Paleoredox Conditions and the Origin of Bedded Barites along the Late Devonian North American Continental Margin[1]

Paul W. Jewell

Department of Geology and Geophysics, University of Utah, Salt Lake City, UT 84112

ABSTRACT

The most important controls of the redox state of natural waters are the flux of organic matter from the photic zone, the degree of physical mixing, and oxygen concentrations of any connecting water masses. In coastal upwelling zones, these factors can be described with a simple box model constrained by data from modern field settings. Onshore-offshore mixing is largely controlled by the intensity of coastal currents that generally are found at depths of <400 m. As a result, onshore-offshore chemical gradients are greater in deeper waters. Application of the mass balance models to Late Devonian paleogeographic reconstructions of western North America illustrates how bedded barites in this setting may have formed in conjunction with a sulfate-reducing coastal upwelling zone. Low-oxygen waters from an extensive equatorial undercurrent entered the upwelling zone during regressive periods of the Late Devonian. The steep bathymetry of emergent bank carbonates to the east meant that the most intense portion of the coastal upwelling system occurred over deep water. Sinking organic matter was remineralized in these deep waters rather than being incorporated into sediments of the continental shelf and shelf break. The influence of coastal currents, and therefore onshore-offshore mixing, was minimal, thereby leading to the depletion of available oxygen and nitrate. Recent geochemical studies of particulate and dissolved barium in the modern ocean in conjunction with the mass balance model illustrate how waters with only minor sulfate-reduction and elevated dissolved barium concentrations may have led to extensive barite flux to the Late Devonian deep-water sediments off the North American continent.

Introduction

The study of oxygen and nutrients in natural waters is critical to understanding a variety of geological and geochemical phenomenon. The cycling and preservation of many elements in water and sediments is dependent on the redox state of the water column (Stumm and Morgan 1981). Barite ($BaSO_4$) is particularly interesting in this regard because its solubility product is low (Church 1979), dissolved barium behaves much like a nutrient (Turekian and Johnson 1966), and sulfate concentrations are dependent on the redox state of the water.

Barite concentrations as high as several weight percent on a carbonate-free basis in oceanic sediments beneath productive areas of the ocean have long been known (Goldberg and Arrhenius 1958). In recent years, considerable attention has been given to the paleoceanographic significance of barite and its relationship to biological productivity in the ocean. Several studies have shown that barite and barium in carbonates is a reliable proxy for surface productivity (Schmitz 1987; Shimmield et al. 1988; Lea et al. 1989; Dymond et al. 1992). Specific relationships of export productivity, dissolved barium concentrations, and barite flux have also been developed (Dymond et al. 1992).

Coastal upwelling zones are characterized by some of the greatest surface productivities found in the modern ocean (Berger 1989) and as such, constitute one of the primary mechanisms by which carbon and other nutrients are removed from the upper ocean and ultimately sequestered in marine sediments. The relationship between barium flux and coastal upwelling has only recently been considered in detail (e.g., von Breymann et al. 1990). This is in contrast to phosphorites (e.g., Burnett et al. 1980; Sheldon 1980; Coles and Snyder 1985; Coles and Varga 1988) and organic carbon-rich shales (e.g., Parrish 1982; Parrish and Curtis 1982; Schopf 1983), which have been

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extensively studied within the context of coastal upwelling throughout the geologic record.

A significant difference between barite deposited in the modern ocean and that found in ancient sedimentary rocks is the form and concentration of the barite. Massive, bedded barite deposition is a common feature of some periods in the geologic record, particularly the early to middle Paleozoic (e.g., Papke 1984; Maynard and Okita 1992). In many of these settings, barite bed thicknesses exceed 1 m and constitute 50% or more of the volume of a given section of rock. Similar massive accumulations of barite are not found in the modern ocean. Any model of barite formation in Paleozoic rocks must therefore account for these abnormally high concentrations of barite.

The fact that barite is a redox-sensitive mineral and intimately associated with the biological cycles of the ocean suggests that the formation of massive bedded barite may be understood by considering the redox controls of highly productive settings such as coastal upwelling. The work presented here consists of a simple mass balance calculations that allow key upwelling processes to be highlighted and permit examination of how redox processes may have been different along the margins of ancient oceans. A specific application of the model is then made to paleogeographic features and the formation of bedded barite of the Late Devonian continental margin of North America. The Late Devonian of North America has long been recognized for its widespread black shale and phosphorite deposition (Conant and Swanson 1961; Ettensohn 1985; Coles and Varga 1988), the occurrence of nodular and bedded barites (Holden and Carlson 1979; Pepper et al. 1985; Dube 1988; Poole 1988; Graber and Chafetz 1990; Jewell and Stallard 1991), and the development of extensive carbonate platforms (Heckel and Witzke 1979; Sandberg et al. 1988). The model presented in this paper is used to explain how these features may have been genetically related.

Oxygen and Phosphorous Mass Balance Models

The physical and chemical controls of dissolved oxygen and nutrients in natural waters are varied and complex. Physical exchange, either with the atmosphere or other water bodies, is one important factor. The flux of organic matter as a result of surface productivity is also very influential. Redox conditions in most bottom waters are the result of some combination of these factors. The goal of the mass balance models presented here is to determine the relative importance of these variables. Particular attention is given to factors that might cause complete oxygen depletion and sulfate-reduction in ancient oceans. Results of the paleoredox model are then used to examine the behavior of dissolved barium and barite flux in a sulfate-reducing environment.

A brief summary of the most important features of coastal upwelling is given as a prelude to the discussion of mass balance models of oxygen, nutrients, and barium. Particular attention is given to the Peru upwelling system, because of its relatively low subsurface oxygen concentrations, extensive data bases, and steep continental margin which allows examination of deep water (>1000 m) geochemistry.

Coastal Upwelling Overview. Most coastal upwelling zones exhibit a two-layer system of currents (Smith 1981, 1992). The surface Ekman layer and associated offshore transport generally occurs in the upper 10–50 m of the ocean. Onshore transport below the surface Ekman layer (typically found between 100–300 m depth) is often divergent, i.e., a certain percentage of the onshore transport becomes entrained in longshore currents (Smith 1981). Poleward undercurrents constitute much of the subsurface, longshore transport in coastal upwelling zones. The dynamic origin of these undercurrents is not well understood, although they are typically strongest near the shelf break of coastal upwelling zones (Johnson and Rockcliff 1986). Poleward undercurrents are responsible for most of the kinetic energy found at depths of <400 m in coastal upwelling zones (e.g., Brockman et al. 1980; Hagan 1981). Currents and kinetic energy below 400 m depth are considerably less than that found at more shallow depths.

