}$  for vein AM-7 appears to record a 100,000-yr Milankovitch cycle.

In summary, the potential of the calcitic veins for deciphering the Pliocene and Pleistocene paleohydrologic history of ground-water discharge at Ash Meadows appears excellent. Deciphering paleoclimatologic signals in the stable isotopic data will be challenging, perhaps formidable, particularly if the postulated major neotectonic effects on  $\delta\text{D}$  are sustained by further study; yet, we have studied only three veins to date and have  $\delta\text{D}$  data for only two of them. Future work will concentrate principally on the D content of fluid inclusions in dated veins from both the recharge areas and the discharge areas of the coincident fossil and modern regional ground-water flow systems of the southern Great Basin.

## PALEOCLIMATE AND MINERAL DEPOSITS

### THE OXYGEN MINIMUM ZONE OF CONTINENTAL MARGINS

By Thomas M. Cronin

The oxygen minimum zone is a feature of the ocean system produced by a combination of high biological productivity and oceanic advective circulation of oxygen-depleted water masses. The depth of the modern O<sub>2</sub> minimum varies throughout the oceans, but it usually occurs in the bathyal zone and is between 200 and 500 m thick (Bubnov, 1966; Menzel and Ryther, 1968). It varies in intensity and is most strongly developed along eastern boundaries of oceans where equatorward winds cause upwelling of cool nutrient-rich subsurface waters that increase biological productivity in the photic zone (Margalef, 1978). In such extreme cases, low dissolved oxygen (0.0-1.0 mL/L) or anoxic conditions prevent organisms from living on the bottom. Sediments deposited in regions of oxygen minimums are characterized by fine laminations consisting of alternating siliceous or calcareous and dark organic-rich layers that reflect anoxic conditions and the absence of bioturbation (Diester-Haass, 1978; Pisciotto and Garrison, 1981). Siliceous material consists of diatoms and radiolarians. Organic content of sediments averages 8 to 17 percent in most regions of upwelling but is as high as 26 percent off Africa. High concentrations of metals such as Ni (35-455 ppm), Zn (18-337 ppm), Cu, P, U, and Mo also characterize these sediments. Phosphorite genesis, which is controlled by warm climates and high sea levels, occurs in regions of strong upwelling and extensive oxygen-depleted water masses. Figure 7 summarizes the biological, sedimentological, and chemical characteristics of the O<sub>2</sub> minimum zones of a nonupwelling coast (I), a coast with deep anoxic silled basins (II), and an upwelling continental margin (III) (Demaison and Moore, 1980; Diester-Haass, 1978; Ingle, 1981; Pisciotto and Garrison, 1981; Rowe and Haedrich, 1979; Margalef, 1978; Douglas and Heitman, 1979).

During the Mesozoic and Cenozoic, climatic and paleogeographic changes have significantly altered the intensity and location of oxygen minimums at various time scales and thereby influenced the extent of ocean floor that was the site of mineral-rich sedimentation. In the Guaymas Basin in the Gulf of California, climatic warming during Pleistocene deglaciations caused a shift from homogenous, bioturbated sediments to finely laminated rhythmites deposited

under anoxic conditions (Schrader and others, 1980). Short-term climatic events such as the little ice age (1550-1830 A.D.) can also be recognized in varved sediments in the Santa Barbara Basin. In the eastern North Atlantic, in the Gulf of Guinea, analyses of benthic faunas allowed accurate documentation of fluctuations in dissolved oxygen during sea-level fluctuations of the last interglacial-glacial cycle (Peypouquet, 1979). Relatively low dissolved-oxygen concentrations correspond to high eustatic sea level, and high oxygen concentrations correspond to low sea level.

Over longer time scales, the Miocene Monterey Formation of California is the prototype of oxygen minimum zone sedimentation in which deposition occurred in bathyal environments under particular climatic, tectonic, and oceanographic conditions. Global cooling during the Miocene (about 15-16 m.y. ago) associated with the buildup of Antarctic ice caused the southward shift of cool waters, intensified upwelling, and the deposition of finely laminated siliceous sediments that are an important petroleum source and, when they are fractured, reservoir beds (Ingle, 1981). Fine-scale Miocene climatic changes are not understood well enough to predict the detailed sequences of laminated and homogeneous sediments; however, information on the frequency and amplitude of climatic events has potential use in the western United States and throughout the Pacific, where similar oceanographic situations developed during the Miocene. For example, oil-bearing Neogene deposits on the Oga Peninsula of Honshu, Japan, formed under environments similar to those of the Monterey (Ingle, 1981).

The formation of Cretaceous black shales has also been attributed to expanded O<sub>2</sub> zones in the open ocean; during periods of black shale formation, high sea levels, warm global climates, and low latitudinal thermal gradients caused ocean stagnation, high terrigenous input, and bottom anoxia (Schlanger and Jenkyns, 1976; Weissert, 1981; Arthur and Schlanger, 1979). Some authors emphasize climatically modulated diminishment in thermohaline circulation as a first-order cause for some black shales in the South Atlantic, Indian, Tethyan, and central North Atlantic Oceans. However, climatic control of terrigenous

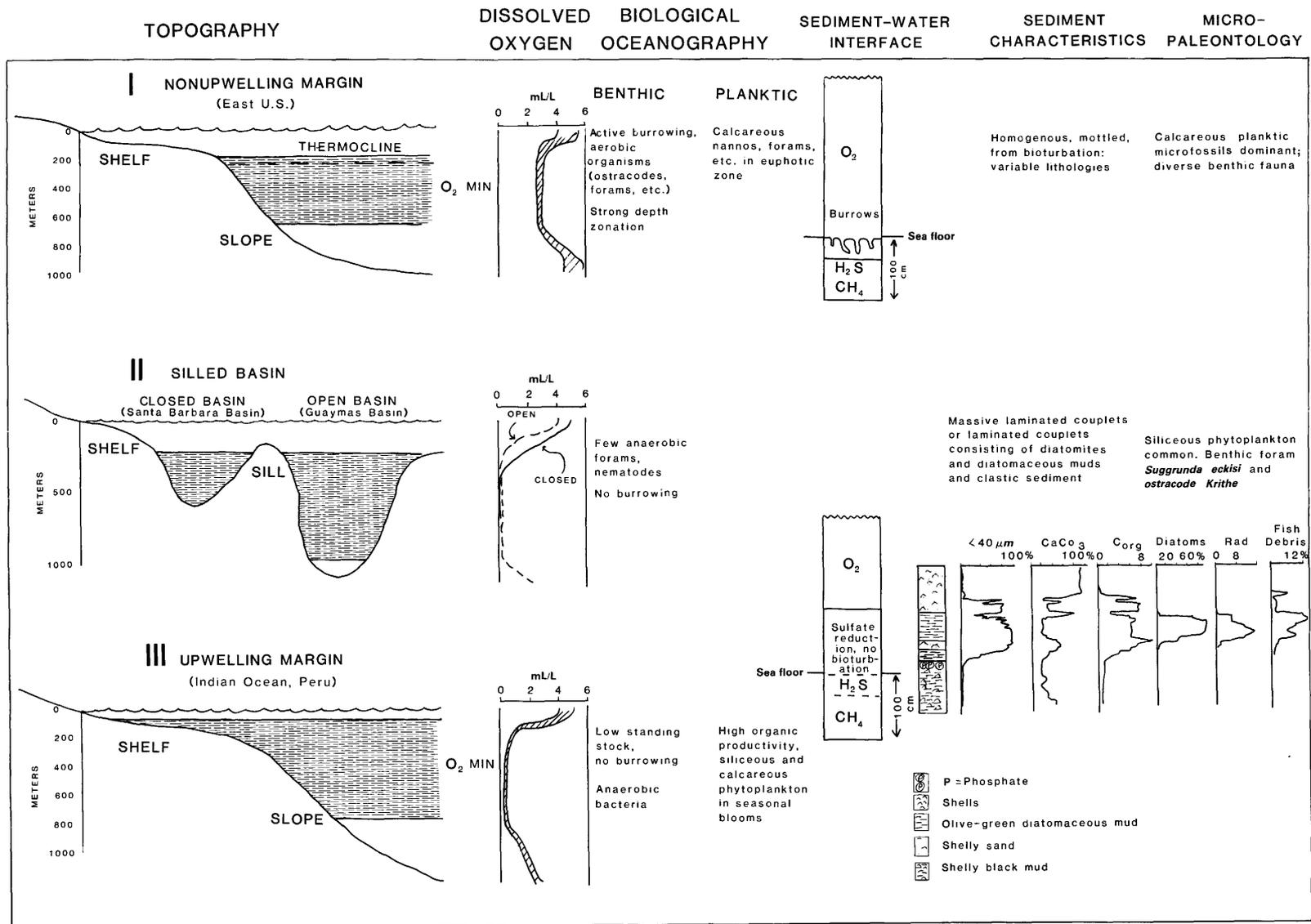


FIGURE 7.—Characteristics of oxygen minimum zones. Nonupwelling margin from data by Cronin (1933). Silled basin and upwelling margin model adapted from Ingle (1981) and Pisciotto and Garrison (1981); published with permission from the Society of Economic Paleontologists and Mineralogists. Sediment-water interface data adapted from Demaison and Moore (1980); published with permission from the American Association of Petroleum Geologists. Sediment characteristics data adapted from Diester-Haass (1978); published with permission from Springer-Verlag.

input also controlled the deposition of northern North Atlantic organic shales in turbidite sequences (Dean and others, 1977).

The following observations must be taken into account in models designed to explain and (or) predict the occurrence of sediments deposited in the O<sub>2</sub> minimum zone:

1. The O<sub>2</sub> minimum zone varies in intensity and depth throughout the world's oceans; it is not necessarily synonymous with anoxic conditions.
2. Temporal changes in the development of oxygen minimum zone and anoxic conditions occur at time scales ranging from 10<sup>1</sup> to 10<sup>6</sup> yr in the geologic record.
3. Different combinations of environmental conditions can cause anoxia; conversely, several sedimentary processes can produce cyclic or rhythmic sediments. Anoxic conditions can result in the concentration of hydrocarbons and metals during relatively warm or cool climatic conditions, depending on local paleogeography
4. Understanding the evolution of the O<sub>2</sub> minimum zone and bottom anoxic conditions in general requires high-resolution climatic records for specific marine basins and more accurate methods of paleoenvironmental reconstruction that allow paleodepth estimation, paleogeographic reconstruction, and estimation of chemical and physical conditions at the sediment-water interface. Benthic organisms having limited tolerances for specific physical and chemical conditions - in particular, certain ostracodes (Peypouquet, 1979; Cronin, 1983) and foraminifera (Ingle, 1981) - hold promise for accurately and quickly delineating bottom paleoceanographic conditions along continental margins.

## PALEOCLIMATE AND MINERAL DEPOSITS

### CENOZOIC PALEOCEANOGRAPHY

By Richard Z. Poore

Marine geological and geophysical studies in concert with more than a decade of studying cores raised by the Deep Sea Drilling Project (DSDP) have led to increased understanding of the evolution of ocean basins and paleoceanography during the Cenozoic. At the start of the Cenozoic, a circumglobal ocean, which allowed latitudinal flow of both surface and deep water, was present at low latitudes. Changing ocean-basin geometry during the Cenozoic, however, resulted in restriction of equatorial circulation and concomitant development of circum-Antarctic circulation. In the Paleogene, northward movement of India and Australia greatly restricted circulation in the Indian Ocean and the western Pacific. Northward movement of Africa caused restriction and finally complete closing of the eastern Mediterranean by the early Miocene. Later, in the Neogene, uplift of the Isthmus of Panama first restricted and then terminated circulation between the Atlantic and the eastern Pacific. The net effect of these events was to greatly enhance the meridional aspect of low-latitude circulation.

The separation of India and Australia from Antarctica, coupled with the opening of the Drake Passage between Antarctica and South America, led to development of a circum-Antarctic current. This current isolated Antarctica and allowed extensive formation of an Antarctic watermass, which provided a source for large quantities of very cold bottom water through formation of sea ice.

Another important development during the Cenozoic was the opening of the Norwegian-Greenland Sea, followed by the sinking of the Iceland-Faeroe Ridge below sea level. Major breaching of the Iceland-Faeroe Ridge during the Miocene provided a route for cold Arctic water to enter the world's oceans and probably initiated formation of significant amounts of North Atlantic deep water.

Knowledge of major changes in ocean-basin geometry has allowed construction of broad features of paleoceanography through the Cenozoic (Haq, 1981; Kennett, 1978; Berggren and Hollister, 1977). Within this framework, details of Cenozoic paleoceanography are being developed primarily from paleontologic, geochemical, and sedimentologic study of DSDP cores.

One of the most important recent developments has been the integration of biostratigraphy, magnetostratigraphy, and isotope stratigraphy with radiometric dates to formulate reliable high-resolution time scales for correlating and dating marine sequences. Accurate correlations mean that time-slice maps showing the distribution of microfossil assemblages or lithologies for specific time intervals can be constructed with confidence and used to infer oceanographic conditions. Under optimum conditions, correlations over portions of the Cenozoic are approaching resolution on the order of 100,000 yr. Similarly, time-series studies done in different regions can be compared with one another with a minimum of ad hoc "curve matching." Another important aspect of the development of high-resolution time scales is the ability to detect relatively brief unconformities and to determine sediment accumulation rates in pelagic sequences. For example, Keller and Barron (1982) identified and mapped the geographic extent of seven Miocene deep-sea unconformities. These unconformities are interpreted to be the result of increased bottom-current activity associated with the expansion of Antarctic glaciation.

Mapping the distribution of planktonic microfossil assemblages can show the distribution and migration of surface-water masses and thus delineate the distribution and migration of climatic belts. For example, Haq and others (1977) demonstrated several poleward migrations of tropical microfossil assemblages in the Atlantic Basin during the Paleocene and Eocene. Moreover, individual species and assemblages of microfossils are indicative of upwelling conditions. For example, the abundance of the diatom genera *Thalassiomena* and *Thalassiothrix* is a reliable indicator of upwelling intensity in Neogene sediments in low and middle latitude areas of the Pacific Basin.

It has been documented for some time that benthic foraminifers can be used to identify low  $O_2$  environments at the sea floor (Ingle, 1981). Quantitative studies have revealed that benthic foraminifers can also be used to identify deep-water masses (Lohmann, 1978). In addition, several distinct large-scale vertical migrations of benthic foraminifers, which probably reflect major changes in

deep-water circulation patterns, have been found in the Miocene of the Pacific (Woodruff and Douglas, 1981).

Oxygen and carbon stable isotope studies of calcareous microfossils also contribute to our understanding of Cenozoic paleoceanography.  $\delta^{18}\text{O}$  were initially interpreted as a temperature index. However, it is now clear that the  $\delta^{18}\text{O}$  signature of marine calcites is a complex signal that contains information on a number of factors such as the isotopic composition of seawater and the life processes of microfossils. Planktonic foraminifers show isotopic evidence of depth stratification in the water column as far back as the Mesozoic (Douglas and Savin, 1978), and benthic foraminifers show evidence of consistent offsets from presumed equilibrium values back to at least the Oligocene (Graham and others, 1981; Poore and Matthews, 1983). Interpretation of  $\delta^{13}\text{C}$  data is more complex, but values obtained from some taxa appear to correlate with the dissolved-oxygen content of seawater (Belanger and others, 1981).

The identification of sea-level cycles in seismic records has important implications for interpreting the geologic history of continental margins (Vail and others, 1977). The timing and magnitude of these cycles, however, are open to question. A number of studies (Keller and Barron, 1982; Poore and Wolfe,

1980) suggest significant correlation between paleoceanographic and sea-level events. Figure 8 correlates terrestrial and marine paleoclimate records from the Atlantic Basin with global sea-level fluctuations during the Paleocene, Eocene, and Oligocene. Cold intervals correlate with sea-level minimums, whereas warm intervals correlate with sea-level maximums. These correlations suggest that some, if not all, of the second-order sea-level fluctuations observed in the Cenozoic may be glacioeustatic. Therefore, oxygen isotope records, which contain information on global ice volume, may be used eventually to quantify the magnitude of sea-level changes seen in seismic records.

In summary, the ability to understand Cenozoic paleoceanography has reached the point where these data can make significant contributions to investigations concerning sedimentary mineral resources. Times of intensified oceanic circulation can be identified, and regional variations in accumulation rates and areas of submarine erosion can be delineated. Areas of high productivity and oceanic climate belts can be mapped. Major oceanographic events can be identified, and the dissolved-oxygen content of deep water can be traced by both faunal and isotopic techniques. Increased understanding of the magnitude, frequency, and multiple causes of eustatic sea-level fluctuations appears near.

