BEDDED BARITE IN THE GEOLOGIC RECORD

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Abstract: Barite occurs throughout the geologic record as massive beds, laminations, rosettes, and nodules. The most important scientific and economic occurrences of barite are stratabound and stratiform massive beds from the Early Archean and the Early to Middle Paleozoic. Paleozoic bedded barites are by far the most volumetrically significant deposits in the geologic record. Additional occurrences have been documented in some Middle Proterozoic, Late Proterozoic, and Mesozoic rocks and in several localities on the modern ocean floor. Bedded barite is believed to have formed as emanations from seafloor sediments, as diagenetic replacements of preexisting minerals, or as direct precipitants due to biological fixation of barium in the water column. Direct field evidence to differentiate between these theories is often lacking or contradictory. Geochemical studies, particularly those that have employed $\delta^{34}S$ and $^{87}Sr/^{86}Sr$ analyses of the barite, have proven very useful in understanding bedded barite genesis.

The low solubility of barite relative to other natural salts has helped barite survive as a pseuodomorph of stratiform evaporite minerals in some Archean sedimentary sequences. Other examples of Archean barite appear to have a shallow water detrital or authigenic origin. Very low $\delta^{34}S$ values of Archean barite are interpreted as indicating a low-sulfate ocean. Large deposits of Paleozoic bedded barite are typically found in fine-grained, organic-rich siliciclastic sequences and are associated with massive and disseminated sulfides, cherts, phosphorites, and less frequently limestones and volcanic rocks. $\delta^{34}S$ analyses indicate that almost all bedded barite had a seawater sulfate source. The genetic link between Paleozoic bedded barites and sedimentary submarine exhalative Pb-Zn sulfide deposits has been established by field and geochemical study of deposits in western Canada and western Europe. $^{87}Sr/^{86}Sr$ analyses suggest that these bedded barites have a continental barium source. Economically important bedded barites in China, Arkansas, and Nevada have no significant sulfides or other hydrothermal manifestations. The clear association of dissolved barium and barite with biological cycles in the modern ocean, associations with phosphorites and cherts, and $^{87}Sr/^{86}Sr$ analyses that are comparable to contemporaneous seawater suggest that the Chinese, Nevada, and Arkansas barite deposits formed as biological precipitates on the seafloor. Bedded barite formed by this mechanism holds promise as an indicator of high paleoproductivity and open ocean sulfate reduction during selected periods of the Paleozoic. The lack of world class examples of bedded barite in Mesozoic and Cenozoic black shale sequences indicates a lack of open ocean sulfate reduction during these periods of geologic time.

INTRODUCTION

Barite ($BaSO_4$) is found throughout the geologic record and is widely documented in modern oceanic environments. Several factors make barite an economically and scientifically interesting mineral. The high specific gravity (4.48 g/cm^3) and widespread occurrence of almost pure barite make it economically useful, particularly in the manufacture of drilling muds for the oil and gas industry. Barite is a common gangue mineral in a variety of hydrothermal ore deposits including volcanic- and sediment-hosted deep-sea hot springs associated with seafloor volcanism. These associations are used as a modern analog for bedded barite in sedimentary exhalative ("sedex") deposits, which are common in many fine-grained siliciclastic sedimentary sequences in the geologic record.

Barium in modern seawater has long been recognized as following biological cycles in a manner similar to elements such as phosphorous and silicon (Chow and Goldberg, 1960; Turekian and Johnson, 1966). Barite and elevated barium concentrations in modern deep water marine sediments have been noted by oceanographers for decades (Goldberg and Arrhenius, 1958). Careful research has shown that barite forms discrete particles in the water column of the open ocean as a result of biological processes (Dehairs et al., 1980; Bishop, 1988). This has led to the development of barite as an important paleoproductivity tracer (e.g., Schmitz, 1987; Dymond et al., 1992).

The solubility of barite is dependent on the redox state of water, which means that barite dissolves in reducing open water and diagenetic environments. This feature has been used to argue that transitions between anoxic, sulfate-reducing, and oxygenated waters are necessary for the formation of bedded barite and associated minerals in a variety of marine settings, including a sulfate-poor Archean ocean (Perry et al., 1971), deep sea hydrothermal emanations (Turner, 1992), and coastal upwelling zones (Jewell and Stallard, 1991; Jewell, 1994).