Upwelling water in coastal settings has widely varying nutrient and oxygen concentrations. In general, these concentrations reflect the character of intermediate-depth water which feeds into the coastal upwelling zone. For instance, the Peru-Chile Undercurrent is the source of upwelled water off the coast of Peru between 5°S and 15°S. The Peru-Chile undercurrent has its origins in the Pacific Equatorial Undercurrent, which traverses much of the Pacific equatorial region between 2°N and 2°S (Pickard and Emery 1983). Divergence of trade winds in the equatorial Pacific causes upwelling across much of the area. Sinking organic matter is remineralized and advected eastward by the underlying equatorial undercurrent. Equatorial waters thus become progressively more nutrient-rich and oxygen-poor to the east. As the undercurrent encounters the South American continental margin and flows southward, coastal upwelling causes additional oxygen depletion and nutrient enrichment in the underlying water. As a result, nitrate reduction is common in deep coastal waters off Peru (e.g., Codispotti 1983). Under certain conditions, sulfate reduction has been observed (Dugdale et al. 1977).

Surface biological productivity of coastal upwelling zones is most intense where intermediate depth water comes to the surface (generally within a few tens of kilometers of the coast) and drops off dramatically in the offshore direction. Cross-shelf gradients in surface productivity (figure 1) tend to produce subsurface, cross-shelf gradients of oxygen and nutrients as a result of organic matter that sinks out of the photic zone. Off the coast of Peru, cross-shelf phosphate and oxygen gradients show considerable variability, but generally increase with depth (figure 2, table 1). This feature is probably the result of decreasing onshore/offshore velocities with depth. Although mean velocities are close to zero, velocity variances are clearly smaller in deeper water (table 2). Measurements of kinetic energy also show marked decreases with depth off of Peru (Hagen 1981). As a result, phosphate which is remineralized by sinking organic matter adjacent to the coastline is less likely to be advected offshore in these deeper waters.

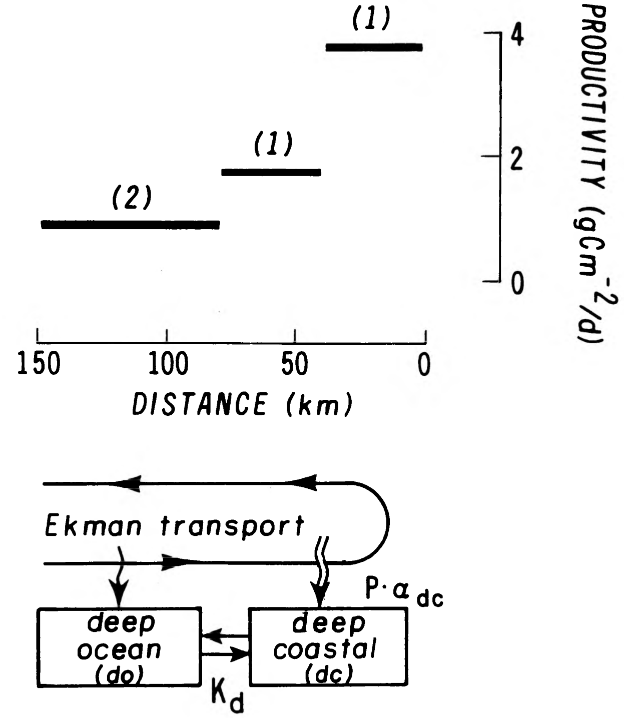

Figure 1. Average primary productivities and a simple onshore-offshore box model of the Peru upwelling zone. 1 = the near shore productivities reported by Packard et al. (1983). 2 = offshore productivities from Suess et al. (1987). Ekman transport represents onshore movement of nutrient-rich water and offshore movement of nutrient-depleted water. A certain fraction of biogenic particles produced at the surface ($\alpha_{dc} \cdot P$) is remineralized in the deep coastal (*dc*) box. The deep coastal box receives a higher amount of biogenic particle flux than does the deep ocean (*do*) box due to higher near-shore surface productivities. Exchange between the two deep-water boxes is represented by the mass flux K_d (m^3/s per unit length of shoreline).

Model Formulation. Many of the features of modern and ancient coastal upwelling chemistry can be explained by simple relationships that describe the vertical and cross-shelf flux of oxygen and nutrients. In this section, surface productivity, organic carbon flux, and onshore-offshore oxygen and nutrient data from the Peru upwelling system and a simple box model are used to examine the fate of organic matter that settles into deep coastal water in coastal upwelling zones. It is important to emphasize that a box model such as this is fundamentally different from advection-dispersion models that calculate continuous variations of properties with differential equations. Among the most simple and effective advection-dispersion models have been 1-dimensional, vertical simulations of oxygen and nutrients in the open ocean (Wyrtki 1962; Southam and Peterson 1985; Wilde 1987). The 2- and 3-dimensional nature of coastal upwelling requires considerably more complex advection-dispersion models (e.g., Walsh 1975). The box model presented here represents a simple yet effective method of examining the deep-water, onshore-offshore biogeochemistry of these settings.

Deep-water (>300 m) coastal upwelling features are modeled with onshore and offshore boxes coupled by onshore-offshore mixing processes (figure 1). Surface water transport is represented by a continuous Ekman transport loop, which moves onshore in the subsurface and offshore in the surface Ekman layer. Ekman transport moves nutrient-rich water into the productive photic zone, which in turn produces biogenic particles, *P*. A small percentage of the organic matter, $\alpha_{dc} \cdot P$, is remineralized in the deep coastal zone. The level of nutrients or oxygen in the deep coastal zone (*dc* box in figure 1) is a function of $\alpha_{dc} \cdot P$, the degree of cross-shelf mixing (K_d), and the chemistry of the water entering the deep coastal zone (i.e., the *do* box). These relationships can be expressed with the mass balance relationship:

$$PO_{4,dc} = PO_{4,do} + \frac{P \cdot \alpha_{dc}}{K_d} \qquad (1)$$

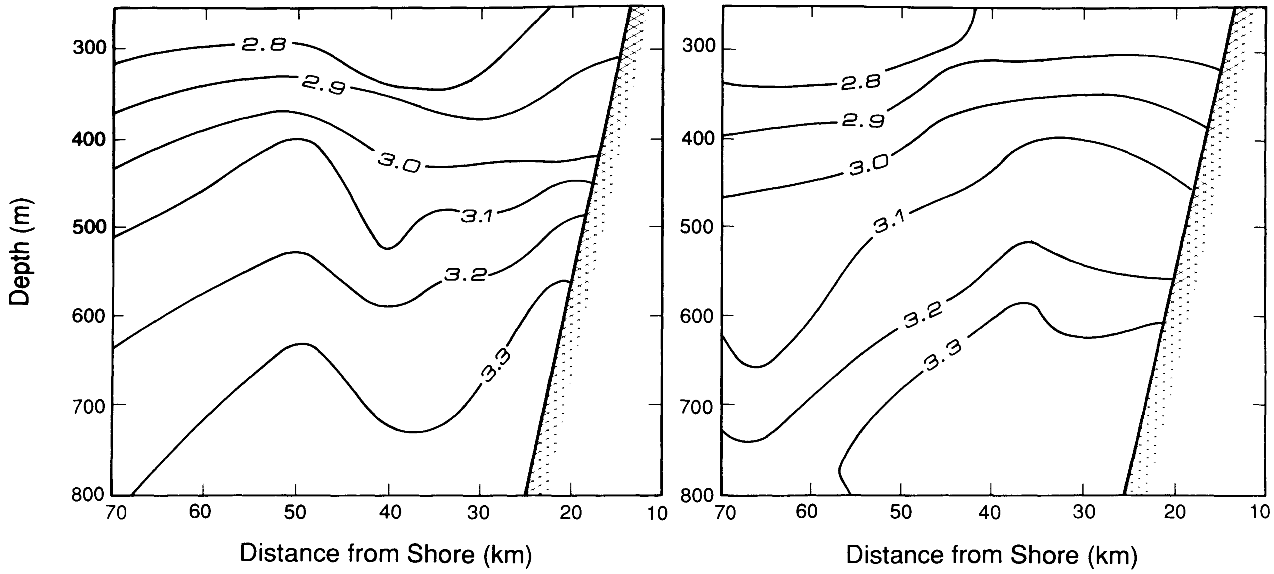

Figure 2. Cross-shelf phosphate concentrations at 15°S off the Peru coast. The left-hand panel is from Stations 411–416 and the right-hand panel is from Stations 367–373 of the JOINT-II data set (Hafferty et al. 1978). Note the increase in onshore-offshore phosphorous gradients with depth.

In equation (1), K_d has the units of m^3/s per meter of longshore distance, i.e., 2-dimensional mass flux (m^2/s). The depth of the deep coastal (*dc*) zone is arbitrary. In other words, the deep coastal zone can be represented as a series of boxes rather than one single box. The analysis presented here considers "slices" of the water column that are 100 m thick and are not in contact with bottom sediments. Comparison of model output is made with chemical data from similar 100-m thick slices of the open ocean portion in the Peru upwelling system which likewise are not in contact with the bottom sediments.

Table 1. Summary of Onshore-offshore Phosphate and Oxygen Gradients at 15°S

Stations	Transect length (km)	Depth (m)	ΔPO^4 (μmol/L)	ΔPO^4 (μmol/L)
81–89	55	355	−.16	. . .
		405	−.03	. . .
		455	.09	10.1
		560	.15	9.6
		810	.06	−16.3
367–373	44	330	.53	. . .
		410	.39	. . .
		510	.24	15.6
		610	.68	0.3
		765	.54	7.3
		1020	.86	−13.2
382–387	51	410	.07	. . .
		510	.01	6.0
		610	−.11	10.8
		765	.10	1.3
		960	−.14	−3.1
411–416	50	510	.14	−7.4
		610	.21	2.1
		770	.20	−10.5
		1025	.20	−8.3

Source. Hafferty et al. (1978).

An expression which is similar to equation (1) can be written for oxygen:

$$O_{2,dc} = O_{2,do} - r \cdot \frac{P \cdot \alpha_{dc}}{K_d} \qquad (2)$$

In this case r represents the $PO_4 : O_2$ ratio of approximately 170 observed in the deep ocean (Takahashi et al. 1985).

Equations (1) and (2) are solved by using modern oceanographic data for all variables except K_d. This variable cannot be measured and must be constrained indirectly.

In modern oceanographic settings, the amount of organic matter fluxed through the water column shows considerable spatial and temporal (seasonal to daily) variability. A few long-term (>2 month) summaries of surface productivity in upwelling zones have been published. Among these data sets, the JOINT-II survey at 15°S off the coast of Peru is noteworthy for its nearly continuous occupation of a series of cross-shelf stations over a 3-month period. Average surface productivity within 40 km of the shore at 15°S is reported to be 1400 gC m^2/yr. Within 40–80 km of the shore, productivity is

Table 2. Summary of Cross-Shelf Velocities in the Peru Upwelling System

Depth (m)	Latitude	Longitude	Cross-shelf velocity (cm/s)
197	5°01′	81°31′	1.5 ± 4.0
560	do.	do.	−.3 ± 3.6
860	do.	do.	−.3 ± 1.9
195	5°00′	81°44′	.0 ± 6.2
235	do.	do.	.0 ± 4.2
415	do.	do.	−2.1 ± 4.0
183	15°11′	75°34′	−.3 ± 3.4
283	do.	do.	−.2 ± 2.1
115	15°10′	75°36′	−1.1 ± 4.7
214	do.	do.	−.3 ± 3.1
512	do.	do.	.9 ± 1.6

Source. Brockmann et al. (1980).

reported to be 630 gC m^2/yr (Packard et al. 1983). In the box model formulation, the width of the *do* and *dc* boxes would thus be 40 km. Box model surface productivity, *P*, would be the observed difference between the 0–40 and 40–80 km widths, i.e., 770 gC m^{-2}/yr.

Over the past three decades, sediment-trap data from a variety of oceanographic stations has been used to construct relationships that relate surface productivity, water depth, and subsurface carbon flux. In general, carbon flux decreases exponentially with depth. A summary of these relationships can be found in Berger et al. (1989). In intermediate-depth water (500–1500 m), approximately 1–3% of sinking organic matter is remineralized while sinking through 100 m of water. For the purpose of solving equations 1 and 2, a value of 2% is assumed (i.e., $\alpha_{dc} = .02$). The value of $\alpha_{dc} \cdot P$ is therefore 15 gC m^{-2}/yr. Estimates of K_d can then be obtained by substituting cross-shelf phosphate concentrations from the Peru upwelling system (table 1) into equation (1). K_d values of approximately 0.05 m^2/s are obtained for deep water (>500 m), while values of >0.30 m^2/s are obtained for shallow water (<500 m). For oxygen data (table 1), K_d is approximately 0.15 m^2/s in deep water.

Model Application. Plots of equations (1) and (2) illustrate the most important controls of nutrient enrichment and oxidant reduction in upwelling zones. In natural waters, certain oxidants which remineralize organic matter are energetically favored over others. In seawater the sequence of oxidation is $O_2 \rightarrow NO_3^- \rightarrow Mn^{+4} \rightarrow Fe^{+3} \rightarrow SO_4^{2-}$ (Stumm and Morgan 1981). Since the amount of dissolved Mn and Fe in seawater is virtually nonexistent, the primary oxidants are generally O_2, NO_3^-, SO_4^{2-}, in that order. NO_3^- concentrations in deep seawater are considerably smaller (20–40 μmoles/L) than either O_2 (0–300 μmoles/L) or SO_4^{2-} (approximately 28 millimoles/L) concentrations. In marine basins with restricted circulation (e.g., the Black Sea and Cariaco Trench), oxygen-depletion and sulfate-reduction are closely related spatially. In highly productive, open marine settings such as the Peru upwelling system, nitrate-reduction is common in intermediate-depth water.