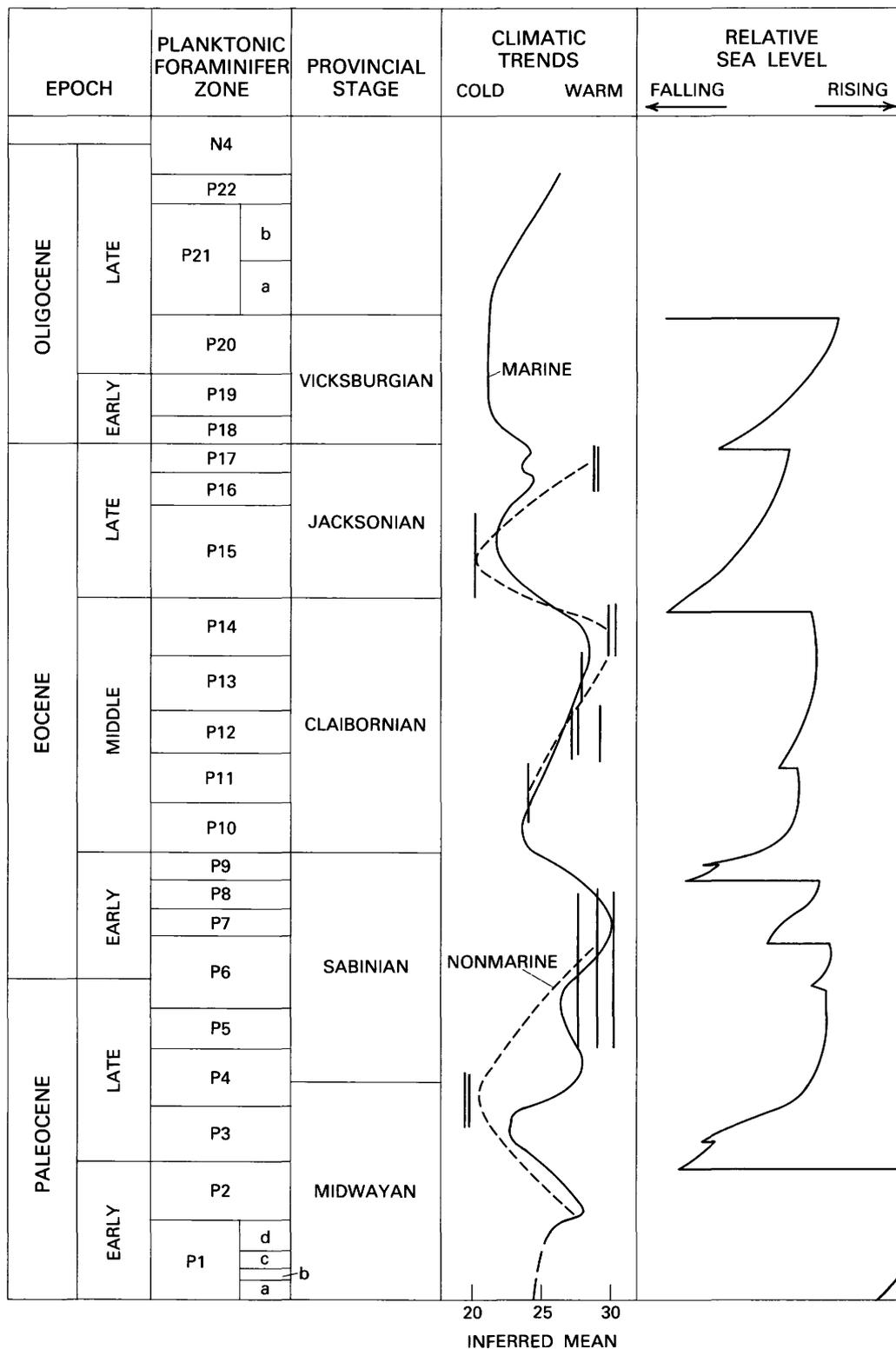


FIGURE 8.—Tertiary sea level and climatic trends (modified after Wolfe and Poore, 1982). P and N refer to standard planktonic foraminiferal zones for the Paleogene and the Neogene, respectively.

## PALEOCLIMATE AND MINERAL DEPOSITS

### THE U.S. ATLANTIC CONTINENTAL MARGIN: EUSTASY, PALEOCEANOGRAPHY AND MINERAL DEPOSITS

By John S. Schlee

The U.S. Continental Margin is a series of elongate sedimentary basins and shallow platforms that originated during the latest opening of the Atlantic Ocean. In the basins, as much as 16 km of sedimentary rock accumulated under marine shallow-water or nonmarine conditions. Although the thickness of Mesozoic-Cenozoic sedimentary rocks changes from basin to basin, the vertical succession and seaward changes in facies appear remarkably similar and point to uniform paleoenvironmental conditions over a large area of the Continental Margin.

The sedimentary sequence has been most closely studied in approximately 75 holes drilled mainly off Nova Scotia. They reveal an older rift sequence of Late Triassic red beds, evaporites, and carbonate rocks that overlies Paleozoic(?) metasedimentary rocks and granite. A conspicuous postrift unconformity, best developed toward the landward edge of the basins, separates the rift sequence from a more extensive "drift" sequence of carbonate and siliclastic rocks of Jurassic age and younger, which accumulated following the separation of North America and West Africa. The postrift section of Jurassic age is mainly limestone and dolomite (with some interbedded anhydrite in the Lower Jurassic part of the section) that interfingers with deltaic clastic-rock facies toward the uppermost part of the Jurassic. Except for the Blake Plateau, most of the carbonate platform buildup ceased in the Early Cretaceous as substantial amounts of siliclastic sediment overspread the margin to build a sedimentary blanket across the shelf and onto the Continental Rise. Clastic sedimentation continued at a diminished rate throughout the Cretaceous and Cenozoic, marked by short-term regressions across the shelf and deposition of thin, widespread transgressive limestones. Beginning in the Tertiary, the Blake Plateau was affected by periodic erosion and reduced sedimentation as flow of the ancestral Gulf Stream shifted into the area. Farther north, a series of marine regressions in the Oligocene, Miocene, and Quaternary resulted in a cutback of the slope to expose rocks as old as Early Cretaceous and build up the Continental Rise wedge.

Sea-level trends for five stratigraphic holes drilled off the eastern United States reveal a pattern of relative sea-level rise during the Jurassic and Cretaceous that reached a maximum in the Late Cretaceous and early Tertiary and dropped thereafter. Superimposed on this broad trend are much shorter shifts in sea level that appear to be nearly synchronous from basin to basin and to have formed interregional unconformities. Major breaks are evident in the Cenomanian, in the late Turonian, in the Campanian-Santonian, at the Cretaceous-Tertiary boundary, at the Paleocene-Eocene boundary, in the late Eocene-early Oligocene, in the early Miocene, and in the Pliocene and Pleistocene. Older interregional unconformities also probably exist, but faunal remains in rocks older than Albian are scarce.

The occurrence of petroleum source beds along the Atlantic margin has been linked to paleoceanic circulation factors and to source factors by Tissot and others (1980) and Hunt (1981). Anoxic events leading to the formation of organic-rich shales in the Cretaceous are thought to have occurred because of the latitudinal elongation of the North Atlantic Ocean basin, a warm global climate in which warm seawater was depleted in oxygen, and a widespread oceanic transgression onto the continents that created shallow, warm seas having high biologic productivity. In terms of paleoceanography and sources of kerogen, these conditions translated into a low total hydrocarbon potential for rocks of Cretaceous age and a humic type of kerogen most likely to produce gas (if maturity, timing of migration, traps, and reservoirs were also favorable). In the Upper Jurassic rocks, Continental Offshore Stratigraphic Test (COST) wells drilled off the northeastern United States showed a similar low concentration of total extractable hydrocarbons of the humic type III (Miller and others, 1980; Miller, 1982).

Phosphorite deposits on the Blake Plateau (Manheim and others, 1980) are the continuation offshore of Miocene sediments that probably originated in a cool, upwelling, shallow-water anoxic environment. Beneath the shelf, the phosphate is a lag gravel that formed from the erosion of phosphatized carbonate-rich sediment. Further seaward where the

unit crops out on the Blake Plateau, the boulders and cobbles of phosphate are impregnated by iron and manganese oxide crusts (todorokite and goethite). The iron-manganese mineralization is a later phase in two modes--as a replacement of preexisting phosphorite and carbonate and as a nodular coating over detrital

phosphatic fragments. Its buildup occurred mainly in the area of lag carbonate and phosphate gravels and under conditions where the rate of oxide deposition exceeded the rate of sediment deposition (Manheim and others, 1982).

## PALEOCLIMATE AND MINERAL DEPOSITS

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### BUILDING A BIOSTRATIGRAPHIC FRAMEWORK AROUND AN ANOXIC-KENOXIC EVENT

By Joseph E. Hazel

In the late Cenomanian and early Turonian (at about  $92 \times 10^6$  yr), sediments with high organic carbon and metal values were deposited at many places in the world. The climate was mild and equable at this time. Warm temperate and subtropical climatic zones extended into high latitudes, and the tropical zone was expanded. As a result, bottom-water conditions were sluggish, and the  $O_2$  minimum zone expanded vertically. A rapid transgression of the seas over the continents occurred (perhaps in response to an increase in volume of the midocean ridge system); the amount of epicontinental sea less than 300 m deep was twice as extensive as it is today. These drowned low-lying areas contributed much plant organic matter to the oceans (Schlanger and Jenkyns, 1976; Jenkyns, 1980; Ryan and Cita, 1977; Arthur and Schlanger, 1979).

This Cenomanian-Turonian event has been termed an oceanic anoxic event (OAE), and it is the second of three such events in the Cretaceous—thus, it is referred to as OAE-2. The event was short lived but intense. It has been widely recognized. However, in part because of the problems inherent in dealing with sediments deposited under  $O_2$  minimum conditions, precise biostratigraphic correlation of many sections is poorly understood. Biostratigraphic frameworks that integrate first-appearance datums (FAD) and last-appearance datums (LAD) from microfossils, both calcareous and organic walled, and megafossils are only now beginning to be developed (for example, Robaszynski and others, 1982).

The sediments of OAE's are or have the potential to be source rocks for much of the world's hydrocarbons (Arthur and Schlanger, 1979) and other natural resources. Exploration for such resources will depend in part on a cogent biostratigraphic framework, developed within the context of paleoclimatic fluctuations and tectonic-paleogeographic events. Without accurate correlations, determining the timing

and frequency of events associated with times of anoxic-kenoxic seas would be prevented.

The integration of various types of biostratigraphic data into one standard model is the key to understanding the timing of events associated with OAE-2 in North America. Such integration is necessary because precise correlation between the various areas in North America where Cenomanian-Turonian seas transgressed requires using a variety of fossil groups. For example, in many parts of the Western Interior and the Rio Grande and East Texas Embayments, ammonites, inocerami, and planktic foraminifers occur in rocks associated with OAE-2. However, these are more rare in the subsurface of the Atlantic Coastal Plain, where pollen, calcareous nannofossils, and ostracodes are the most useful tools. Thus, for example, it is important to know how datums of these latter groups of organisms correlate with foraminiferal or molluscan datums.

A modeling technique based on the graphic correlation method of Shaw (1964) (see also Miller, 1977; Murphy and Edwards, 1977) has proved successful in building robust biostratigraphic models (or frameworks) for several Geological Survey projects. Preliminary results suggest that it can be used to produce a biostratigraphic framework for OAE-2.

Graphic correlation is a technique that uses two-dimensional successive approximations to produce a scaled solution. That is, the FAD's and LAD's for fossils are placed in sequence, and the amount of spacing, expressed in either rock thickness or in a time sense, is apparent. If radiometric dates can be obtained for events in the scaled solution (usually termed the standard reference section), the arbitrary scale can be converted to time, and the position of biostratigraphic datums and sedimentary and other geologic events observed in the studied sections can be expressed in easily understood numbers.

## PALEOCLIMATE AND MINERAL DEPOSITS

### INORGANIC GEOCHEMISTRY OF DEEP-SEA BLACK SHALES

By Walter E. Dean

Cretaceous strata containing organic carbon in the Atlantic Ocean provide considerable insight into the general problem of incorporating trace metals into sediments rich in organic carbon. Such marine sediments and rocks are known to be significantly enriched in a variety of redox-sensitive trace elements (Vine and Tourtelot, 1970) relative to average marine sediment and shale, but the degree of enrichment varies greatly. Although few systematic studies have been made of major- and trace-element concentrations in Cretaceous deep-sea lithologies rich in organic carbon, such lithologies may be important as potential sinks for organic carbon, sulfur, and trace elements, particularly As, Ba, Cd, Co, Cr, Cu, Mo, Ni, Pb, V, and Zn. During the deposition of these sediments, it is possible that trace elements, organic carbon, and sulfur are extracted from the oceans at rates greater than steady state and that the chemical and isotopic balances of the ocean are thereby perturbed. Average deep-sea accumulation rates of organic carbon were as much as 7 times greater during the peak of Aptian-Albian black-shale deposition than they are today (Dean and others, 1983). The reasons for the enhanced preservation of organic carbon in the Cretaceous deep-sea basins, however, are still a matter of debate.

The enrichment of certain trace elements—especially Cu, Zn, Mo, V, Ni, and Cr—in sediments and rocks enriched in organic matter has been reported by many investigators (Tourtelot, 1964; Calvert and Price, 1970; Vine and Tourtelot, 1970; Chester and others, 1978; Leinen and Stakes, 1979; Brongersma-Sanders and others, 1980; Dean and Gardner, 1982; Dean and Parduhn, 1983) (fig. 9). The association of high trace-element concentrations with organic matter may be the result of concentration of these elements by organisms (bioconcentration) or by chemical sorption and precipitation under anoxic conditions created by a flux of excess organic carbon. Marine

plankton are known to concentrate trace elements—especially Ba, Pb, Ni, Cu, Zn, Mn, and Fe (Boyle and Lynch, 1968; Knauer and Martin, 1973; Chester and others, 1978; Leinen and Stakes, 1979)—and the suggestion is that bioconcentration is a potentially important mechanism for incorporating certain trace elements into marine sediments rich in organic carbon. However, the great effectiveness of trace-metal adsorption by clay minerals and organic matter and the coprecipitation of trace metals, particularly as sulfide minerals, suggests that these processes may play a more important role in the removal of trace metals from seawater (Tourtelot, 1964b; Holland, 1979). Detailed trace-element profiles from thick sequences of organic-rich strata suggest that there is differential mobility of trace elements, accompanied by diffusion of some elements over distances of at least tens of meters (fig. 10). The sequence of trace-element mobility, from highest to lowest, is approximately Ba, Mn, Pb, Ni, Co, Cr, Cu, Zn, V, Cd, and Mo.

Although bottom-water anoxia may have occurred during periods when strata rich in organic carbon were accumulating, it was not necessarily a cause of accumulation of these strata. The main reason for the accumulation of these strata was an increase in the relative amount of organic debris being deposited. This organic debris was derived from continental margin areas where the production and accumulation of organic matter from marine, terrestrial, or mixed sources were increased; the debris was then transported to slope and basinal sites by turbidity currents (fig. 11). But why was the supply of organic debris so much greater during the middle Cretaceous? Local pockets of accumulated organic matter in continental margin areas today are the result of local circulation patterns (for example, Walvis Bay off southwest Africa and Santa Barbara

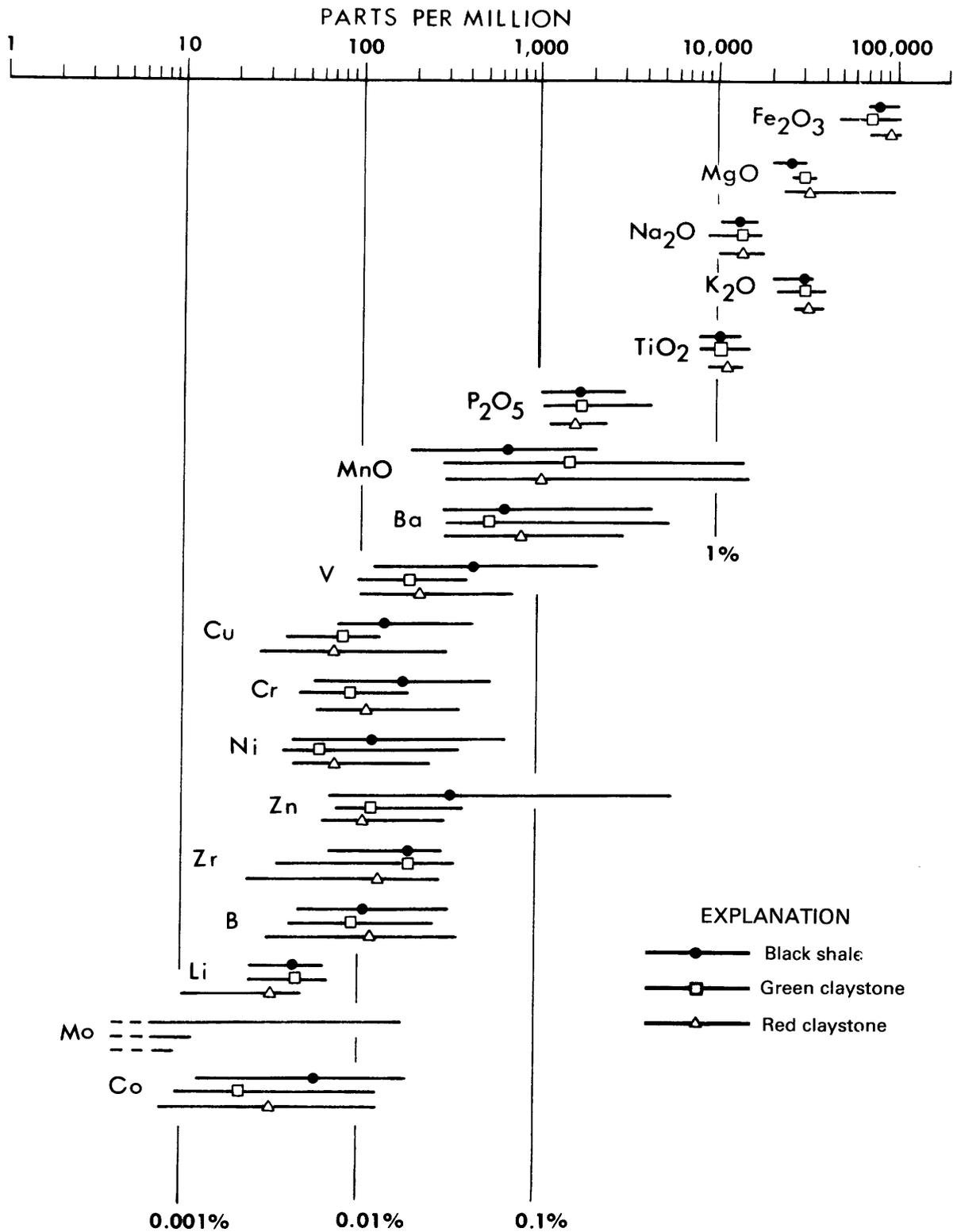


FIGURE 9.—Observed range (length of bar) and geometric mean (symbol) of concentrations of major-element oxides and trace elements in samples of red and green claystone and black shale from Deep Sea Drilling Project (DSDP) Hole 530A, cores 89-105 (adapted from Dean and Parduhn, 1983).