Barite has the useful characteristic of containing two elements (barium and sulfur) that can be interpreted within the context of well-established isotopic techniques. Stable isotopes of sulfur have a long history of being used to interpret both the source and genesis of a wide variety of sulfide and sulfate minerals. Within this context, barite has played a role in understanding the global history of the sulfur cycle (e.g., Schidlowski et al., 1983). Also, the chemistry of barium is sufficiently similar to that of strontium that $^{87}Sr/^{86}Sr$ techniques have been extensively used to understand the parentage (for example, continental versus mantle versus seawater source) of barite. For instance, detailed geochemical analysis of the biologically produced barite fraction of deep-sea modern to Miocene sediments shows that barite tracks the $^{87}Sr/^{86}Sr$ composition of contemporaneous seawater (Paytan et al., 1993; Martin et al., 1995). On the other hand, barites that precipitate from fluids discharging on the seafloor tend to reflect the $^{87}Sr/^{86}Sr$ values of minerals that reacted with the formation fluids (e.g., Aquilina et al., 1997). These studies provide confidence that the large number of $^{87}Sr/^{86}Sr$ analyses of older bedded barites accurately reflect the parentage of the fluids from which they formed.

All of these features have combined to produce a wealth of studies on barite geology and geochemistry. In spite of this, many aspects of bedded barite genesis remain poorly under-

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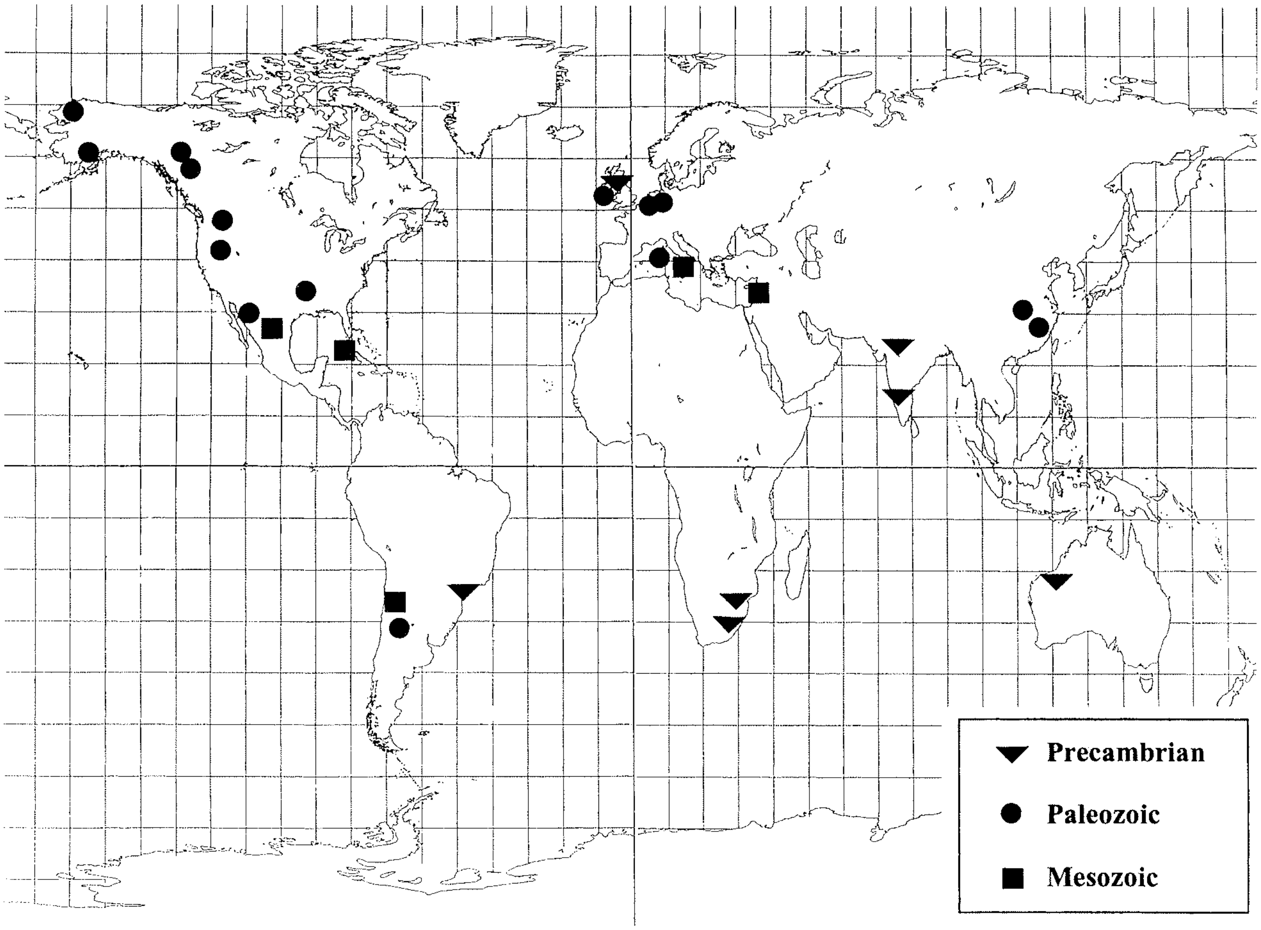