In equation (2), "O_2" values of 0 to −30 μmoles/L are therefore taken to represent nitrate-reduction, while values <−30 μmoles/L represent sulfate-reduction. This is a simplification of actual geochemical processes. For instance, nitrate-reduction commences when O_2 concentrations are low, yet greater than zero. For the sake of the present discussion, the simplification is useful for illustrating processes which occur in the deep coastal waters of upwelling zones.

The degree of phosphate enrichment and oxygen depletion is relatively minor at high values of K_d (figure 3*a*). At low values of K_d (approximately .05 m^2/s), phosphate enrichments up to 0.5 μmoles/L in the *dc* box are possible (figure 3*a*). Nitrate- and sulfate-reduction can be brought on by increasing the amount of oxidants feeding into the *do* box (i.e., $O_{2,do}$) or by decreasing the amount of onshore-offshore mixing, K_d (figure 3*b*). It is interesting to note that nitrate- and sulfate-reduction is possible at low onshore-offshore mixing rates, regardless of the deep ocean oxygen concentrations which feed into the deep coastal zone.

Late Devonian Paleogeography of Western North America

Bedded barites, bedded cherts, phosphorites, and black shales are common constituents of the Late Devonian rocks of western North America. A brief overview of these rocks is given as a prelude to consideration of the possible paleoceanographic conditions which led to the formation of the massive bedded barites.

Late Devonian sedimentary rocks of the westward-facing continental margin of the North American continent in the present-day Great Basin of the United States are characterized by a deep-water siliceous facies, a shallow-water carbonate facies, and a poorly-exposed, transitional facies between the shallow and deep water rocks. These facies have been structurally juxtaposed against each other by the Roberts Mountains thrust fault. The thrusting has typically been considered to be correlative with the Antler orogeny of Late Devonian-

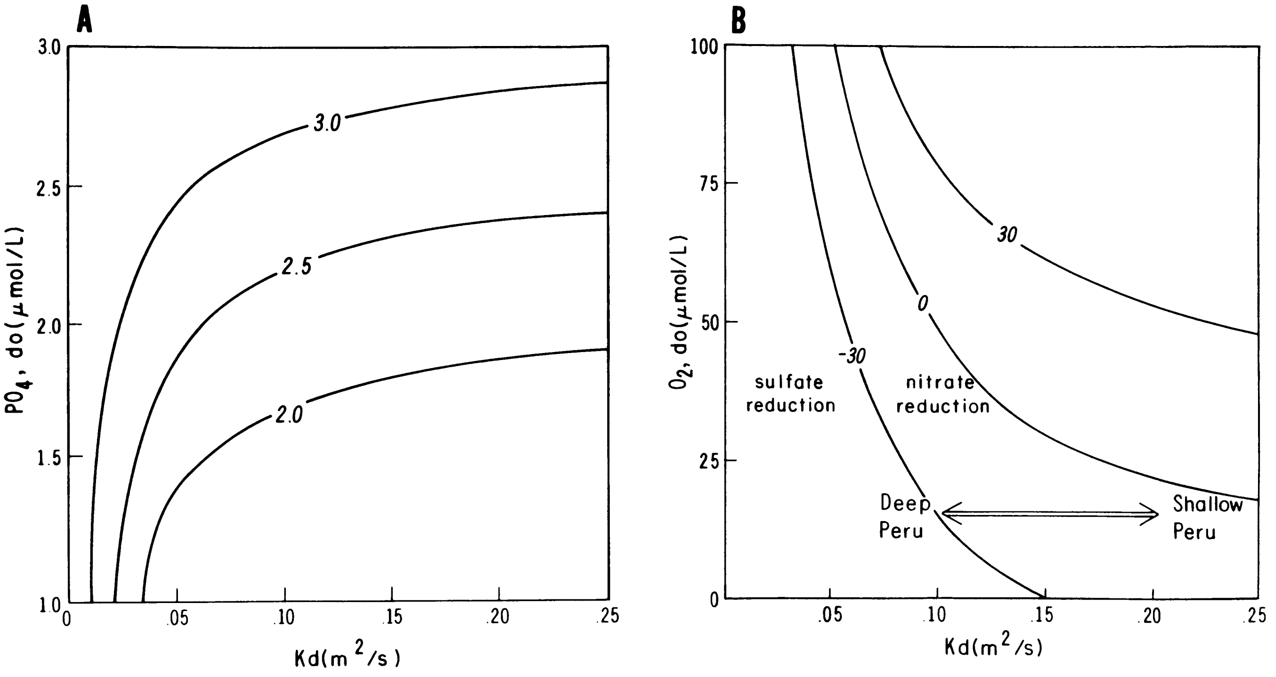

Figure 3. Calculated concentrations of (*a*) phosphate (μmoles/L) and (*b*) oxygen (μmoles/L) in the deep coastal (*dc*) zone as a function of cross shelf mixing (K_d) and the phosphate and oxygen concentrations which enter from the deep offshore (*do*) layer of the box model in figure 1.

Early Mississippian age (Roberts et al. 1958), although a Mesozoic age of the fault is advocated by some workers (e.g., Ketner and Smith 1982). The allochthonous, western assemblage rocks are known as the Roberts Mountains Allochthon, a term retained here.

The deep-water siliceous rocks of the Roberts Mountains allochthon are composed primarily of Ordovician through Devonian shales, cherts, and siltstones with lesser amounts of greenstone, limestone, bedded barite, and phosphorite. A major, barite-bearing Devonian unit within the Roberts Mountain allochthon is the Slaven Chert, which is exposed extensively in central Nevada. The Slaven Chert spans most of the Devonian (Stewart 1980), although the phosphorite- and barite-bearing portions appear to be late Late Devonian (Famennian) (Sandberg et al. 1988). Additional phosphorite- and barite-bearing sequences in the Roberts Mountain allochthon include the Late Devonian-Early Mississippian Pinecone sequence in the Toquima Range (Coles 1991) and the Late Devonian Beacon and lower to middle Devonian South Creek units in the Tuscarora Mountains (Dube 1988). The depositional environment of these rocks appears to be that of siliciclastic-starved, pelagic, and hemipelagic sedimentation beneath a zone of high surface productivity (Coles 1991).

Several studies suggest that the Late Devonian deep-water marine facies in central Nevada were deposited under a coastal upwelling system off the North American continent. Evidence includes the abundance of black shales with very high organic carbon contents (up to 12 wt %) (Poole and Claypool 1984), phosphorite lenses and nodules in shales and chert (Coles and Snyder 1985; Coles and Varga 1988; Graber and Chafetz 1990; Jewell and Stallard 1991), and paleogeographic reconstructions which demonstrate an appropriate west-facing, low-latitude position of these rocks during the Late Devonian (Scotese and McKerrow 1990). The presence of calc-alkalic lamprophyres of apparent continental or transitional affinity that cross-cut the deep water facies (Dube 1988), siliciclastic facies gradational into shallow water carbonates to the east (Stewart and Poole 1974; Smith and Ketner 1975), and minor detrital carbonate (Coles 1991) suggest that the deep-water facies were formed adjacent to a continent.