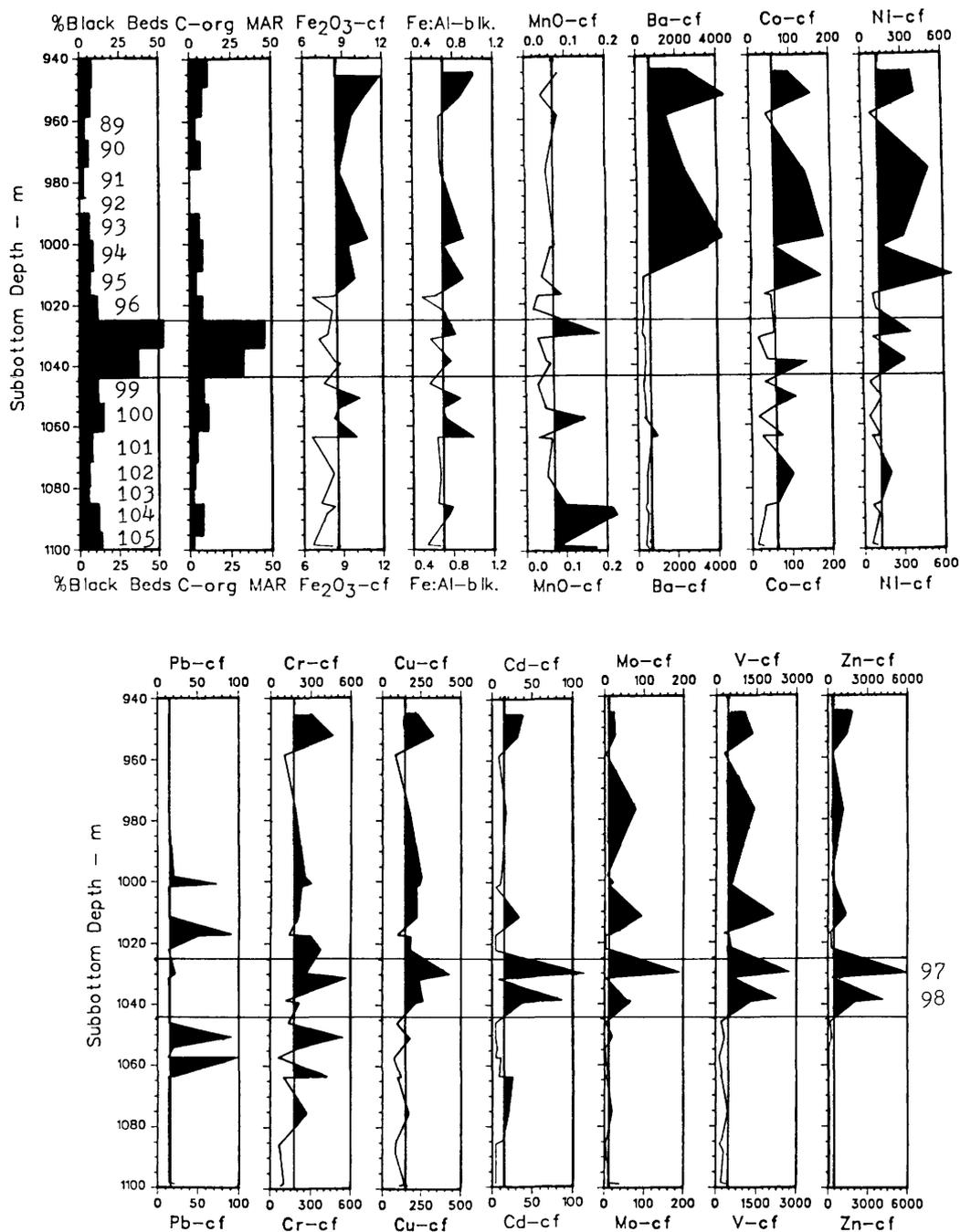


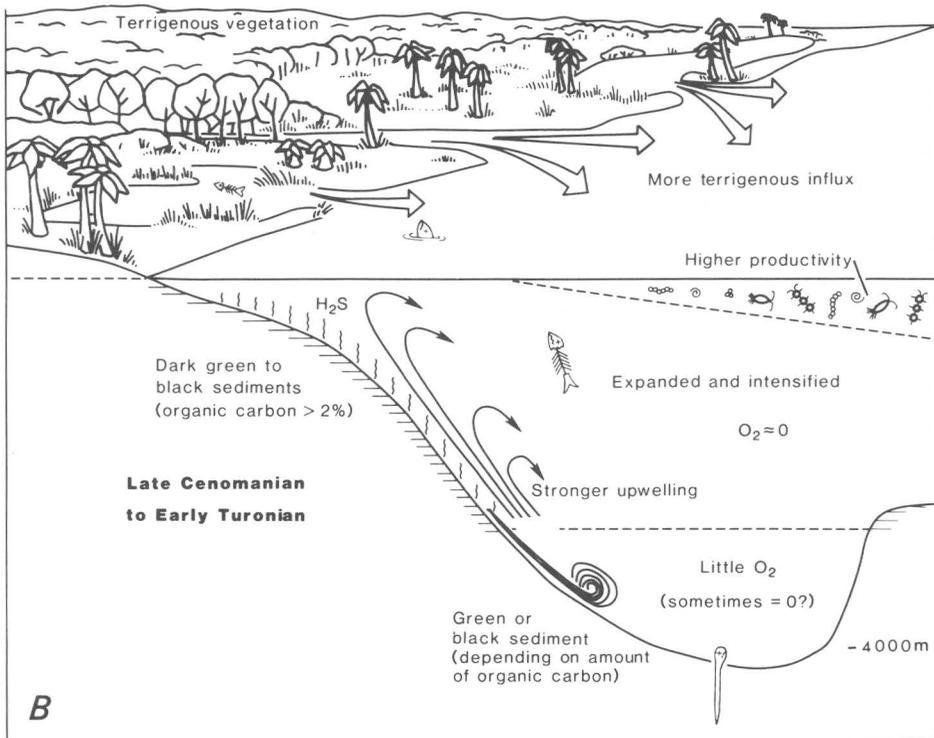
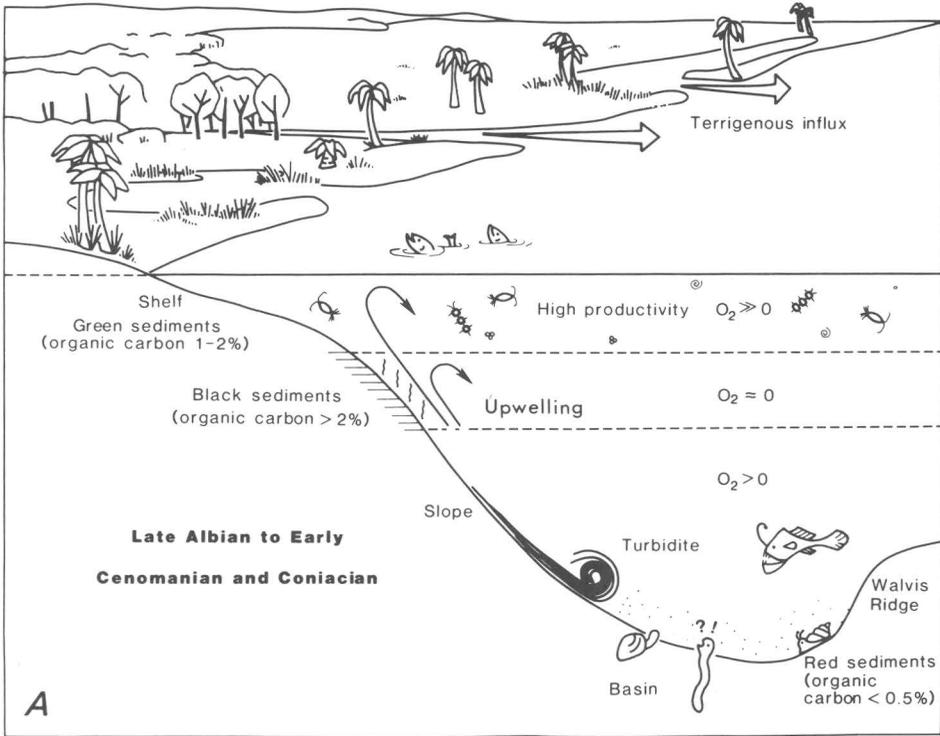
FIGURE 10.—Plots of carbonate-free (cf) concentrations versus depth for  $\text{Fe}_2\text{O}_3$ , MnO, Ba, Co, Ni, Pb, Cr, Cu, Cd, Mo, V, and Zn in samples of black shale from Deep Sea Drilling Project (DSDP) Site 530A in the southern Angola basin. Concentrations of  $\text{Fe}_2\text{O}_3$  and MnO are in percent; all other concentrations are in parts per million. The Fe:Al ratio in black-shale samples, the percentage of black-shale beds in each 9.5-m cored interval, and the mass accumulation rate (MAR) (in grams per square centimeter per million years) of organic carbon for each 9.5-m cored interval also are plotted. The vertical line through each plot is at the geometric mean concentration for that element or oxide. All values greater than the geometric mean are shaded. The numbers (89-105) within the plot for percentage of black-shale beds are the numbers of each core. The two horizontal lines through all plots are drawn at the top of core 97 and the bottom of core 98 and mark the zone of maximum black-shale bed concentration (from Dean and Parduh, 1983).

Basin off southern California). It is unlikely that such conditions would have existed around the entire margin of the middle Cretaceous Atlantic Ocean as well as on isolated plateaus and seamounts in the Pacific (Schlanger and Jenkyns, 1976; Dean and others, 1981) without the aid of some worldwide conditions of ocean circulation and productivity. Global climate during the middle Cretaceous was warm, eustatic sea levels were high, spreading rates were fast, pelagic sediments in the world ocean were accumulating rapidly, and oceanic surface- and bottom-water temperatures were high (Douglas and Savin, 1975; Fischer and Arthur, 1977; Brass and others, 1982). Increased surface-water temperatures would have had two main effects. First, thermohaline deep-water circulation, driven today by the sinking of cold, oxygen-rich surface waters in high latitudes, would have been more sluggish; second, the warmer water would have contained lower concentrations of dissolved oxygen. Bottom-water circulation was sufficient to supply some oxygen to maintain oxidizing conditions in the deep basins of the Pacific but slow enough to permit depletion of dissolved oxygen at midwater depths in areas of high productivity of organic matter. Accumulations of sediments rich in

organic carbon at many places in the world ocean undoubtedly are the results of coincidences of several factors acting to produce and preserve organic matter (fig. 11). During the middle Cretaceous, much of the world ocean may have been poised such that relatively small changes in the flux of organic matter and (or) circulation at any one place would have caused anoxia or near anoxia within midwater oxygen minimum zones and possibly, under extreme conditions, throughout much of the bottom-water mass. An expanded and intensified oxygen minimum would explain the excellent preservation of organic carbon and the increase in the accumulation rate of organic carbon over a much larger area in slope and deep-sea (largely by redeposition) environments during much of the Early and middle Cretaceous. It is not inconceivable that the intensified oxygen minimum zone extended as deep as 2,500 to 3,000 m; such an extent would help to explain the presence of Albian black shales containing well-preserved organic carbon on or near the crest of the Mid-Atlantic Ridge in the North Atlantic, where it is unlikely that turbidites derived from the continental margin could have been the supply of the organic matter.

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FIGURE 11.—Diagrams showing how the influx of terrigenous organic matter, surface-water organic productivity, upwelling, and turbidity currents may contribute to the accumulation and redeposition of sediments containing various amounts of organic carbon and, therefore, ranging in color from red to black. A, Period of moderate supply of organic detritus from autochthonous marine and terrigenous sources and moderate upwelling resulting in accumulation of green sediment in shelf areas, sediment with high organic-carbon concentrations (perhaps black in color) within the O<sub>2</sub> minimum zone, and dominantly red clays in the deep basin. Such conditions might be representative of the later Cretaceous (for example, Santonian-Coniacian) in the Atlantic Ocean. B, Period of rapid rate of supply of organic detritus and stronger upwelling resulting in an expanded and more intense O<sub>2</sub> minimum zone that may include much of the water mass and allow sediment rich in organic carbon to accumulate over a much greater area and provide a greater source area for supply of such sediment to the deep basin by downslope transport. Such conditions might be representative of periods of accumulation of strata rich in organic carbon in the Atlantic Ocean (Aptian-Albian and Cenomanian-Turonian) (from Dean and others, 1983).



## PALEOCLIMATE AND MINERAL DEPOSITS

### SOME CLIMATIC AND OCEANOGRAPHIC CONTROLS ON THE TIME AND PLACE OF MINERALIZATION

By W. F. Cannon

In the past decade, substantial advances have been made in understanding secular variations in climate and in the nature of the oceans and the interplay of the two. Examples include work by Arthur and Schlanger (1979), Degens and Stoffers (1976), Demaison and Moore (1980), Jenkyns (1980), and Schlanger and Jenkyns (1976). In general, eustatic sea-level rise favors climatic warming because the sea surface generally has a greater capacity to retain solar energy than the land surface does. Warm climate and low pole-to-equator thermal gradients tend to diminish deep oceanic circulation and favor the development of widespread stratified oceans that are anoxic below the zone of surface mixing. Hence, there is both a theoretically predictable as well as an observed correlation between periods of ocean stagnation and anoxia. The recognition in recent years of "ocean anoxic events," periods when oceans became largely anoxic on a regional or perhaps even a worldwide scale, has been a major advance both scientifically and practically and is now a widely applied principal in petroleum exploration because the products of anoxic oceans—black organic-rich shales—form the source beds for petroleum. Such considerations of paleoclimate and paleoceanography have not yet had as substantial an impact on mineral exploration, but

their promise is great. For instance, knowing when oceans underwent major climatic-controlled changes in Eh and pH and what the effects of those changes on the solubility of metals were is an obvious application of the principals to mineral exploration. An intriguing possibility is that relatively discrete regionwide or even worldwide time lines for high mineral favorability can be defined.

The present-day Black Sea offers a good and relatively well studied scale model of former anoxic oceans. It is anoxic below about 200 m. The oxidized surface layer has an Eh of about +0.4 v and a pH of about 8.3. The deeper anoxic water has an Eh of about -0.2 v and a pH of about 7.5 (Grasshoff, 1975). These changes place surface water and deep water on opposite sides of a major solubility boundary for manganese minerals. The dissolved manganese in deep water is about 500 times greater than that in surface water (Brewer and Spencer, 1974). Where deep anoxic water is welling up onto a flanking shelf, a manganese deposit is forming just above the anoxic-oxic interface. Such conditions during major ocean anoxic events may account for the formation of important marine sedimentary manganese deposits such as Groote Eylandt (Cenomanian) in Australia.

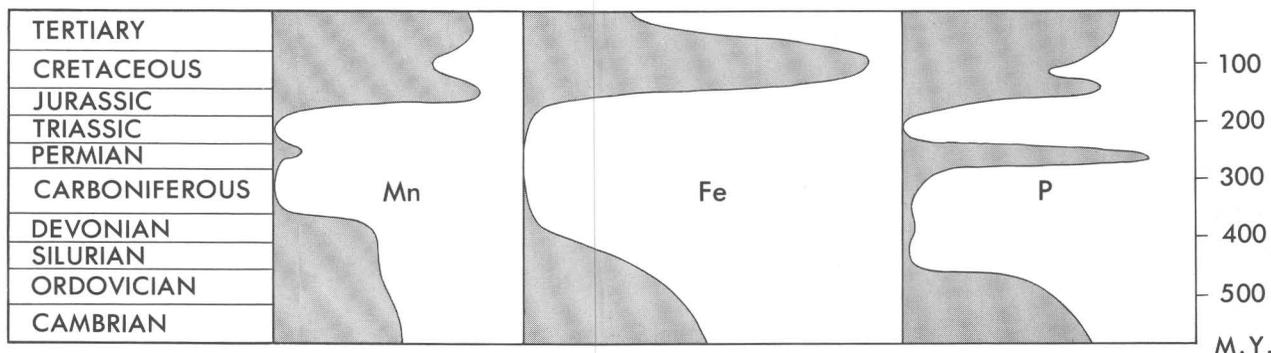


FIGURE 12.—Relative rates of accumulation of marine sedimentary deposits of manganese, iron, and phosphate on a worldwide scale approximated from resource figures compiled from many sources. Horizontal (rate) axis is sketched on logarithmic scale.

Similar solubility controls are also possible for iron and phosphate, so there is a predictable direct relationship between the times of formation of important marine sedimentary deposits of iron, manganese, and phosphate. Figure 12 shows at least a crude correlation between the times of formation of deposits of these three commodities on a worldwide scale. Many deposits formed in the early Paleozoic (until the end of the Devonian), very few formed from early Carboniferous until the beginning of the Jurassic (with the exception of a sharp worldwide phosphate peak in Late Permian), and then very extensive major deposits throughout the world formed from Early Jurassic to the present. This temporal distribution is also remarkably similar to that for petroleum source beds. Figure 13 compares the temporal distribution of marine sedimentary iron deposits and petroleum source beds and also illustrates that both were favored when sea level was considerably higher than it is at present.

There may also be a correlation between ocean anoxic events and the temporal distribution of massive sulfide deposits, particularly deposits formed at spreading centers. Such deposits forming today are oxidizing rapidly on the sea floor, and it appears that

they would be difficult to preserve in the geologic record. Those that formed during anoxic events, on the other hand, would not oxidize and would have a much higher probability of persisting until they could be buried and preserved.

Warm, humid climate also plays an obvious role in forming many continental deposits, including bauxite, nickel laterites, residual and supergene deposits of iron and manganese, and heavy-mineral placers. Identifying periods of exceptionally warm climate in the relatively complete Mesozoic and Cenozoic marine record should allow a more efficient search for these deposits in the less complete continental record.

The above are only a few examples of how the genesis of mineral deposits might be linked to fluctuations in climate and oceanographic conditions. Improving our ability to interpret paleoclimate and paleoceanography from the rock record and understanding the interplay of the two and their effect on the physical and chemical processes that form ore promise to greatly improve our ability to predict and discover deposits of many types of ores.