An extremely thick sequence of lower- to middle-Paleozoic carbonate rocks is found throughout central Nevada and western Utah. These carbonates represent more or less continuous deposition along a stable cratonic margin from Late Cambrian through Late Devonian (Stewart 1980). Carbonate units dated as Late Devonian in central Nevada were deposited in environments that ranged from deep subtidal to supratidal (Sandberg et al. 1988).

Detailed Late Devonian chronostratigraphic correlations of carbonate rocks in Nevada and Europe suggests a series of eustatic transgressions and regressions (Johnson et al. 1985; Sandberg et al. 1988). The overall trend through the Famennian appears to be regressive (figure 4).

One persistent feature of Devonian rocks in western North America is a seaward zone of bank carbonates from Alberta to Nevada as late as the *marginifera* conodont zone (middle Famennian) (figure 5). These bank carbonates form the upper portion of the Guilmette Formation, which is extensively exposed throughout central Nevada. A less extensive, subtidal bank is believed to have been deposited during the *expansa* conodont zone (figure 5) (late Famennian). Following this time, carbonate deposition along the continental margin of North America ceased (Sandberg et al. 1988).

Proposed Climatic and Bathymetric Setting. Deposition of carbonates generally takes place in warm water (>20°C) at latitudes within 30° of the equator (Lees 1975). Bank carbonate deposition along the North American margin appears to have occurred during relatively high sea level stands of a warm climate (Heckel and Witzke 1979; Sandberg et al. 1988). The regressive portions of the late Late Devonian of North America (figure 4) may have been the result of glaciation on the Gondwana continent (Caputo and Crowell 1985), changes in mid-ocean spreading center rates (Johnson et al. 1985), or localized tectonic uplift as a result of the Antler orogeny in the late Late Devonian (Coles 1991).

Coastal upwelling would have brought relatively cool water into the continental shelf areas of North America, and for this reason it is unlikely that bank carbonate deposition and upwelling occurred concurrently. Although evidence for extensive continental glaciation during the Late Devonian is sketchy (Caputo and Crowell 1985), it is very likely that warm-cool, Milankovitch-type climate cycles were operative during the 10 m.y. time span of the Fammenian. If so, then the close spatial association of coastal upwelling zone and bank carbonates suggested by field evidence from the Late Devonian record in North America is not necessarily contradictory.

Modern coastal upwelling zones are located along continental margins dominated by siliciclastic deposition. These margins often have more gentle slopes than margins dominated by carbonate deposition (Schlanger and Camber 1986). For instance, in the Bahamas banks the steepest slopes (up to 20–30°) are located on the seaward-facing, north slope of the Little Bahamas (Mullins and Neuman 1979). The area is bordered by a 10 km-

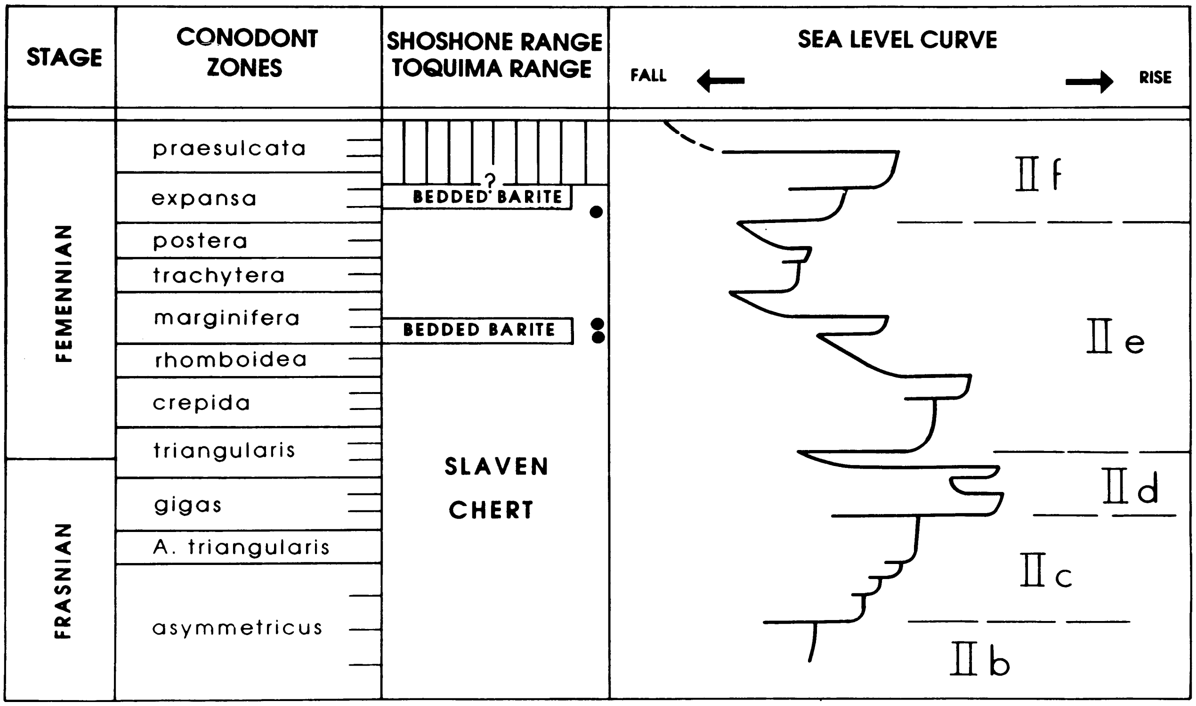

Figure 4. Conodont zones, dated portions of the upper Slaven Chert, and general sea level curve of the late Frasnian and Famennian stages. Adapted from Johnson et al. (1985) and Sandberg et al. (1988). Symbols IIb–IIf refer to specific transgressive-regressive cycles of the Late Devonian

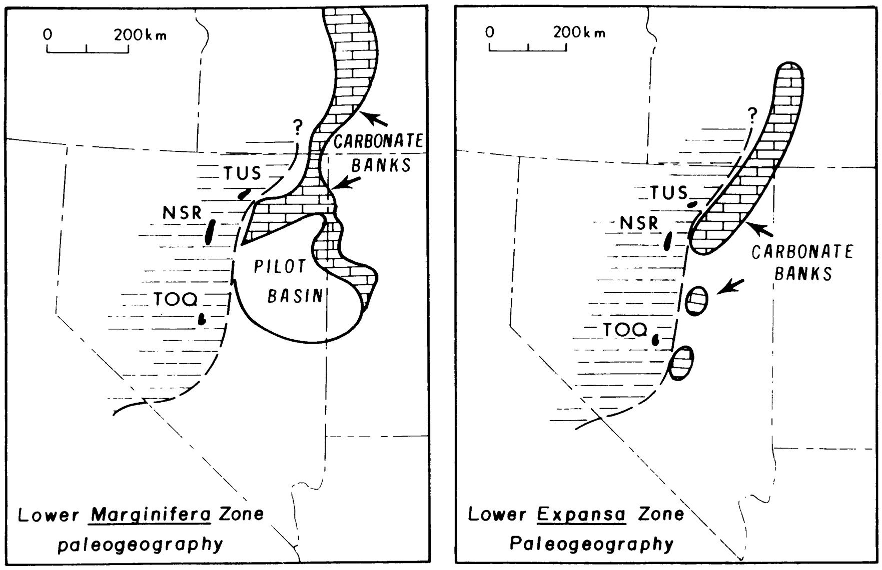

Figure 5. General paleogeographic reconstruction showing the position of the proposed phosphogenic province and bank carbonates in the western United States during the Late Devonian. Lower *marginifera* conodont zone and lower *expansa* conodont zone are adapted from Sandberg et al. (1988) and Coles (1991). Abbreviated locations (TUS = Tuscarora Mountains, NSR = Northern Shoshone Range, TOQ = Toquima Range) refer to dated bedded barite deposits shown in figure 4 and described by Dube (1988). Dashed pattern represents the Late Devonian phosphogenic province described by Coles (1991). The positions of the TUS, NSR, and TOQ locations relative to the carbonate banks are only approximate and are not palinispastically reconstructed. Deposition of the carbonate banks and phosphatic sediments is not necessarily contemporaneous (see text).

wide zone of carbonate talus accumulation. Similar talus zones have not been observed in Late Devonian rocks of central Nevada, although Coles (1991) does report detrital limestone and rare carbonate slide blocks in some of the deep-water facies rocks.

If the bathymetry of the shallow-water Nevada carbonates was similar to that of the modern-day Bahamas, then the locus of upwelling would occur over relatively deep water. This is in contrast to the high sea-level stands of the modern interglacial ocean in which the most intense productivity of upwelling systems is located over the outer continental shelf (e.g., northwest Africa) or over the shelf break and slope (e.g., Peru). In the Late Devonian, upwelling adjacent to an inactive carbonate bank would cause significant amounts of organic matter to be fluxed into the deep ocean rather than being sequestered on the relatively shallow continental shelf.

Origin of the Bedded Barite

As shown above, oxygen-depletion and nitrate-reduction is an observed feature of the subsurface waters beneath coastal upwelling zones. In modern settings, complete oxygen- and nitrate-depletion and subsequent sulfate-reduction is only rarely observed (Dugdale 1977). In the Late Devonian ocean off North America, factors not present in the modern ocean may have caused sulfate-reduction to be more common, however.

Formation of Sulfate-Reducing Water. As mentioned above, water that feeds into the modern Peru upwelling system has undergone significant nutrient-enrichment and oxygen-depletion as a result of the "nutrient-trapping" effect of equatorial wind divergence and eastward advection by the Pacific Equatorial Undercurrent. The longer the residence time of water in this undercurrent, the greater the nutrient-trapping effect (figure 6). In the Late Devonian, the equatorial ocean circled much of the entire globe (Scotese and McKerrow 1990). As such, the equatorial nutrient-trapping mechanism observed in the modern Pacific Equatorial Undercurrent would have been very pronounced prior to encountering the west-facing, Laurasian land mass, of which modern North America was a part. Water entering the Late Devonian coastal upwelling system would logically have undergone greater oxygen- and/or nitrate-reduction than that which enters the modern Peru coastal upwelling system.

A second factor which may have enhanced ni-

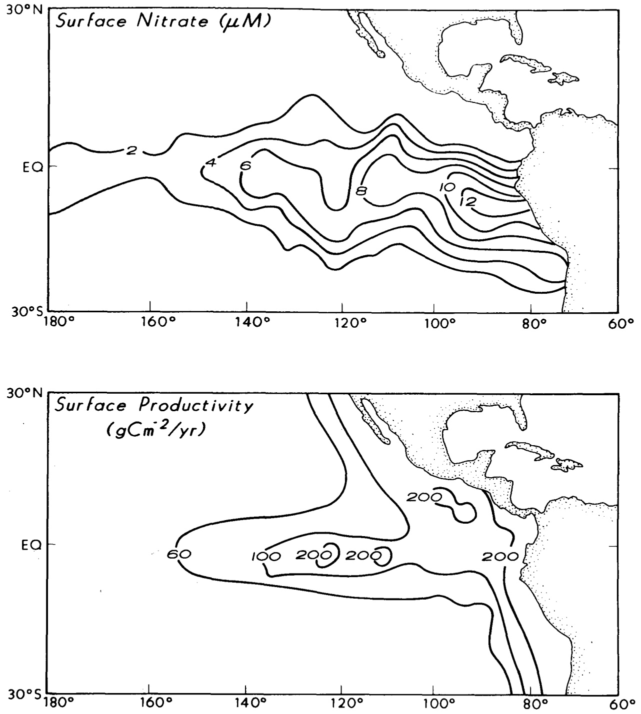

Figure 6. Surface nitrate concentrations in the equatorial Pacific (from Toggweiler et al. 1991). Surface productivity in the equatorial Pacific (from Berger et al. 1989 and Najjar 1992).

trate- and/or sulfate-reduction was the bathymetry of the inactive carbonate bank along the North American continental margin. The zone of greatest surface productivity would overlie relatively deep water, rather than shallow water of the continental shelf (figure 7). Relatively high amounts of organic matter would sink into deep water (>400 m) and thus not be under the influence of coastal undercurrents (table 2). Cross-shelf mixing at these depths would be minimal, and the water would have been more likely to be nitrate- or sulfate-reducing (figure 3*b*). As shown previously, nitrate- and/or sulfate-reduction and phosphorous enrichment is a natural consequence of low cross-shelf mixing, even when the oxygen concentrations which feed into it are relatively high (figure 3*b*).

It is important to re-emphasize that while nitrate-reduction is widespread in the Peru upwelling system, the total amount of nitrate available as an oxidant in seawater is quite small (<40 μmoles/L). Even though sulfate reduction has only rarely been observed in open ocean settings, factors peculiar to certain paleoceanographic configurations (a globe-encircling equatorial undercurrent and steep carbonate bank bathymetry) could easily consume nitrate and bring about sulfate reduction.