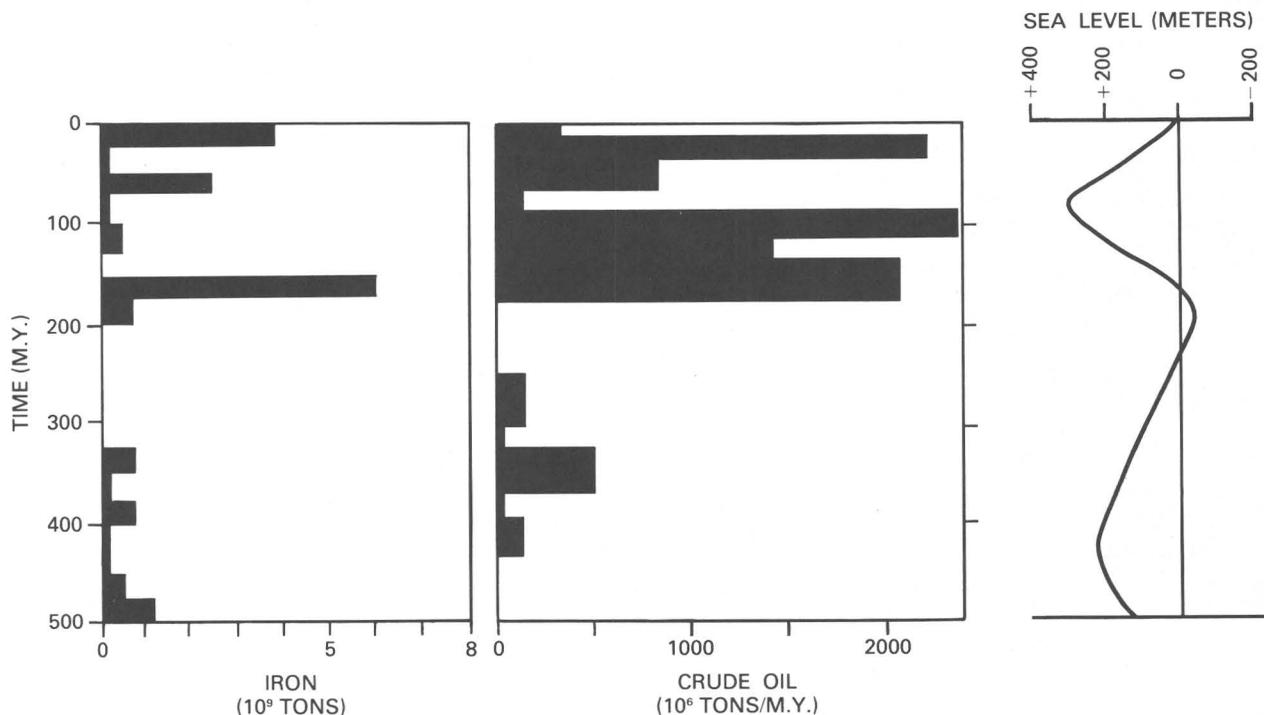


FIGURE 13.—Tons of iron in known deposits of marine sedimentary type in Europe, the Soviet Union, the Middle East, and North Africa (total of 111 deposits) as a function of time in comparison with accumulation of crude oil in source rocks as a function of time (from Tissot, 1979). Age shown is age of petroleum source rock.

PALEOCLIMATE AND MINERAL DEPOSITS

INFLUENCES OF OCEAN ANOXIC EVENTS ON MANGANESE DEPOSITION AND OPHIOLITE-HOSTED SULFIDE PRESERVATION

By Eric R. Force, William F. Cannon, Randolph A. Koski, Keith T. Passmore, and Bruce R. Doe

Periods of widespread warm climate correspond to eustatic transgressions and to ocean anoxic events (Schlanger and Jenkyns, 1976; Arthur and Schlanger, 1979; Jenkyns, 1980). The concurrence is well documented and has implications for sedimentary manganese deposits and for ophiolite-hosted sulfides.

Shallow marine environment

Consider first the situation in shallow seas during an anoxic event. A surface mixed zone of oxygenated water overlies anoxic water with a sharp interface at depths of as little as 100 m. Dissolved manganese concentration below the interface is as much as 500 times greater than that in the normal oxidized seawater above it (fig. 14). Mixing of the water masses across the interface (for example, by upwelling) and diffusion cause manganese precipitation. The precipitate is preserved in sheltered sites landward of the intersection with the shelf owing to slow manganese precipitation (fig. 14). Coincident transgression causes the oxic-anoxic

interface itself to sweep up the shelf; the locus of manganese precipitation shifts landward, and previous deposits may be remobilized. The preserved manganese deposit thus ranges from basal to maximum transgressive in stratigraphic setting. In this model for "bathtub-ring" manganese deposits, manganese can be derived from a variety of sources, and anoxic seawater serves as ore-forming fluid.

The process can also be represented on an Eh-pH diagram constructed for stratified seas like the present Black Sea (fig. 15). The deep anoxic water mass lies in the stability field of pyrite, where iron is removed from solution. Oxidation of this water mass takes it through a solution field, a manganese carbonate field, and finally into a manganese oxide field at high Eh in shallow-water environments. Note that both Eh and pH increase from deep anoxic water to shallow oxygenated water.

Shallow marine (nonvolcanic) manganese deposits comprise 75 percent of the world's present manganese reserves and show stratigraphic features (fig. 16) in accordance with our model (Cannon and

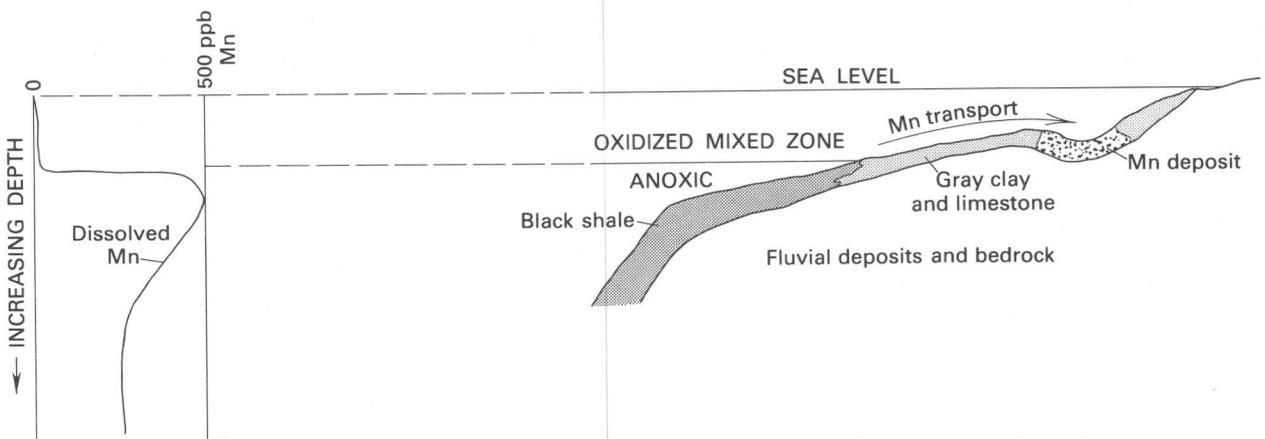


FIGURE 14.—Profile of dissolved manganese (after Brewer and Spencer, 1974) and depositional model for an anoxic event.

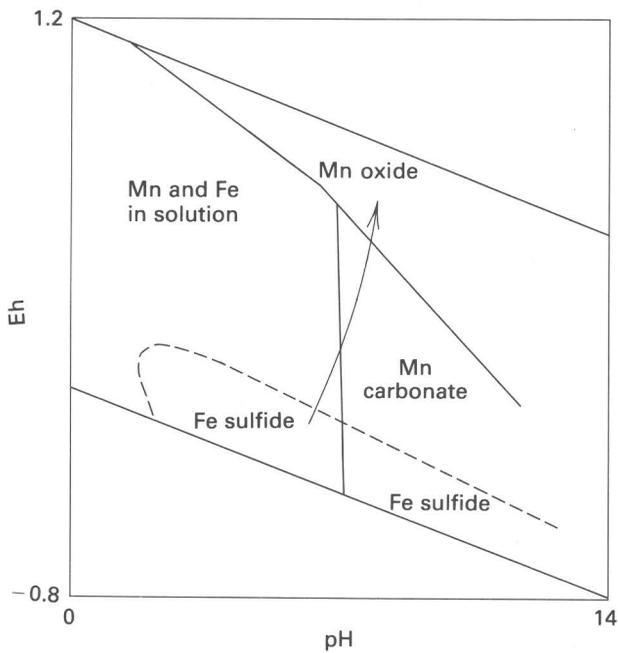


FIGURE 15.—Eh-pH diagram (after Hem, 1972) showing oxidation path of an anoxic water mass (data from Grasshoff, 1975).

Force, in press). Transgressive setting is apparent. The deposits are both clay and carbonate hosted and tend to be oxide facies above and landward of carbonate facies. They follow or correspond in age to anoxic events where this information is available (fig. 17). In some deposits, there are coeval black-shale basins nearby or a carbon isotope signature of an anoxic seawater reservoir.

There is no reason why the United States should not have some deposits of this type. We have not looked for them, and manganese mineralization (especially  $MnCO_3$ ) can be inconspicuous.

#### Deep sea

Now consider the situation in the deep sea at a spreading center. Assume continuous hydrothermal venting during and after an anoxic event (fig. 18). During the anoxic event, anoxic water reached down to some, if not all, oceanic rises, and sulfides were vented into water in which they were stable and thus were preserved.

Anoxic events ended when renewed bottom currents resulted in thinner and weaker oxygen minimum zones (fig. 18). The base of the anoxic layer lifted off the bottom and the situation became analogous to the modern-day North Pacific, which has a widespread midwater oxygen minimum layer. Manganese precipitated both from hydrothermal fluids

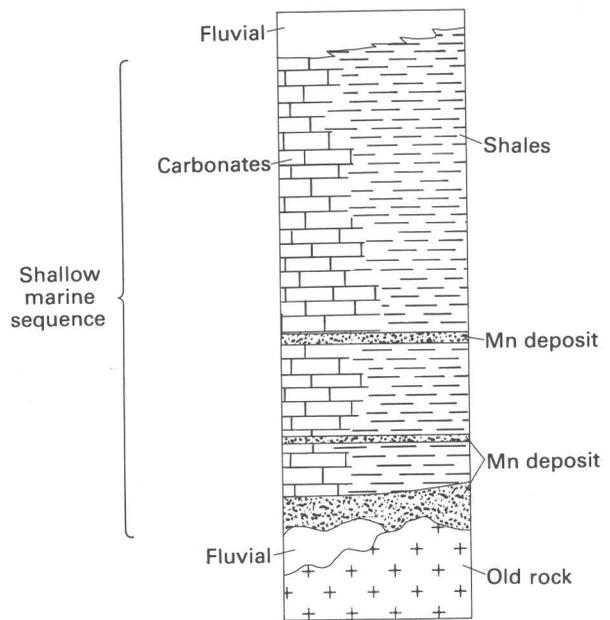


FIGURE 16.—Composite shallow marine manganese deposit (data from Cannon and Force, in press).

and from seawater at the bottom of the oxygen minimum layer (explaining the gradual change in lead isotopes in manganese oxides away from the vent) and forms a manganese halo around the vent. Vented sulfides are unstable, develop syngenetic corrosion features, and eventually dissolve (unless they are rapidly buried by lava). Two products of corrosion are goethite and elemental sulfur. Oxygenated bottom water support the diverse "vent faunas" that function without light but that cannot exist in totally anoxic water.

The stratigraphy resulting from this sequence of events is that seen in the Troodos ophiolite of Cyprus (figs. 17, 19). The lower pillow lavas contain simple sulfides and no manganese halos. The upper pillow lavas contain manganiferous umbers. The onset of oxidizing conditions on the sea floor is recorded by ochers, iron-oxide deposits representing postdepositional corrosion of the sulfides at the top of the lower pillow lava. The umber deposits just postdate the long Aptian-Albian anoxic event (fig. 19), consistent with our hypothesis that sulfides were preserved only during anoxic events.

The model should be subjected to faunal, isotopic, and petrographic tests. However, the sulfide potential of ophiolitic pillow lavas formed during anoxic events appears to be higher than that of those formed at other times. The parts of pillow lava sequences containing umbers may be systematically impoverished in sulfides.

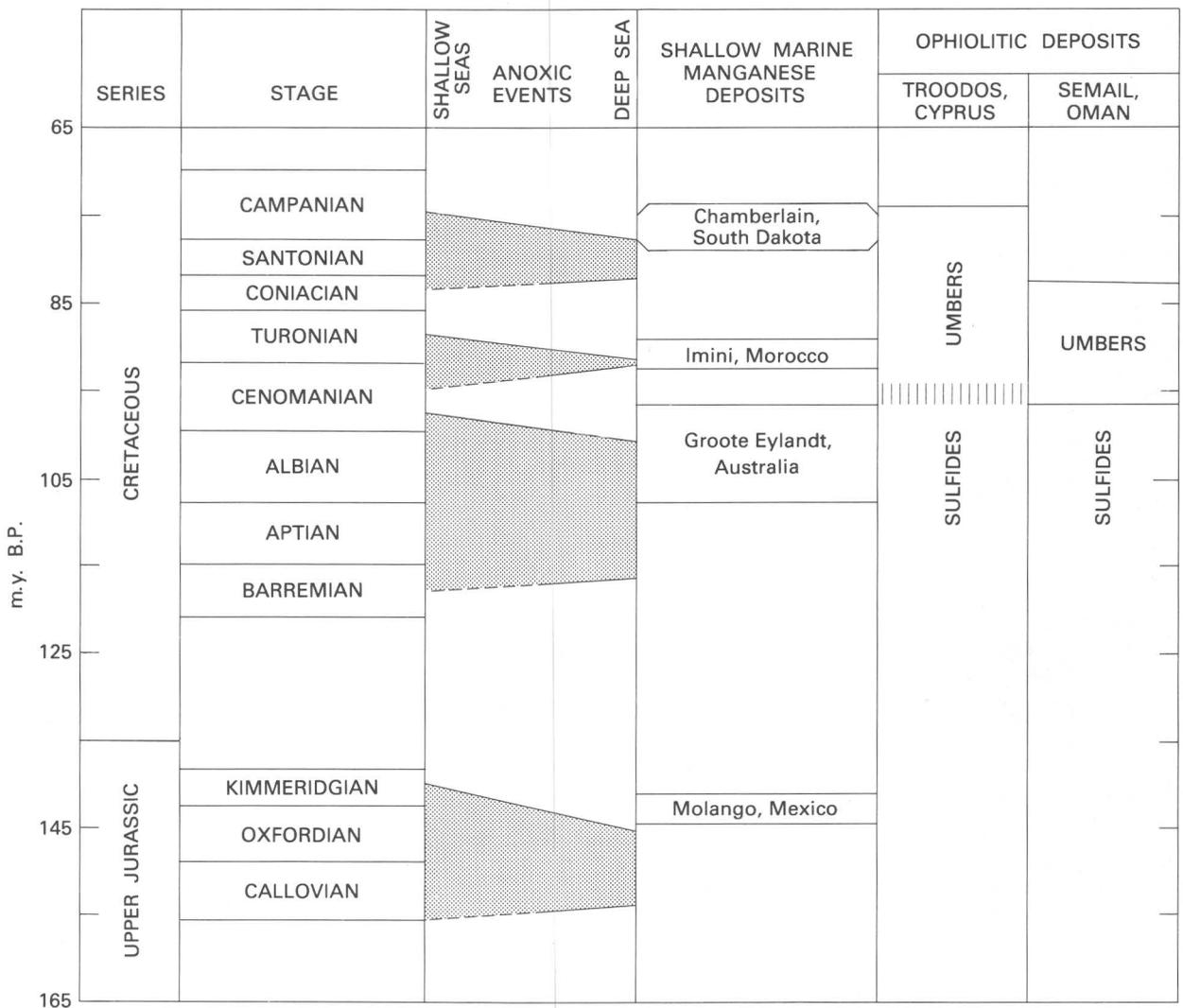


FIGURE 17.—Age correspondence of ocean anoxic events, shallow marine manganese deposits, and ophiolitic sulfides. Dashed lines indicate no data; short vertical lines indicate range of uncertainty.

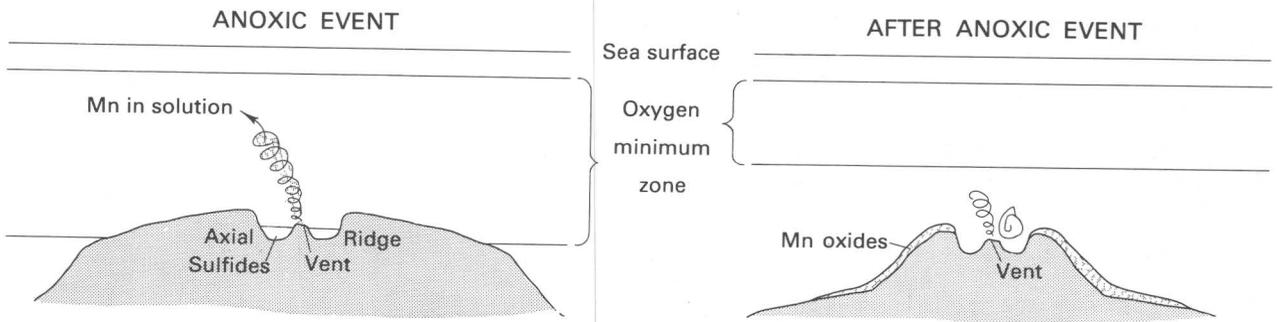


FIGURE 18.—Comparison of axial ridge vents during and after anoxic events.