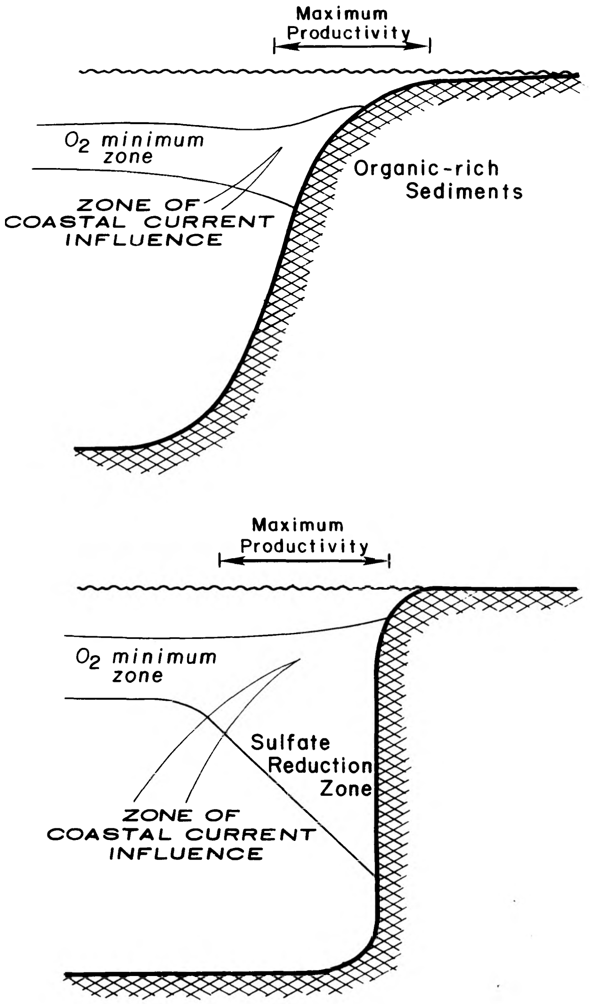

Figure 7. Idealized cross-shelf bathymetry for a modern siliciclastic margin and a steep slope carbonate margin which may have existed off North America during the Late Devonian.

Barium-Productivity Relationships. Bishop (1988) has shown that particulate barite in sinking organic matter in the water column is the result of sulfate-rich microenvironments in the sinking organic matter. Although most areas of the ocean are undersaturated with respect to pure barite (Church 1979), decaying organic matter provides the necessary sulfate to achieve barite supersaturation on a microscopic scale. Uptake of barium into sinking organic matter does not alter the nutrient-like, dissolved barium profiles observed in the deep ocean (e.g., Chan et al. 1976).

Dymond et al. (1992) show that the C_{org}/Ba ratio of three open ocean localities decreases with respect to depth. As sinking organic matter is remineralized, additional sulfate is released, thereby fixing additional barite. Dymond et al.'s observations are therefore consistent with Bishop's (1988) theory of how particulate barite forms in the water column. A relationship that relates new productivity (i.e., the flux of organic matter that leaves the photic zone under steady state conditions) to barium flux, water-column barium concentrations, and depth has been proposed by Dymond et al. (1992).

$$F_{Ba} = \frac{2056(P_{new})^{0.665} z^{-0.476+.00478Ba}}{0.171Ba^{2.218}} \quad (3)$$

F_{Ba} is particulate barium flux (μgrams cm^{-2}/yr), P_{new} is export productivity, and Ba is dissolved barium in nanomoles/L.

Recently, Falkner et al. (1993) found that the barite-forming mechanism of Bishop (1988) was reversed (i.e., dissolved barium increases) when sinking organic matter encountered deep anoxic seawater in the Cariaco Trench, Black Sea, and an anoxic fjord in Norway. The increase in dissolved barium is pronounced at low H_2S concentrations (figure 8). Implications of the Dymond et al. (1992) and Falkner et al. (1993) studies are directly applicable to the formation of bedded barites in the Late Devonian ocean.

Formation of Bedded Barites. Many previous researchers consider the barites in deep water facies of the Roberts Mountain allochthon to have a hydrothermal exhalative origin (e.g., Papke 1984; Poole 1988; Dube 1988; Maynard and Okita 1992). Other than small amounts of diagenetic pyrite, base metal sulfides are very rare in these sediments, however. Furthermore, stable isotope data suggest that ^{34}S and possibly $^{87}Sr/^{86}Sr$ in the bedded barite was equivalent to that of contemporaneous Devonian seawater (Rye et al. 1978). Jewell and Stallard (1991) recently elaborated on an idea originally proposed by Shawe et al. (1969) that bedded barite in the Shoshone and Toquima Ranges of central Nevada was formed by biogenic processes in a highly productive marine setting. Here, a depositional model for the bedded barite is outlined within the context of a sulfate-reducing upwelling system outlined above and geochemical studies of barium from the modern ocean.

Organic particles formed by export productivity (i.e., the net loss of organic carbon from the photic zone) would scavenge dissolved barium from the oxygenated, upper portions of the water column. As the waters were advected in the longshore direction and encountered sulfate-reducing waters at depth, barium would be released from the organic particles in a manner similar to that observed in modern anoxic settings (figure 8). The sulfate-reduction zone of the upwelling system would cause dissolved barium concentrations in water exiting the sulfate-reduction zone to increase dramatically (figure 9). Organic particles settling through oxygenated, barium-rich water outside the sulfate-reduction zone would result in very high barium flux to the sediments (equation 3, figure 10). The net effect of the upwelling zone would therefore be an "upgrade" of barium flux to sediments downstream from the upwelling zone.

Two points of this genetic model for bedded barites merit special emphasis. First, increased dissolved Ba in the sulfate-reduction zone could occur at very low (tens of μmoles/L) H_2S concentrations (figure 8). In other words, because (O_2 + NO_3^-) concentrations are low in some modern upwelling zones, only minimal additional oxidant (O_2 + NO_3^- + SO_4^{2-}) reduction (the order of tens of μmoles/L) would be necessary to bring about significantly higher barite flux. Second, modest increases in dissolved barium exiting a sulfate-reduction zone would dramatically increase barite flux to the sediments (figure 10). For instance, if

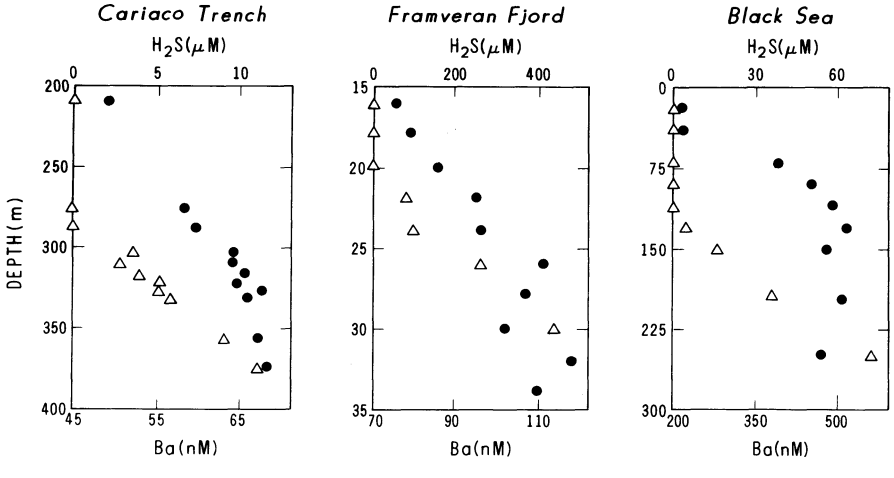

Figure 8. Plots of dissolved H_2S (closed circles) and dissolved Ba (open triangles) for three modern anoxic settings (data from Falkner et al. 1993 and Millero 1991).