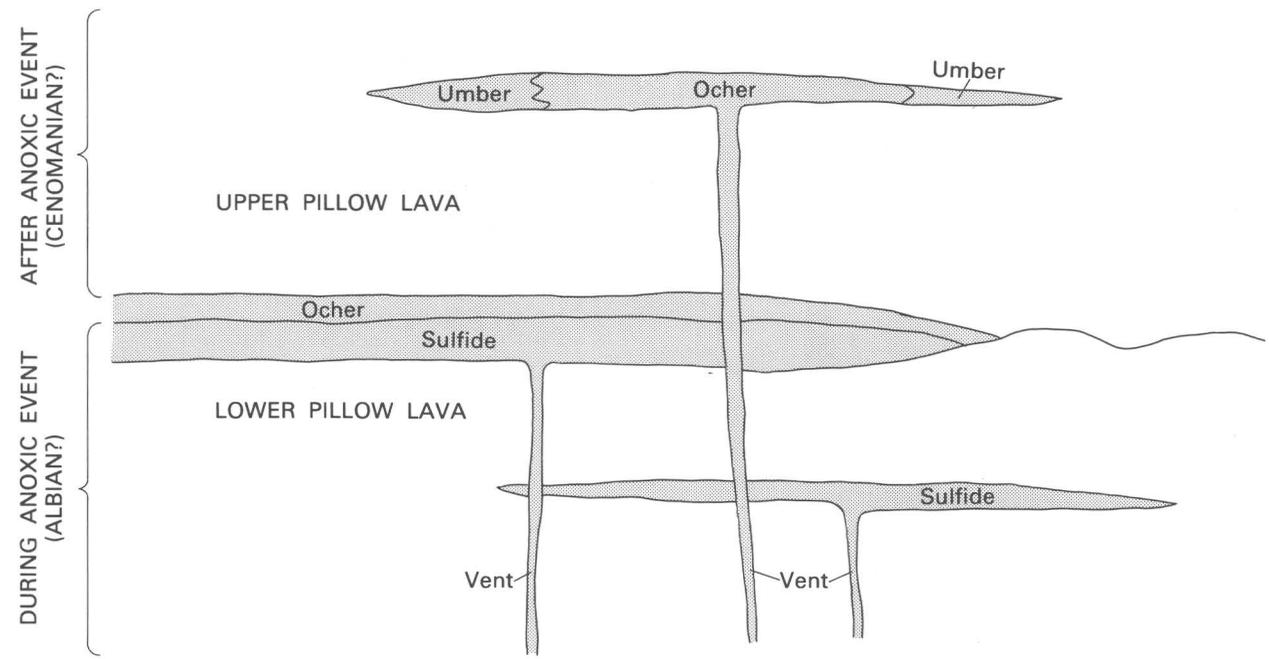


FIGURE 19.—Stratigraphic record of waning anoxic event at Cyprus (relations mostly after Robertson, 1975).

## PALEOCLIMATE AND MINERAL DEPOSITS

### LATE CRETACEOUS AND PALEOGENE NONMARINE CLIMATES IN NORTH AMERICA

By Jack A. Wolfe

Nonmarine climates have some parameters that are of major significance and that are unique, or nearly so, to such climates. In contrast to the aqueous and generally equable marine realm, where the major climatic component is mean temperature, a discussion of nonmarine climates must include annual precipitation patterns and temperature extremes. Indeed, the present distribution of major vegetation types is primarily controlled by mean annual temperature, mean of the cold month, mean of the warm month, and precipitation (Wolfe, 1979). Thus, the valid recognition of certain vegetation types in the fossil record affords a ready means of inferring the past distribution of climatic parameters on the continents.

Most paleoclimatic inferences based on plants rely on the accurate identification of organisms in terms of extant relatives and the assumption that the environmental tolerances of the fossil organisms were fundamentally the same as those of their extant relatives (Wolfe, 1971). Although this floristic approach perhaps has some validity for Neogene and Quaternary organisms, it yields only gross paleoclimatic approximations for older assemblages, which display greater "paleoecologic dissonance" with increasing age. From evolutionary theory, the floristic approach cannot be rigorously applied because one of the major factors driving evolution is the environment; that is, a given lineage diversifies in response to changing environmental parameters, and thus tolerances must have changed through time.

The most valid paleoclimatic inferences based on plants rely on the morphologic (physiognomic) convergences that result from adaptations to particular environments. For example, tropical rain forest in Indonesia is physiognomically similar to tropical rain forest in the Amazon, despite the considerable differences in floristic content. The broad-leaved evergreen rain forests of North Island, New Zealand, physiognomically resemble those of upland Central America, despite the almost total floristic differences. Emphasis on the physiognomy—particularly foliar—of fossil assemblages will yield the most valid paleoclimatic inferences. The physiognomic approach is also largely independent of identifying fossils in terms of extant relatives, an

important consideration in dealing with Cretaceous and Paleogene floras that contain representatives of many extinct genera (and of even higher level taxonomic groups that are now extinct). Among the foliar characteristics that can be used for paleoclimatic inferences are leaf size, type of leaf margin, leaf shape, leaf texture, and certain venation characteristics (Wolfe, 1971, 1981).

Application of physiognomic analyses to Paleogene floras of North America leads to several major conclusions (Wolfe, 1978):

1. The mean annual temperature fluctuated by 7° to 8°C between the four warm and three cool intervals during the Paleocene and Eocene; these intervals apparently correlate with similar intervals based on Deep Sea Drilling Project work (Wolfe and Poore, 1982).
2. A major drop of about 10°C occurred in mean annual temperature at the end of the Eocene.
3. Mean annual temperatures in excess of 20°C occurred at paleolatitudes greater than 60°N. during some warm intervals (Wolfe, 1977, 1980).
4. Truly tropical (mean annual temperature,  $\geq 25^\circ\text{C}$ ) climates extended at times to about latitude 47° N.
5. The mean annual range of temperature (that is, the difference between the means of warm months and those of cold months) was much less during the Paleocene and Eocene than it is today.
6. The mean annual range of temperature increased drastically at the end of the Eocene and has since been gradually decreasing (Wolfe, 1981).
7. The Mississippi Embayment assemblages indicate a pronounced drying trend from the Paleocene into the late Eocene.
8. At the time of drying in the southeast, Pacific Coast assemblages indicate humid climates (the reverse of the present precipitation pattern).

Late Cretaceous leaf assemblages generally have not been physiognomically analyzed. That the Paleogene fluctuations in mean annual temperature may have Late Cretaceous analogs is indicated by pollen analysis of Santonian (84 m.y.) through Maestrichtian samples from the Atlantic Coastal Plain (Wolfe, 1976); these samples show that periods during which conifers were abundant alternate with periods during which angiosperms were abundant. Physiognomic analyses of some described leaf

assemblages from southeastern North America also indicate some major temperature fluctuations. Cenomanian assemblages from the Alaskan North Slope (a paleolatitude almost at the pole) indicate polar temperatures at least 15°C higher than those at present. Late Cretaceous leaf assemblages are obviously in great need of study in order to infer additional information on Late Cretaceous nonmarine climates.

## PALEOCLIMATE AND MINERAL DEPOSITS

### VOLCANIC MANGANESE DEPOSITS IN THE WESTERN CORDILLERA: LITHOLOGIC ASSOCIATIONS AND PALEOCEANOGRAPHIC SETTINGS AND ECONOMIC DEPOSITS ASSOCIATED WITH BIOGENIC SILICEOUS ROCKS

By James R. Hein and Randolph A. Koski

Preliminary investigations suggest that numerous stratiform manganese deposits in the Western United States were formed by hydrothermal-volcanogenic processes. These deposits can be grouped into five categories on the basis of manganese mineral assemblage, lithologic association, and tectonic settings:

1. Deposits in chert-graywacke sequences—for example, parts of the Franciscan Complex of California, where lenses and beds of manganese carbonate and manganiferous opal are associated with bedded chert within thick sequences of graywacke and conglomerate. Manganese minerals from the Buckeye Mine in the Franciscan Complex include rhodochrosite, braunite, bementite, birnessite, and pennantite.
2. Deposits in chert-greenstone (ophiolite) sequences—for example, the late Paleozoic Havallah sequence in Nevada, parts of the Franciscan Complex of California, and the Nicoya Complex in Costa Rica. Manganese jasper, manganese oxides, and manganese silicates occur in lenses within bedded chert, at the interface between basalt and chert, and within basalt. Manganese minerals from the Nicoya Complex in Costa Rica include pyrolusite, hollandite, romanechite, braunite,  $\delta$ - $MnO_2$ , and bixbyite. Chemically, these ores are rich in Ba (to 5.0 percent), Cu (to 0.2 percent), and Ni (to 0.1 percent) but poor in Fe, Co, and Zn (Hein and others, 1982). The Costa Rica manganese deposits have not been exploited since 1920 and have produced about 32,000 tons of ore having an average grade of 50 percent manganese (Roberts, 1944). The largest deposits in the Franciscan, the Ladd and the Buckeye, produced 30,000 tons and 26,000 tons of high-grade manganese ore, respectively, at grades between 35 and 55 percent manganese (Trask, 1950).
3. Deposits in metachert-metavolcanic sequences—for example, late Paleozoic to Jurassic strata of the Sierra Nevada and Klamath Mountains. These deposits are similar in occurrence and general lithology to those in the Franciscan and Havallah sequences but have undergone a higher grade of metamorphism, so that the manganese mineral assemblage includes rhodochrosite, rhodonite, spessartine, piemontite, and manganese-rich pyroxene and amphiboles.
4. Deposits in limestone-argillite-basalt sequences—for example, the Eocene Crescent Formation on the Olympic Peninsula of Washington, where marine carbonate and spilitized volcanic rocks host a diverse manganese mineralogy dominated by silicates and oxides. Soren and Gunn (1967) determined the manganese oxides to be braunite, hausmannite, jacobsonite, and crednerite, whereas the manganese silicates include alleghanyite, bementite, inesite, johannsenite, rhodonite, and tephroite.
5. Deposits in Miocene and Pliocene sequences of conglomerate-sandstone-tuff-gypsum of the Colorado River-Lake Mead area of Nevada and Arizona, where high-tonnage low-grade stratiform and largely strata-bound deposits consist mainly of poorly crystalline manganese oxide cement in clastic sedimentary rocks. Manganese minerals from the Lake Mead area include pyrolusite, todorokite, cryptomelane, and ramsdellite, whereas minerals from the Artillery Mountains in Arizona include these minerals plus hollandite, romanechite, and coronadite. Chemically, these deposits are rich in Pb (to 1.5 percent), Cu (to 0.2 percent), Zn (to 0.45 percent), and Ba (to 11.0 percent) but poor in Co, Ni, and Fe. The Artillery Mountains contain about 175 million tons of manganiferous rocks

averaging 3.5 to 4 percent manganese and 70,000 tons at +20 percent manganese (Lasky and Webber, 1949). The Three Kids district near Lake Mead in Nevada produced over 2,225,000 long tons of ore averaging 18 percent manganese, which yielded more than 600,000 tons of concentrate averaging 45 percent (Crittenden, 1964).

Our preliminary interpretation concerning manganese deposits in the western Cordillera, based on lithologic associations, mineralogy, chemistry, and regional settings, is that most deposits formed in incipient oceanic rifts or at spreading centers close to a continental margin. Contemporary settings of this nature include the type of incipient oceanic rifts and back-arc basins found in the Gulf of California and the Red Sea. This concept can be best tested in the Arizona-Nevada deposits, where spreading associated with the proto-Gulf of California rift may be the source for the sandstone- and conglomerate-hosted manganese deposits. Deposition of manganese in shallow-water environments over the rift may be related to paleoclimatic and paleoceanographic factors. Sedimentological characteristics of bedded cherts and comparisons with open-ocean deep-sea chert sequences support a deep-water near-continent environment for most chert sequences (Hein and Karl, 1982) and presumably for the enclosed manganese deposits. The bedded cherts formed in areas of oceanic upwelling, probably similar to the oceanic conditions presently found in offshore Peru, southern California, or the Gulf of California. In addition, the red limestones and argillites hosting manganese deposits in the Olympic Peninsula and the red-bedded

cherts at other localities suggest an oxidizing paleoceanographic environment.

In addition to manganese, biogenic siliceous deposits host important accumulations of iron, uranium, barium, phosphates, and petroleum. Paleozoic and Mesozoic bedded chert sequences and Tertiary siliceous deposits, mainly diatomite, porcellanite, and chert, occur in several circum-Pacific orogenic belts. These siliceous deposits are derived from biogenic debris--radiolarians, diatoms, and sponge spicules.

Tertiary siliceous deposits form the source and reservoir rocks for petroleum in many places. occur with important deposits of phosphate, and may be source rocks for uranium accumulation, whereas Mesozoic and older bedded chert sequences host iron, manganese, and barium accumulations. Laminated diatomites were deposited in basins on continental shelves and slopes in areas of oceanic upwelling; bottom-water conditions were commonly anoxic.

The rhythmic bedding in Mesozoic and Paleozoic bedded cherts probably resulted from deposition by turbidity currents that carried mainly siliceous biogenic debris. Interbedded shales represent ambient hemipelagic sedimentation. Some chert sections in Japan, however, are thought to show an opposite relation; their shale beds are identified as turbidites and their cherts as ambient pelagic deposits. As mentioned, on the basis of sedimentary structures, chemical compositions, and regional settings, many bedded chert sequences apparently were deposited in deep water but near a continental margin. Bedded cherts show few similarities with open-ocean deep-sea cherts recovered from the Pacific.

## PALEOCLIMATE AND MINERAL DEPOSITS

### ORGANIC CARBON, SULFUR, AND IRON RELATIONSHIPS AS AN AID TO UNDERSTANDING DEPOSITIONAL ENVIRONMENTS AND SYNGENETIC METALS IN RECENT AND ANCIENT SEDIMENTS

By Joel S. Leventhal

Syngenetic iron sulfide phases in sediments are generally formed from aqueous sulfide resulting from catabolism of organic matter by anaerobic sulfate-reducing bacteria. It has been shown that recent marine sediments below oxygenated depositional waters show a constant relationship of carbon to sulfur (Berner, 1970; Sweeney, 1972; Goldhaber and Kaplan, 1974). When the weight percent of organic carbon is plotted on the x axis and the weight percent of sulfur is plotted on the y axis and the data are fitted by the linear least-squares method to  $y = a + bx$ , the S/C slope is approximately 0.3, and the line passes through the origin (fig. 20). New interpretation of data from recent sediments from euxinic marine environments (for example, the Black Sea) also shows a linear relationship between carbon and sulfur, but the slope is variable, and the lines for individual cores can intercept the y axis anywhere from 0.7 to 2 percent sulfur (Leventhal, 1979). Thus, the presence of an anaerobic  $H_2S$ -laden water column leads to an extra increment of sulfide without a corresponding fraction of residual organic carbon in the sediment. The extra sulfide is probably due to metal sulfide formation in the water column (Sweeney and Kaplan, 1980) and at the water-sediment interface; some is formed diagenetically in the sediment. Data from the two most recent sedimentary units of the Black Sea illustrate the effect of the evolving  $H_2S$  layer on sulfur geochemistry by producing a more positive sulfur intercept for the youngest unit having the thickest  $H_2S$  layer. Between-core comparison of data from several sites shows variable S/C slopes, which can be related to location and (or) deposition rate. The larger S/C slope is associated with higher rates of deposition nearer the edge of the basin at shallower depths (Leventhal, 1983).

New data from cores of Upper Devonian black shales from the Appalachian Basin show carbon and sulfur relationships similar to those found in modern euxinic environments. The S/C slopes for the ancient shales can be interpreted in relation to deposition rate, availability of iron, and perhaps the type of organic matter and the thickness of the aqueous sulfide layer.

These carbon and sulfur data from the Devonian black shales of the Appalachian Basin and the Cambrian Alum Shale of Sweden are used as distinct prototypes to examine the enrichment controls for metals. These samples are contrasted with the Permian Kupferschiefer of central Europe. Major controls are a relatively low sedimentation rate and a relatively high input of organic matter and metals. Organic carbon and sulfide-sulfur relationships can be used to establish the presence of an  $H_2S$ -laden water column for these ancient shales by analogy with the Recent Black Sea. However, in the Alum Shale, it is shown that all of the iron is sulfidized; thus, the normal carbon-sulfur relationship is disturbed (Leventhal, 1981b).

Trace-element abundances (Vine and Tourtelot, 1970) are closely related to organic carbon (U, Mo) and (or) sulfide sulfur (As, Hg) in the Devonian shales. Somewhat different element-association patterns are present for the Alum Shale. For the Devonian shale (Swanson, 1961), the type of organic matter is also a control for the uranium. In particular, the terrestrially derived organic matter is specific as a control and residence site of the uranium (Leventhal, 1981a). These relationships are illustrated in the diagram in figure 21. Trace element-organic and trace element-sulfide ratios vary by less than a factor of 2, whereas the sedimentation rate varies by more than an order of magnitude in the Appalachian Basin samples. Uranium and organic carbon contents for individual stratigraphic units from various parts of the basin show an inverse relation to the thickness of the unit (Leventhal and Kepferle, 1982).

The source of the uranium and certain trace elements is in part related to leaching of volcanic ash (near its source, on land), as demonstrated by increased contents of metals in samples stratigraphically above the ash in comparison with those below the ash (Leventhal and Kepferle, 1982; Leventhal and Hosterman, 1982).