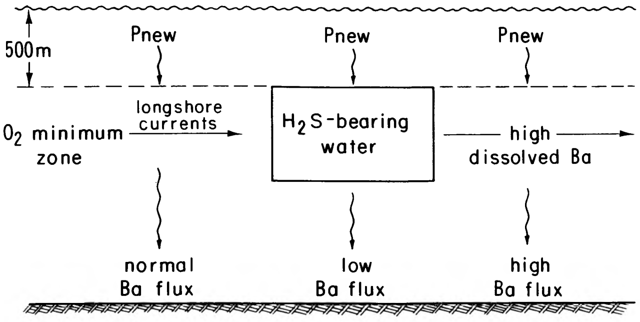

Figure 9. Diagrammatic representation of the longshore dimension of a sulfate-reducing coastal upwelling zone. Normal Ba flux to the sediments would be expected below an O_2 minimum zone similar to that found in the modern ocean. If the upwelling resulted in H_2S production, barite particles produced by export productivity (P_{new}) would dissolve, resulting in low Ba flux to the underlying sediments. Longshore currents would advect the Ba-rich water out of the sulfate-reducing zone, where sinking organic matter would produce elevated Ba flux to the sediments.

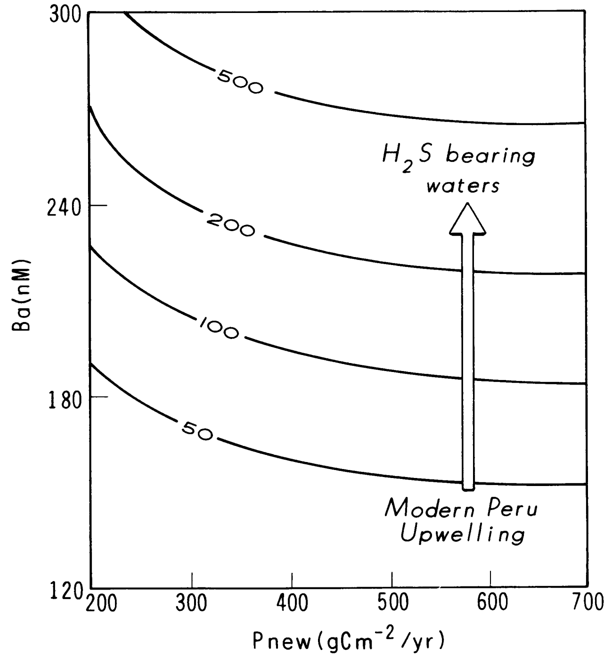

Figure 10. Barite flux (μgrams cm^{-2}/yr) as a function of new productivity (P_{new}) (gC m^{-2}/yr) and dissolved barium concentrations (nanomoles/L) in the water column. New productivity is assumed to be one-half of nearshore productivity reported by Packard et al. (1983) for the Peru upwelling system. Arrow shows the expected dissolved barium increases which would result from modest sulfate reduction (figure 8).

the dissolved barium concentrations in the modern Pacific Ocean were doubled, barite mass flux rates computed with equation 3 would be comparable to published rates of Mesozoic bedded chert deposition (table 3). This is consistent with field observations of economic barite deposits in the Roberts Mountains allochthon, which often show roughly equal barite-to-(chert + shale) volumes (Papke 1984).

Discussion

Many mid-Paleozoic rocks of North America other than the Roberts Mountains allochthon are characterized by abundant black shale, barite, phosphorite, and chert deposition. Examples of Middle Devonian to Middle Mississippian barite occurrences with no associated metal sulfides include the Jefferson Formation of Montana (Berg 1988), the Lower Earn Group of the Yukon Territory (Lydon et al. 1985), the Hanover Shale of upstate New York (Pepper et al. 1985), the Cleveland and Bedford Shales of Ohio (Holden and Carlson 1979), the Stanley Formation of Arkansas (Howard and Hanor 1987), and the Needmore Shale, Marcellus-Millboro Shale, and the Tully Limestone of the central Appalachians (Nuelle and Shelton 1986; Clark and Mosier 1989). Many of these occurrences are thought to have been formed by seafloor hydrothermal processes (e.g., Lydon et al. 1985; Nuelle and Shelton 1986), while others are believed to be the result of cycling through anoxic zones in a manner similar to that described here (e.g., Clark and Mosier 1989). Most of the barite occurrences mentioned above are associated with phosphatic black shales and cherts. Circumstantial evidence of highly productive, nutrient-rich surface waters therefore exists in these rock sequences, although most are not adjacent to bank carbonates.

It is interesting to note that all barite occurrences mentioned above occur along continental

Table 3. Summary of Bedded Chert Sedimentation Rates and Possible Barite Sedimentation Rates

Age/Location	Sedimentation rate (g cm^{-2}/10^3 yr)
Upper Jurassic/Austria-Germany	.3–3.0
Upper Jurassic/Italy-Switzerland	1.0
Upper Jurassic/California	1.5
Upper Triassic/Japan	8
Bedded barite	.05–.8

Source. Chert sedimentation rates from data of Jenkyns and Winterer (1982); barite sedimentation rates from Dymond et al. (1992) and figure 10.

margins within 30° of the proposed Middle Devonian to Late Mississippian paleo-equator (e.g., paleogeographic reconstructions of Scotese and McKerrow 1990). The chemistry of these tropical/subtropical waters may have become oxygen-depleted and nutrient-rich in the same manner as modern waters from similar latitudes. In both the modern Pacific and Atlantic Oceans, equatorial undercurrents move water from west-to-east beneath productive waters of equatorial upwelling. In a single large, mid-Paleozoic ocean, this equatorial "nutrient-trap" phenomenon may have been more pronounced than it is in modern ocean basins.

Upon intersecting continental margins, nutrient-rich equatorial waters of the modern ocean are deflected north and south, where coastal upwelling causes even higher productivity (figure 6), adds additional nutrients, and further depletes available oxidants. If the coastal upwelling system were located next to a steep, inactive carbonate bank during the Late Devonian, additional factors would come into play. The most intense portion of the upwelling zone would overlie deep water, and sinking organic matter would be remineralized in the deep portions of the water column. Onshore-offshore mixing in these deep waters would be minimal, further depleting the oxygen and nitrate concentrations. Given the low (O_2 + NO_3^-) concentrations in modern upwelling systems such as the one off Peru (<30 μmoles/L; Hafferty et al. 1978), sulfate reduction in a late Late Devonian upwelling system could be brought on by a decrease in deep water mixing rates, a decrease in the oxygen concentrations feeding into the upwelling zone (figure 6), an increase in upwelling intensity due to increased zonal winds of a cool climate, or a combination of these three factors.

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