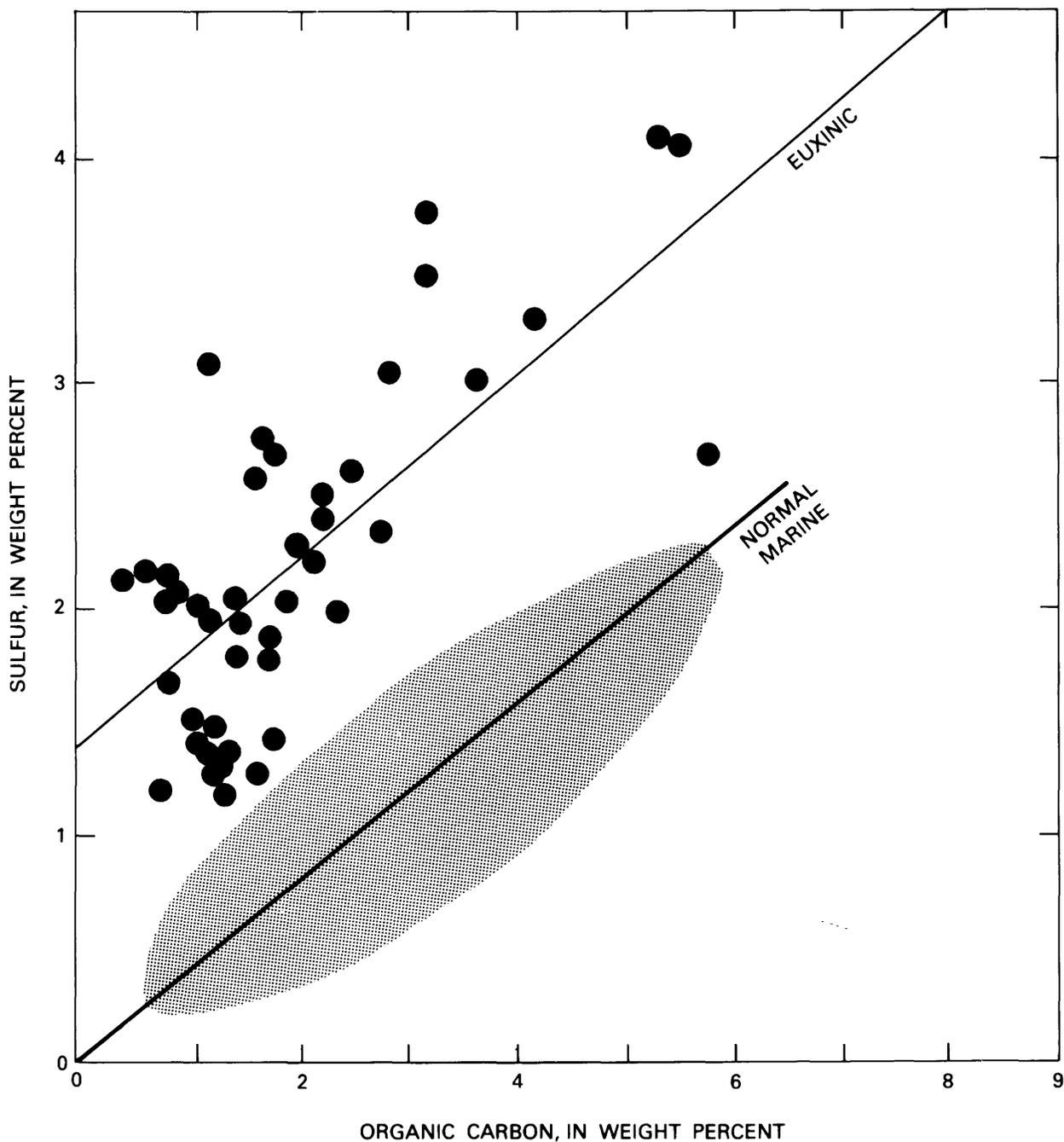


FIGURE 20.—Relationship of carbon to sulfur in Black Sea marine sediments deposited below oxygenated water (normal marine) and  $H_2S$ -containing water (euxinic) (Leventhal, 1983). Patterned area represents about 500 samples from modern normal marine sediments.

These black shales are important because they can be the host for Kupferschiefer-type ore deposits or the source of the metals for metamorphic-type ore deposits or higher grade mineralization and because their high organic content can provide an in-place

source of energy for mining and milling metals of the black shale itself when higher grade metal deposits without such associated energy sources become uneconomic (Leventhal and others, 1981; Hatch and Leventhal, 1981).

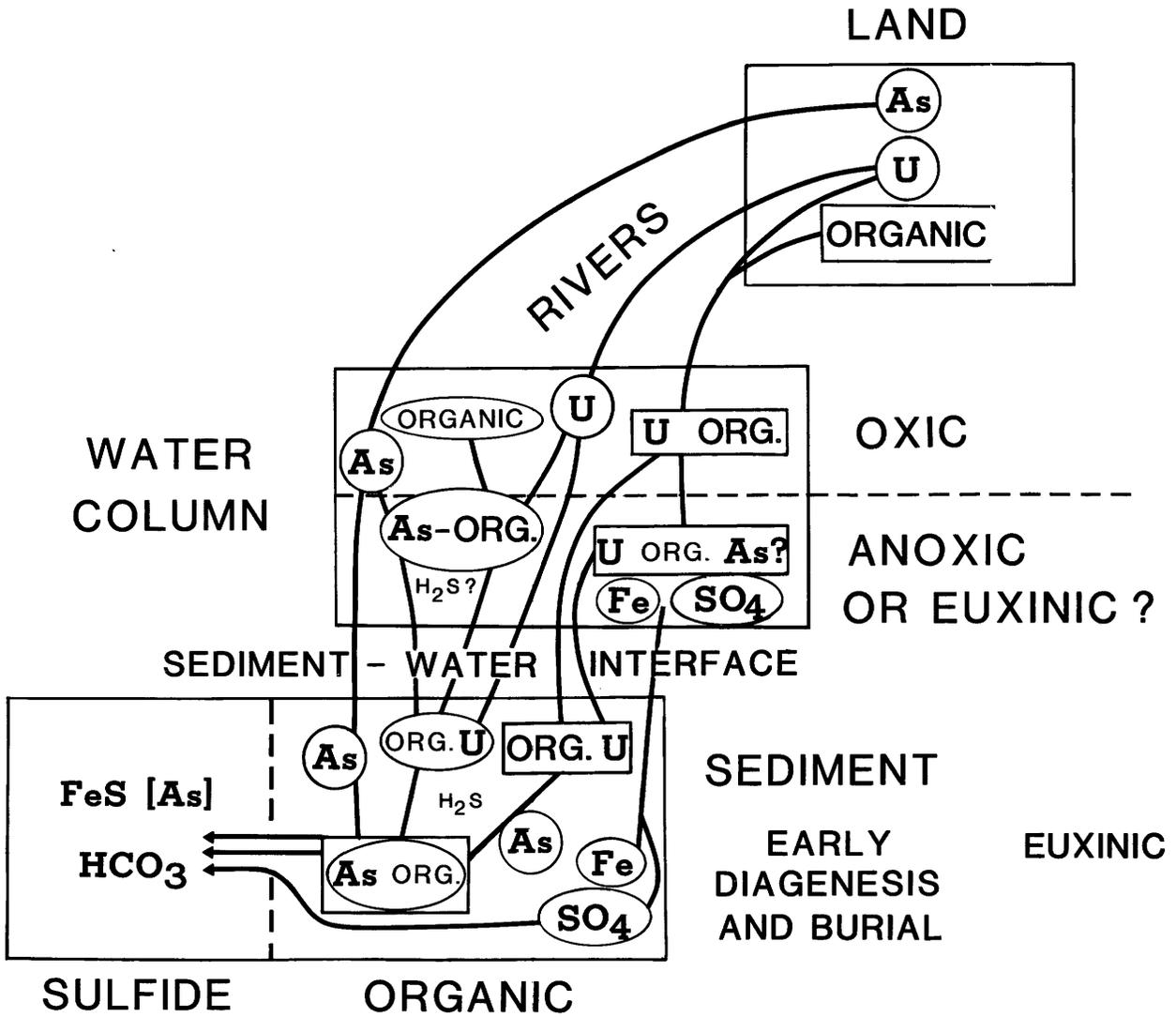


FIGURE 21.—Geochemical relationships in oxic, anoxic, and euxinic sedimentary environments (modified from Leventhal and others, 1981).

## PALEOCLIMATE AND MINERAL DEPOSITS

### PALEOZOIC ATMOSPHERIC CIRCULATION AND OCEANIC UPWELLING

By Judith Totman Parrish

Paleoclimatological models traditionally have been based on the latitudinal components of climatic patterns and their effects on the distribution of organisms and (or) climatically significant sedimentary rocks. The latitudinal components of climate include an equator-to-poles temperature gradient and a latitudinal distribution of atmospheric pressure, wind, and precipitation. The distribution of climatic patterns parallel to latitude results from the rotation of the Earth (that is, the Coriolis effect) and the existence of a temperature gradient. The rotation of the Earth prevents a direct exchange of heat between the equator and the poles. Three first-order vertical circulation cells parallel to latitude in each hemisphere are required to effect the heat exchange. The resulting surface wind pattern consists of easterly winds between about 20° N. and S., westerlies between 35° and 50° N. and S., and easterlies above 65° N. and S. High-pressure (descending air) belts occur at the poles and at about 30° N. and S., and low pressure (ascending air) occurs at about 60° N. and S. and at the equator. Precipitation is higher in the low-pressure regions and lower in the high-pressure regions.

The latitudinal model explains only the coarsest components of the global climatic pattern; it corresponds to the pattern that would be seen if the Earth had a homogeneous surface. The contrasting thermal properties (that is, specific heat capacity) of land and sea greatly complicate the simple latitudinal thermal regime imposed by the equator-to-poles temperature gradient. Fortunately, the role of land-sea circulation in disrupting the latitudinal components of atmospheric circulation to create large-scale cellular features such as the subtropical high-pressure cells at low midlatitudes in the oceans is fairly well understood, at least for the present-day global thermal regime. Moreover, global paleogeographic reconstructions, especially for the Paleozoic, are becoming more reliable, as the convergence in reconstructions published by different research groups indicates. Therefore, ancient atmospheric and oceanic circulation patterns can be modeled with some confidence, and we can thereby begin to examine some of the elements of paleoclimatic patterns that were

different from present ones because of different paleogeography.

An example of the use of such models is the prediction of the locations of ancient upwelling zones (that is, zones of high biologic productivity in the oceans) (Parrish, 1982). Because of the large input of organic matter to the sediment, upwelling zones are important settings for the deposition of very organic rich sediments and of phosphorites. The most persistent upwelling currents are wind driven—hence, the necessity of first modeling the atmospheric circulation. Upwelling currents occur in two major forms—as coastal upwelling zones and as oceanic divergences. Coastal upwelling zones occur where persistent winds flow parallel to a coastline so that the net transport of water, which is at right angles to the wind owing to the Coriolis effect, is offshore. At present, coastal upwelling zones occur primarily along the west coasts of continents (for example, California and Peru) and are driven by winds that compose the eastern limbs of the subtropical high-pressure cells. Coastal upwelling also occurs off Somalia during the summer monsoon in Asia and off Venezuela. The predominance of west coast upwelling zones is partly an artifact of present geography. Theoretically, zonal coastal upwelling currents, such as the current off Venezuela, are potentially more extensive. Zonal coasts were more prevalent in the Paleozoic; consequently, the potential for zonal coastal upwellings was higher then (fig. 22). Oceanic divergences have been almost completely ignored by geologists because, in the present world, the divergences tend to occur over very deep water and leave little mark in the sediment except a higher biogenic silica content. However, the very wide continental shelves that characterized many past geographies, particularly during the early Paleozoic, would have permitted the development of oceanic divergences in settings where high biologic productivity could have resulted in the preservation of organic carbon and phosphorites as well as of biogenic silica (fig. 22).

The following table compares the distribution of predicted Paleozoic upwelling zones with the distribution of phosphorites, organic-rich rocks, and chert.

*Comparison of distribution of predicted upwelling zones with the distribution of phosphorites, organic-rich rocks, and cherts*

[Number in parentheses is the total number of deposits for that time; first number is the number of deposits that fell into the predicted upwelling zones. \*, statistically significant correspondences]

Time	Organic-rich rocks	Phosphorites	Chert
Permian:		8 (12)*	11 (12)*
Late-----	4 (11)*		
Early-----	3 (4)*		
Pennsylvanian:		2 (5)	4 (7)
Late-----	2 (2)*		
Early-----	3 (3)*		
Mississippian:		2 (4)	6 (22)
Late-----	4 (4)*		
Early-----	3 (5)*		
Devonian:		8 (15)*	14(30)*
Late-----	13 (17)		
Middle-----	5 (7)*		
Early-----	3 (8)*		
Silurian-----	1 (4)	1 (5)	5 (9)
Ordovician-----	3 (6)	10 (22)	12 (20)*
Cambrian-----	2 (6)	19 (40)*	10 (19)*

With the exception of phosphorites in the Ordovician, wherever sample sizes are large enough to give meaningful statistical results, there is a significant correspondence between upwelling and the three types of deposits commonly found in upwelling zones. Particularly interesting is the fact that cherts correspond so well, because biogenic silica in modern upwelling zones is almost entirely derived from diatoms, which did not evolve until much later. Some of the Paleozoic cherts are radiolarites, and radiolarians tend to concentrate in upwelling zones in

the present world. However, other Paleozoic cherts either have undergone so much diagenesis that their origin cannot be determined or are derived from sponge spicules. The relation of siliceous sponges to upwelling is not well known.

The results presented in the table suggest that, despite undoubted differences in climatic parameters, such as the absolute value of the equator-to-poles temperature gradient, past atmospheric circulation patterns were governed by the same factors that govern them today.

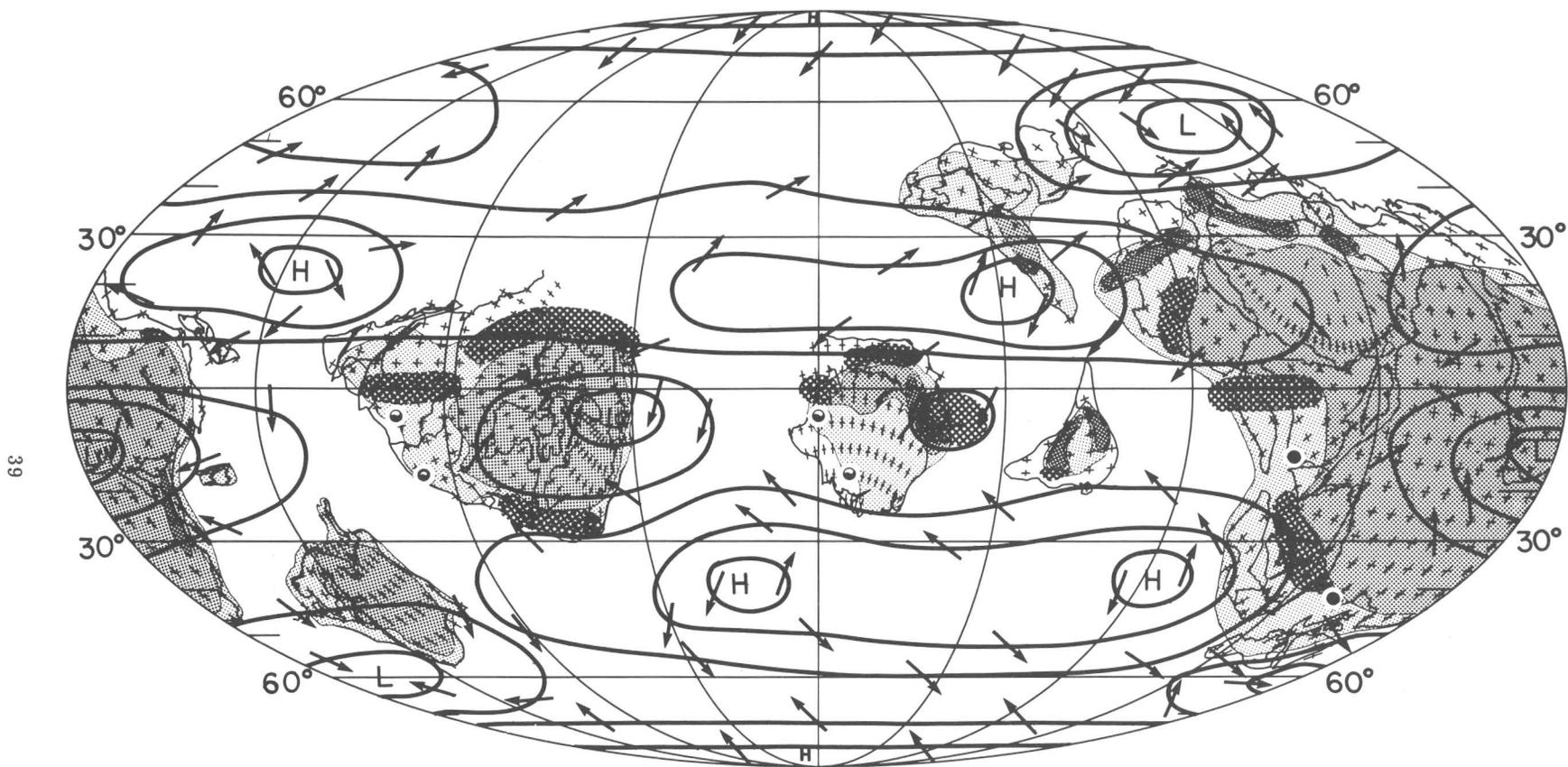


FIGURE 22.—Atmospheric circulation in the Late Cambrian northern winter (adapted from Parrish, 1982; published with permission from the American Association of Petroleum Geologists). H, high pressure; L, low pressure; hatching, upwelling zones; dark shading, highlands; medium shading, lowlands; light shading, continental shelf (reconstruction from Scotese and others, 1979). Dark lines are isobars; arrows indicate wind direction. Note the zonal coastal upwelling zones predicted for the north and south paleocoasts of North America (left center) and the equatorial divergence over the shelf in western Gondwana. Solid circles indicate organic-rich rocks with marine organic matter; half-solid circles indicate organic-rich rocks of unknown origin; plus signs represent 5° longitude-latitude tick marks.

## PALEOCLIMATE AND MINERAL DEPOSITS

### PALEOCLIMATIC CONTROLS ON THE OCCURRENCE AND QUALITY OF COAL

By C. B. Cecil, R. W. Stanton, S. G. Neuzil, F. T. Dulong, and L. F. Ruppert

The industrial nations of the world have devoted many years of research to understanding coal quality; however, the geologic factors that control the origin and distribution of mineral matter in coal are still poorly understood. In a broad sense, paleoclimate is recognized as one controlling factor in the worldwide distribution of coal. Although the quality of coal deposits varies worldwide, there are three general "families" of coal deposits (Stach and others, 1982): (1) banded bituminous coals of Carboniferous age of the Northern Hemisphere, (2) banded bituminous coals known as Gondwana coals of Permian, Triassic, and Jurassic age in India, southern Africa, eastern Australia, South America, Madagascar, and Antarctica, and (3) high-moisture lignite and subbituminous coals of late Mesozoic or Tertiary age in Europe, western North America, and southeastern Australia. The Carboniferous coals formed under a humid tropical and subtropical climate. In contrast, climate conditions were cold temperate during the formation of the Gondwana coals (Stach and others, 1982). Climate conditions that prevailed during the formation of coals of Cretaceous age and younger are not well documented. However, paleoclimates directly and indirectly affect and (or) control both the occurrence and the quality of these three broad "families" of coal deposits.

On a local or regional scale, attempts to predict the quality and thickness of coal beds are generally unsuccessful without data from closely spaced drilling. Models to explain variations in thickness and quality are limited to physical depositional environments such as alluvial plain, upper delta plain, lower delta plain, or back barrier. Coal beds whose origins are traced to an alluvial plain or upper delta plain depositional setting are generally believed to be low in ash and sulfur, whereas coal beds of lower delta plain or back barrier origin are generally believed to be high in ash and sulfur as a result of proximity to marine conditions. High-sulfur coal has been related to superjacent strata of marine origin (White and others, 1913; Horne and others, 1978). Williams and Keith (1963) and Gluskoter and Hopkins (1970) demonstrated that sulfur content is higher in areas where a coal bed is overlain by marine sediments than it is in areas where the same bed is overlain by sediments of nonmarine origin. In contrast, recent

work by Cecil and others (1982) has shown that the variation in sulfur is far greater among coal beds of strictly nonmarine origin than it is for a given coal bed that is overlain by both marine and nonmarine sediments.

Geochemical and paleoclimatic models provide a more comprehensive explanation for the systematic variation of ash and sulfur in coal beds of the central Appalachian Basin. In the Upper Mississippian, coal beds are thin, discontinuous, and generally of poor quality. In the Lower and lower Middle Pennsylvanian, coal beds are generally low in both ash (<10 percent) and sulfur (<1 percent), whereas, in the upper Middle and Upper Pennsylvanian, coal beds contain high amounts of ash (>1 percent) and sulfur (>1 percent). Sedimentary rocks associated with the low-ash low-sulfur coal beds are noncalcareous—sandstone, siltstone, and shale. Coal beds that are high in ash and sulfur are associated with calcareous sandstone and shales as well as with nonmarine limestone. The mineralogy of the low-ash coal beds is dominantly kaolinite and quartz; the mineralogy of the high-ash high-sulfur coal beds is dominantly kaolinite, illite, quartz, pyrite, and calcite. In the sedimentary sequence of the upper Middle Pennsylvanian, flint clays are present that, in places, grade laterally into nonmarine carbonates; these sediments were subaerially exposed and, as a result, contain microkarst zones that are brecciated and have subaerial crusts. The Upper Pennsylvanian also contains nonmarine carbonates that were subaerially exposed; however, flint clays are not present. In addition, red beds as well as paleosols are present. The paleosols are somewhat similar to caliches because they contain teepee or pseudoanticlinal structures and are highly enriched in nodular carbonate at the top.

The stratigraphic occurrence of coal, changes in coal quality, and changes in the lithologies of associated sediments in the Appalachian Basin indicate at least two major climatic changes during Pennsylvanian time. In Late Mississippian time, evaporation was high relative to precipitation, as the presence of nonmarine carbonates, red beds, and paleosols having the characteristics of caliches indicates. In the latest Mississippian or Early Pennsylvanian, the first climatic change occurred as

rainfall increased relative to evaporation. From Early to late Middle Pennsylvanian time, precipitation was high relative to evaporation; thus, highly acid conditions ( $\text{pH} > 4.5$ ) were produced in the paleo-peat-forming environments. Coal derived from peat that formed under these acid conditions is in general low in both ash and sulfur (Cecil and others, 1981).

In the upper Middle Pennsylvanian, the second climatic change occurred when evaporation increased relative to precipitation. These relatively drier conditions resulted in an increase of dissolved solids and pH in surface and near-surface waters and thereby changed the geochemical conditions in peat-forming and associated depositional environments. Coal derived from peat that accumulated under nearly neutral conditions is relatively high in both ash and sulfur (Cecil and others, 1981). Changing climatic conditions are also indicated by the presence of (1) nonmarine limestones that have shallow-water and subaerial features and (2) paleosols similar to caliche. The climatic changes interpreted from lithologic and coal-quality characteristics are summarized in figure 23. The inferred paleoclimatic changes from the Late Mississippian through the Late Pennsylvanian are consistent with paleobotanical data (White, 1925; Phillips, 1978; Pfefferkorn and Thomson, 1982).

Paleoclimate was one of the principal factors that controlled the geochemistry of the Pennsylvanian peat-forming environments. In turn, these geochemical conditions controlled the quality of the resulting coal. In the Early and lower Middle Pennsylvanian, water in the peat-forming

environments was dominantly derived from rainfall. Organic acids maintained the waters at low pH values because the concentration of dissolved solids was low, and the resulting buffering capacity was also low. In the upper Middle and Late Pennsylvanian, rainfall was reduced, and the climate became more seasonal (White, 1925). Water in the peat-forming environments was derived chiefly from surface or ground water. Interstitial water contained increased concentrations of dissolved solids; buffering capacity was increased, and pH values increased in interstitial water of the peats. These latter conditions were more conducive to sulfur and ash fixation in the peat.

The climate changes and the subsequent shift in geochemical conditions account for the stratigraphic variation in the ash and sulfur contents of coal beds in the Appalachian Basin. This variation cannot be explained by physical depositional models. The marine influence model generally used to explain the high-sulfur content of coal (Williams and Keith, 1963) is nothing more than a special case within a more encompassing geochemical model (Cecil and others, 1982).

The continued development and application of paleoclimatic-geochemical modeling will expedite coal-resource assessments and quantify resource estimates. Such modeling can also be applied to exploration, reserve characterization, mine planning, coal preparation, and the successful prediction of coal properties as related to coking, combustion, and synthetic fuels.

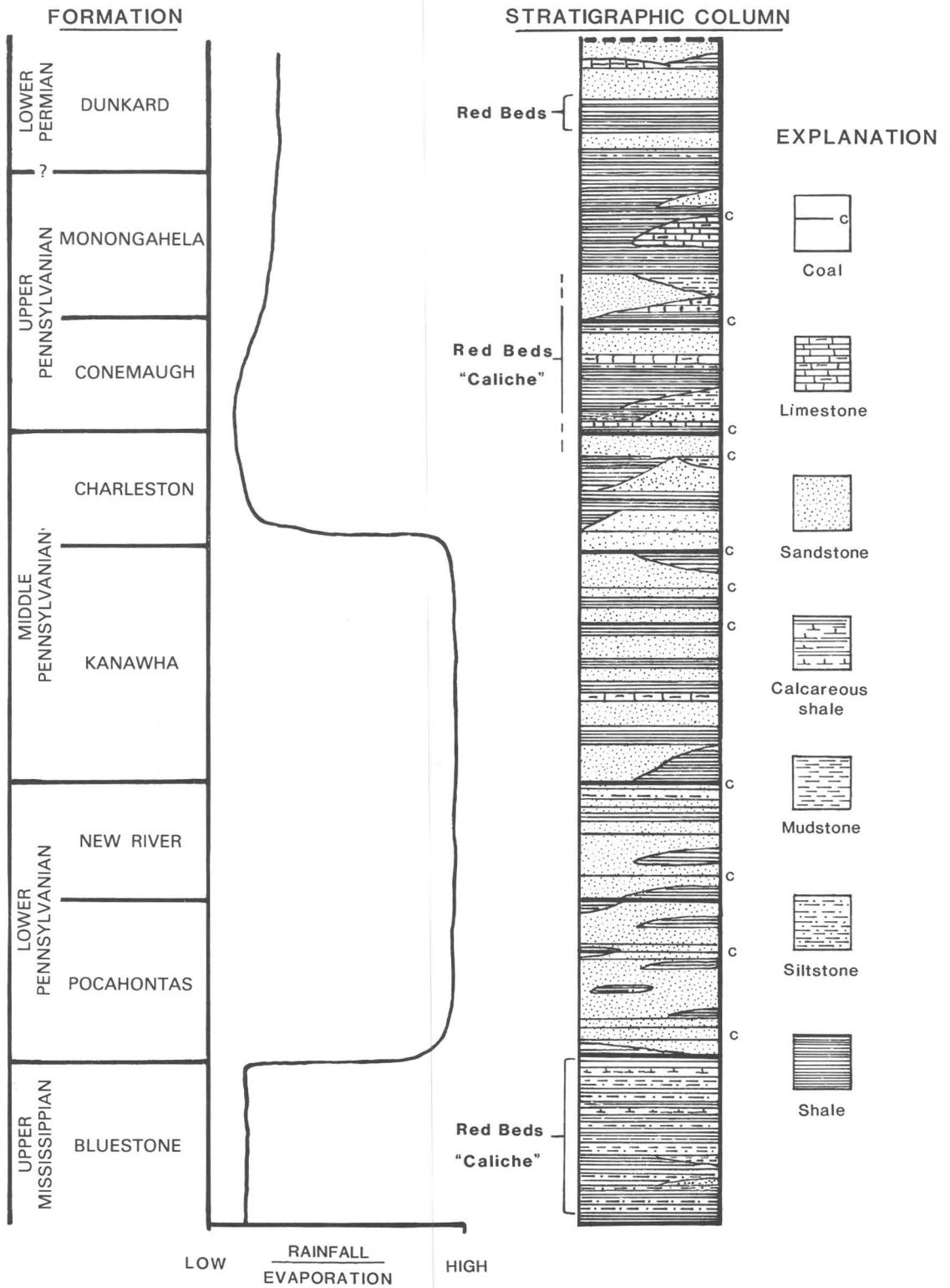


FIGURE 23.—Inferred paleoclimate changes and generalized stratigraphic column from the Upper Mississippian to the Lower Permian(?) central Appalachian Basin.

## PALEOCLIMATE AND MINERAL DEPOSITS

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### CARBON DIOXIDE, GEOCHEMICAL MODELING, AND PALEOENVIRONMENTAL RECONSTRUCTIONS

By Eric T. Sundquist

Paleoclimate is sometimes linked to other paleoenvironmental factors by means of geochemical speculation on a regional or global scale. For example, several investigators have suggested various relationships among past climate, atmospheric CO<sub>2</sub>, carbonate dissolution, organic carbon burial, and biological productivity. In order to develop geochemical models of these relationships, it is useful to draw upon recent improvements in modeling atmospheric CO<sub>2</sub>.

During the past 25 years, atmospheric CO<sub>2</sub> concentrations have increased from about 315 to about 340 ppm. Extrapolation to future levels of fossil-fuel consumption suggests that atmospheric CO<sub>2</sub> will be twice its preindustrial level before the year 2050. The best climate modeling available indicates that this increase will enhance atmospheric absorption of infrared radiation enough to raise the mean global surface temperature by about 2° to 3°C and the polar surface temperature by about 5° to 8°C. Concern for these potential climatic effects has stimulated a broad international effort to understand the factors that control atmospheric CO<sub>2</sub> concentrations.

The measured atmospheric increase accounts for only about half of the CO<sub>2</sub> produced by burning fossil fuels. Accounting for the other half is very difficult because it requires understanding the oceans and the biosphere, the two major reservoirs that exchange carbon rapidly with the atmosphere. The problem is further complicated because it is not clear whether the biosphere is a net CO<sub>2</sub> sink or an additional source; thus, the fossil-fuel CO<sub>2</sub> problem is a fundamental carbon-cycle problem.

Because of their long-standing interest in geochemical cycles, geologists can offer unique and important perspectives on the CO<sub>2</sub> problem. One particularly geological concern is the long time scale of response to anthropogenic CO<sub>2</sub> production. Whereas most public attention has focused on effects that may occur during the next few decades or centuries, geochemical models suggest that some effects may persist for thousands or even tens of

thousands of years. Another geological concern is the potential for significant geochemical effects, such as enhanced marine carbonate dissolution. These effects are implied by geochemical principles that will operate even if there are no climatic effects. Finally, the geological record contains abundant evidence for past nonanthropogenic variations in the global carbon cycle. Many of these variations appear to have been associated with changes in climate and some strongly influenced the deposition and preservation of fossil fuels. The sedimentary record of past fluctuations also necessitates a careful reexamination of the steady-state assumption that underlies all predictive CO<sub>2</sub> and climate modeling.

Geochemical modeling is a powerful and essential tool for approaching these geological aspects of the CO<sub>2</sub> problem. Geochemical models provide a way of integrating numerous kinds of geological evidence into paleoenvironmental reconstructions and predicting how geological processes will respond to future CO<sub>2</sub> emissions. The models are invariably rooted in the fundamental principles of chemical equilibrium, chemical kinetics, and mass and energy conservation. If they are to be applied to the integration of stratigraphic evidence or future effects, they must be time dependent. These characteristics are shared by many predictive carbon-cycle models developed by the CO<sub>2</sub> research community. Predictive CO<sub>2</sub> models provide a valuable starting point for geochemical modeling.

However, the development of geochemical carbon-cycle models from CO<sub>2</sub> models is not straightforward. Three very important considerations are (1) the interdependence of processes and time scales, (2) the multiplicity and unreality of steady states, and (3) continuity with the present. These considerations imply very specific constraints on the form of geochemical carbon-cycle models and the way that the models are applied. They also have important implications for predictive CO<sub>2</sub> models and for other geochemical models.

## PALEOCLIMATE AND MINERAL DEPOSITS

### ISOTOPIC RESEARCH, CLIMATE, AND THE GENESIS OF MINERAL DEPOSITS

By Bruce R. Doe

There are several fundamental climatic factors that we need to study to document the history of past climates and to understand the relationship of paleoclimates to the genesis of mineral deposits. These climatic factors include temperature, temperature distribution, humidity (including cloudiness and windiness), oxidation state of waters, pH, salinity, and saline species. In addition, several factors that may be indirectly related to climate and the influence of climate on mineralization are source materials (mountains versus plains of various materials such as volcanic rocks or sediments) and plate tectonic configurations. A number of other factors that may be important as mechanisms for climate change include changes in solar luminosity, variations of the Earth's magnetic field, and a change in the Moon's distance from the Earth. Isotopes have played a large role in resolving many of these paleoclimatic problems. The following is a survey of some of these applications.

#### Oceans

Because temperature exerts a primary control on the isotopic composition of benthic and planktonic foraminifers, oxygen isotopes have been the workhorse for determining paleotemperatures in the oceans. The use of oxygen isotopes of benthic and planktonic foraminifers for paleothermometry culminated in delineating the temperature history of the oceans over the last 100 m.y. (Savin, 1977). Belemnites have also been important because of the ease in identifying recrystallization in thin section, and foraminifera have shown broad applicability for the Cenozoic. Several factors influence the application of oxygen isotopes to paleothermometry: diagenesis, disequilibrium, oxygen isotopic composition of the water in which the animals grow, water density in the case of planktic foraminifera, and salinity. Identifying the contribution of each parameter is essential in isotopic studies. For example, the extent of diagenetic recrystallization can often be determined through thin-section study. Also, some foraminifera secrete their tests out of equilibrium with seawater, so that some taxa are more

reliable as paleotemperature indicators. Increasing salinity tends to result in heavier oxygen isotopic compositions, so that taking the lightest values from several analyses can help compensate for this problem. The oxygen isotopic composition of ocean water is itself a problem because it is controlled by the growth and decay of icecaps, local evaporation, or precipitation, large-scale atmospheric circulation, and nearby continental runoff. Berger (1979) gives a useful review of the use of stable isotopes in foraminifers and how they reflect various hydrologic and climatologic conditions.

In the case of carbon isotopes in carbonate rocks, the thermal fractionation effect is very small (about 0.035 permil/ $^{\circ}$ C) and, in rocks or sediments poor in carbon, carbon isotopes are less susceptible to diagenetic effects than oxygen isotopes are (Scholle and Arthur, 1980). Carbon is concentrated into two main reservoirs: carbonate and organic carbon. Although carbon isotopes do not vary as much in the geologic marine record as oxygen isotopes do, Cretaceous variations have been found to correlate with ocean anoxic events (Scholle and Arthur, 1980). Because organic matter contains very light carbon ( $\sim -25 \delta^{13}\text{C}$ ), carbonates formed in the oxic layer during anoxic events can be expected to trend toward heavy values. Recent studies confirm this trend in the heavy carbon isotopic ratios found in the Albian and Turonian stages of the Cretaceous. Carbon isotopes are also governed by the following secondary reservoirs: carbonate from the oxidation of old organic carbonate, sedimentary and marine sulfates formed from oxidation of sulfide, ferric oxides formed from oxidation of iron, and the Earth's atmosphere.

Sulfur is thought to be partitioned into an oxidized inorganic sulfate reservoir and a reduced, biologically mediated sulfide reservoir containing the lighter values of  $\delta^{34}\text{S}$ . Secular variations in the  $\delta^{34}\text{S}$  in sulfate are well documented (Claypool and others, 1980). The reduced sulfur in mineral deposits depends on several parameters, some of which are shown in figure 24. There is a tendency for sulfate-sulfur and carbonate-carbon isotopes to be inversely correlated

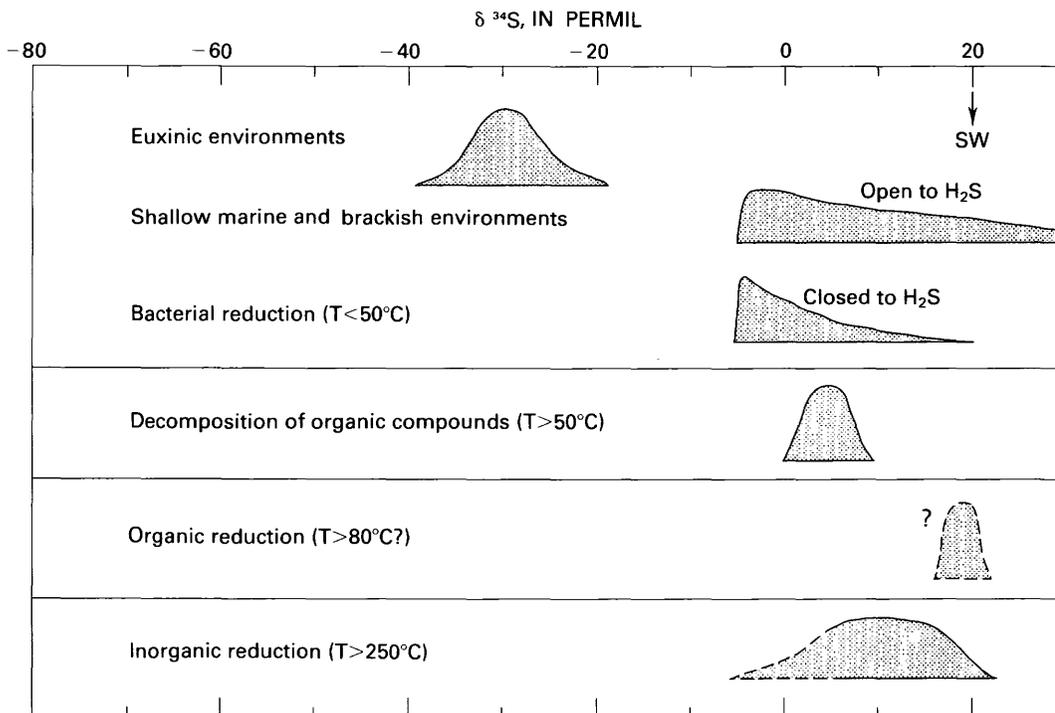


FIGURE 24.--Distribution pattern for  $\delta^{34}\text{S}$  values of  $\text{H}_2\text{S}$  and sulfide minerals when sulfate  $\delta^{34}\text{S}=+20$  percent is reduced by various mechanisms. (From Ohmoto and Rye, 1979.) (Reproduced with permission as modified *Geochemistry of Hydrothermal Ore Deposits*, copyright 1979 by John Wiley and Sons, Inc.)

with each other (Veizer and others, 1980), and this tendency has led to hypotheses involving control of both isotopes by biologic means. There is also a correlation of sulfur with  $^{87}\text{Sr}/^{86}\text{Sr}$  in marine fossils. For example, strontium in the oceans is radiogenic at the present time and was also in the Mississippian but was nonradiogenic in the Jurassic and Cretaceous (Peterman and others, 1970). Sulfate-sulfur is relatively heavy at the present time and was in the Mississippian but lighter in the Jurassic and Cretaceous. Nonradiogenic strontium and light sulfur are compatible with a young igneous component because of either submarine activity or erosion from magmatic arcs (George Claypool, oral commun., 1981). The inverse correlation of sulfate-sulfur with carbonate-carbon may therefore be more complex than current accounts indicate.

Lead isotopes in sedimentary manganese deposits might indicate the importance of volcanism in providing manganese to anoxic seas because, as Doe and Zartman (1979) pointed out, there is a large isotopic difference between mantle lead and the lead in seawater and pelagic sediments. The Cretaceous is a period of unusually great volcanic activity and also hosts some of the best-documented oceanic anoxic events. Radiogenic isotopes such as those of lead and strontium may help distinguish climatic effects from nonclimatic effects.

#### Continents

Deuterium (fig. 25) and oxygen isotopes in continental surface water vary in a systematic fashion. There is a tendency for deuterium to decrease northward because precipitation is enriched in the light isotope, and the remaining vapor becomes depleted (Taylor, 1979). A decreasing temperature trend also tends to make the precipitation heavier. This trend is well illustrated in the midcontinent from the Gulf of Mexico northward. On the east coast, the trend is modified by the Atlantic Ocean and mountain ranges. The trends caused by jet-stream-related precipitation coming eastward across mountains in the western United States add additional complexities. For example, as clouds moving up the mountains cause precipitation, the vapor becomes depleted in the heavy isotope. Increasing elevation is accompanied by a temperature drop that accentuates the isotopic change. East of the highest elevations, the isotopic composition of surface water begins to become heavier because sinking clouds become warmer, and there is mixing with precipitation from the Gulf of Mexico.

Because precipitation is a process approaching equilibrium, oxygen varies systematically with deuterium isotopes (fig. 26), deuterium being about  $8 \delta^{18}\text{O} + 10$  (in permil). This line is called the meteoric water line (Taylor, 1979). Most surface

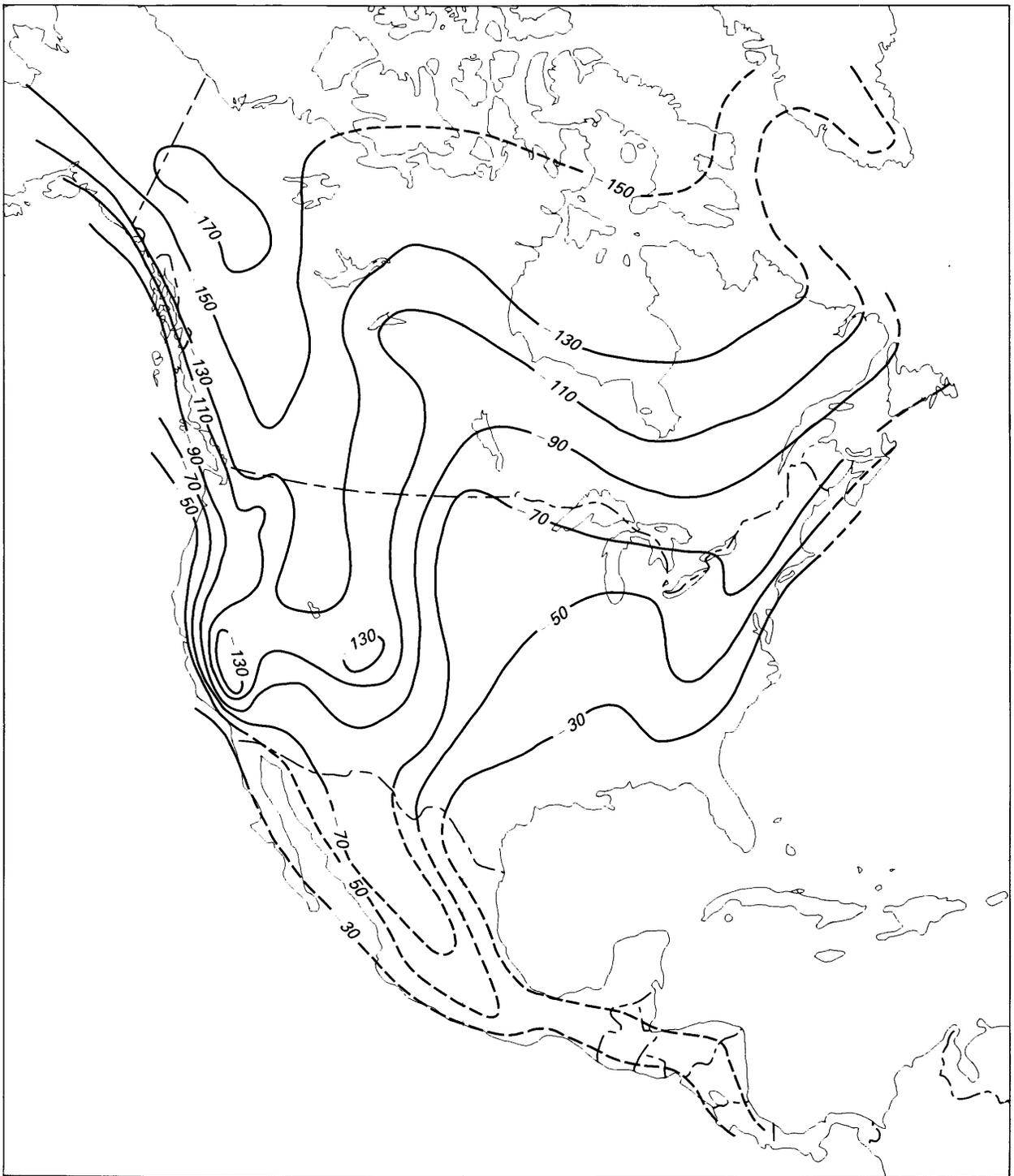


FIGURE 25.—Map of North America showing contours of the approximate average  $\delta D$  values of meteoric water. (From Taylor, 1979.) (Reproduced with permission from *Geochemistry of Hydrothermal Ore Deposits*, copyright 1979, by John Wiley and Sons, Inc.)

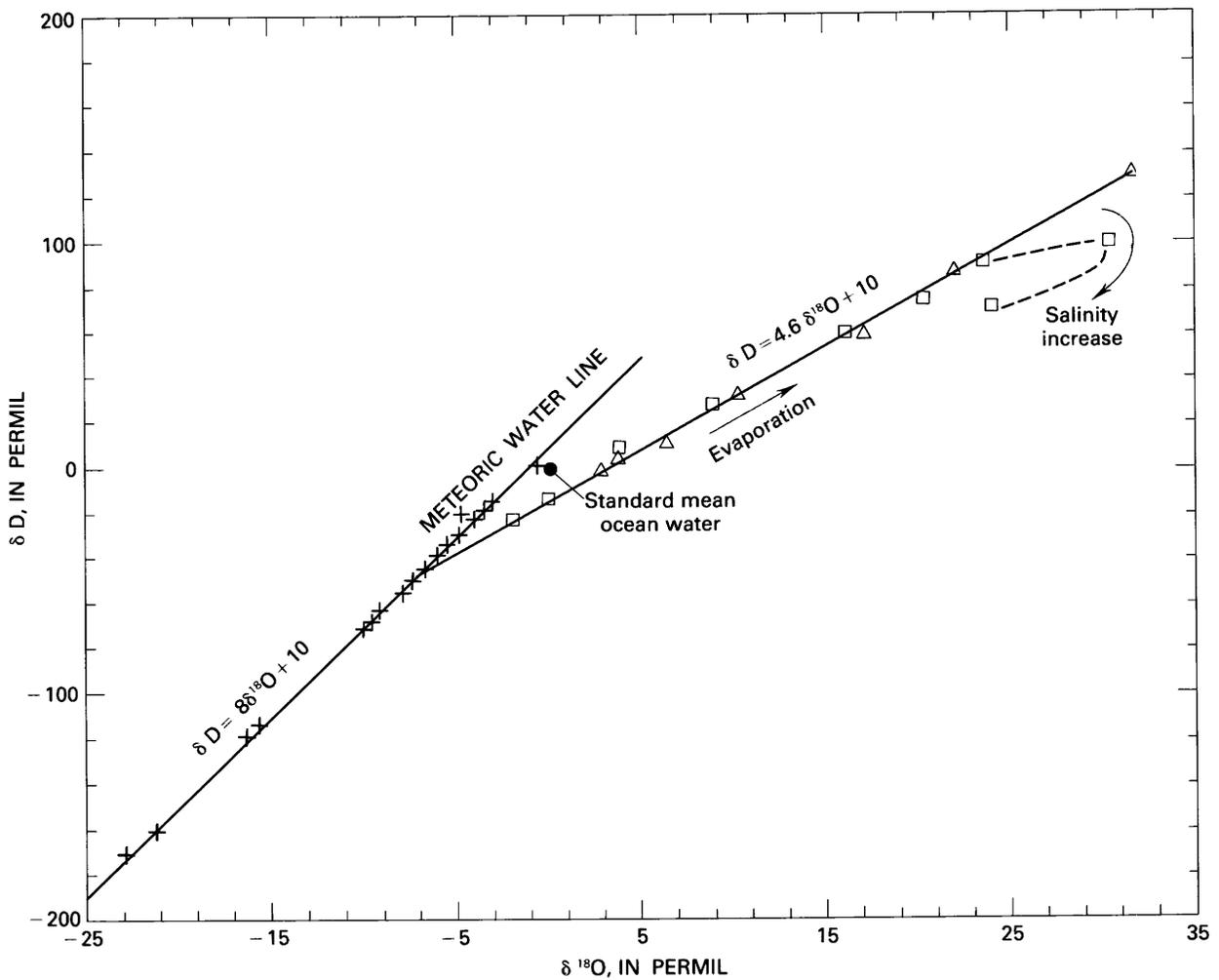


FIGURE 26.—Behavior of  $\delta D$  and  $\delta^{18}O$  in meteoric water. Crosses are values for precipitation at various places throughout the world. Values for Antarctic lakes can be more negative. Squares and triangles represent data from two lakes in the northwestern Sahara that are typical of evaporating water. Note reversal of data on lake represented by squares, caused by the effect of dissolved salts on the activity of free water. (From Pearson and Coplen, 1978.)

water lies to the right of this line (fig. 26) because of surface evaporation and evaporation of the falling precipitation in arid areas. These relationships are expressed as a  $\delta D$  of about  $5 \delta^{18}O + 10$  (in permil). At very high salinities, the trend is reversed because of absorption effects on ions. In general, meteoric water can also be distinguished from magmatic or metamorphic water except in the case of highly evaporated systems at high latitudes. However, in the eastern Triassic basins, which were near the equator at the time they were formed, the meteoric water trends probably followed a heavier isotopic path than that shown for primary magmatic water in figure 27. These

data, coupled with data on fluid inclusions or alteration minerals on magmatothermal ore deposits, have been used to identify a major meteoric water component in many hydrothermal mineralizing systems. The full significance of this important finding is not yet completely realized in ore genesis or as a guide to ore, but a number of economic geologists are now considering topography and climatic conditions during igneous activities.

Detailed analysis of the light stable isotope geochemistry of lakes is highly complex (Pearson and Coplen, 1978) but has the potential to yield significant paleoenvironmental information. It is possible to

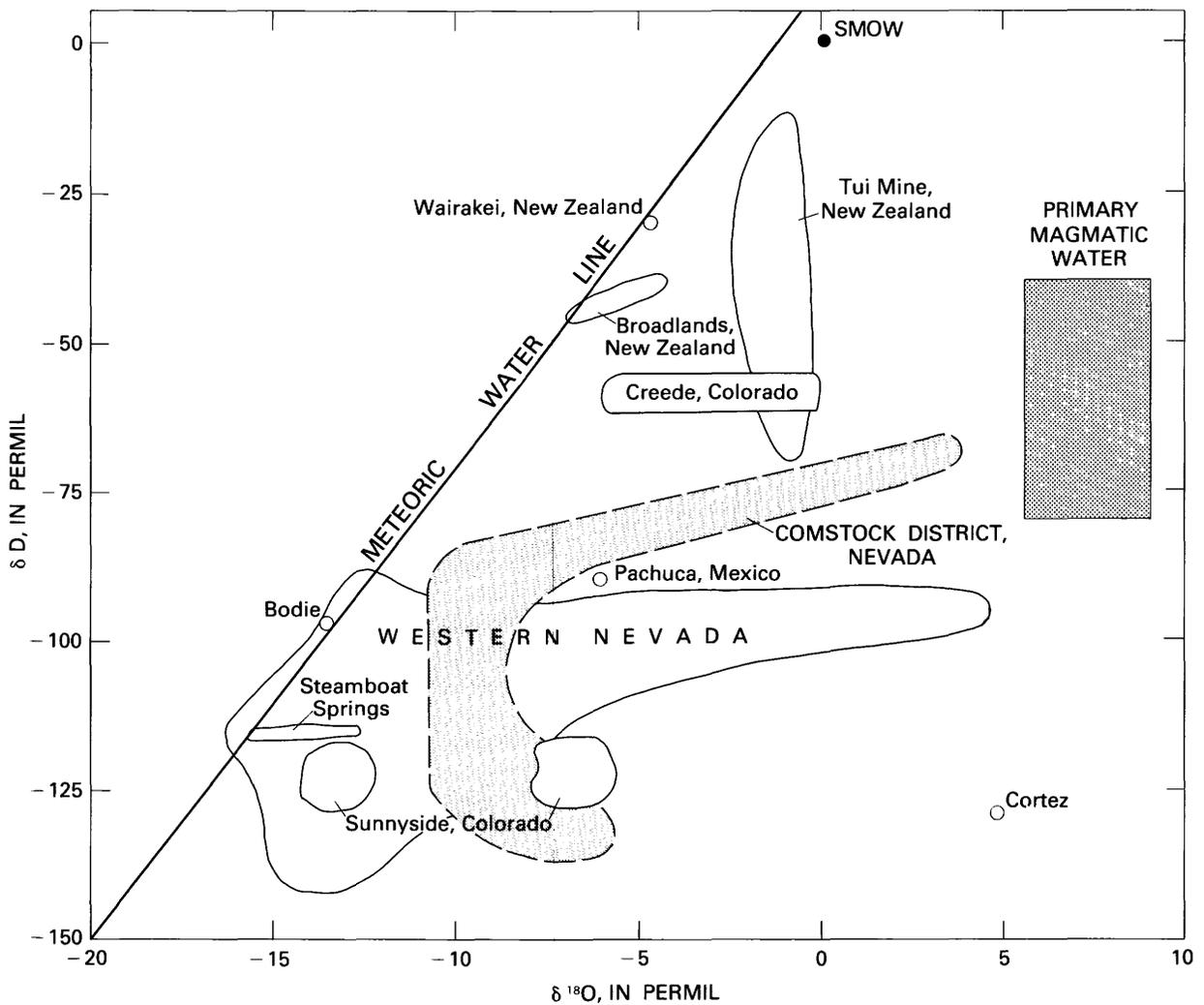


FIGURE 27.--Plot of  $\delta D$  of fluid inclusions versus calculated  $\delta^{18}O$  values of hydrothermal fluids for various epithermal ore deposits. Offset to the left of the primary magmatic water field shows influence of meteoric water. SMOW, standard mean ocean water. (From Taylor, 1979.) (Reproduced with permission as modified from *Geochemistry of Hydrothermal Ore Deposits*, copyright 1979, by John Wiley and Sons, Inc.)

determine parameters such as temperature, pH, and salinity of lake waters in some cases through studies of fluid inclusions, fossils, travertine, chert, sanidine, and zeolite-type minerals formed in many lakes (Cerling and others, 1977).

Preliminary investigations of cosmogenic radionuclides other than radiocarbon indicate that we may be able to date some oilfield brines and other old

fluids. Two such radionuclides currently under investigation are  $^{36}Cl$ , which has a half-life of 0.31 m.y., and  $^{129}I$ , which has a half-life of 15.7 m.y.

In conclusion, the use of stable isotopes, both radiogenic and nonradiogenic, should play a major role in unraveling the importance of climate in the formation of many kinds of mineral deposits.

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