FIG. 1.—Geographic distribution of major bedded barite deposits on the continents.

stood. Although summary articles of some aspects of barite formation have been undertaken (e.g., Brodtkorb, 1989; Maynard and Okita, 1991), no systematic attempt has been made to synthesize theories of barite genesis throughout the geologic record. This paper will focus on massive bedded or stratiform barite in sedimentary rocks in an effort to understand the genesis of this important worldwide economic and scientific resource. Although the discussion is not meant to include all bedded barite occurrences, specific examples are discussed from all of the most important geologic eras and localities where bedded barite has been found. Particular attention is paid to Paleozoic bedded barites, which constitute the largest deposits in the world. The emphasis in this paper is on deposits that are well described in mainstream scientific literature. Lesser emphasis is given to bedded barite occurrences that have only been documented in abstracts or less accessible publications. It should also be noted that nodular barite occurs with many of the massive, bedded barites that are discussed. In some cases, these two contrasting barite morphologies have been used to make specific inferences about environments of deposition (e.g., Graber and Chafetz, 1990) and the isotope chemistry of the two morphologies is often distinctly different (e.g., Rye et al., 1978). A comprehensive discussion of nodular barite would have significantly expanded the scope of this review and for the sake of brevity, the emphasis is placed on bedded barite.

PRECAMBRIAN BEDDED BARITE

Isolated bedded barite occurrences are described from a small number of Precambrian shields throughout the world (Fig. 1, Table 1). Since many Precambrian barite deposits have been extensively metamorphosed, it is often difficult to ascertain their precise genesis. Nevertheless, these barites have sparked considerable scientific interest because of their possible role in interpreting Archean evaporites and the evolution of the redox state of the Archean atmosphere and ocean. The best documented Archean barite occurrences are in Australia, South Africa, and India, all of which have ages >3200 m.y. The paucity of documented bedded barite in rocks from the Late Archean through the Late Proterozoic is puzzling and has been noted by at least one author (Thorpe, 1979).

Archean Barite

Archean bedded barite from the Pilbara block of western Australia (Lambert et al., 1978; Barely et al., 1979; Dunlop and Buick, 1981) and the Barberton Mountain Land of South Africa (Perry et al., 1971; Lowe and Knauth, 1977) represent the oldest bedded barites in the geologic record (Table 1). Measurement of interfacial angles of individual crystals of the Australian barite demonstrate that they are pseudomorphs of

TABLE 1.— SUMMARY OF AGE LITHOLOGIC AND DEPOSITIONAL CHARACTERISTICS OF IMPORTANT PRECAMBRIAN AND PALEOZOIC BEDDED BARITE DEPOSITS

Location and geologic formation	Age	Lithologic associations	Depositional setting
Western Australia			
Warrawoona Group[1]	~3450 m.y.	Cherts, fine-grained metasiliciclastic rocks	Shallow water to subaerial evaporitic shelf
South Africa			
Onverwacht Group[2,3]	~3450 m.y.	Cherts, quartzitic micaceous amphibolites	Shallow water evaporitic shelf
Fig Tree Group[3,4]	~3200 m.y.	Cherts, dolomitic conglomerates	Submarine ridge
India			
Sagur Group[5,6]	>3300 m.y	Quartzites, talc schists, phyllites, metavolcanics	Shallow water evaporitic shelf
Aravalli Supergroup[6]	~2000 m.y.	Quartzites, metabasalts	Alluvial, shallow marine shelf
Scotland			
Argyll Group[7]	610-640 m.y.	Quartzites, phyllites, schists	Epicratonic rift basin
Southern China			
Niutitang, Lujiaping, Longmaxi Formations[8]	Early Cambrian	Black shales, cherts, phosphorites	Continental shelf (south), deep water siliciclastic basin (north)
Western Canada			
Mount Mye Unit[9]	Cambrian	Noncalcareous phyllites, schists	Epicratonic rift basin
Vangorda Unit[9]	Cambro-Ordovician	Calcereous phyllites, schists	Epicratonic rift basin
Road River Formation[10]	Ordovician-Silurian	Black shales, cherts	Epicratonic rift basin
Lower Earn Group[10]	Devonian	Black shales, cherts	Epicratonic rift basin
Nevada, U.S.A.			
Vinini Formation[11]	Ordovician	Shales, cherts, siltstones	Deep water continental margin
Slaven Chert[11]	Late Devonian	Cherts, shales	Deep water continental margin
Germany			
Meggan Beds[12]	Middle Devonian	Black shales, siltstones	Epicratonic starved basin
Wissenbach Shales[13]	Middle Devonian	Black shales, siltstones	Shallow water shelf
Belgium			
Unnamed[14]	Late Devonian	Shales, argillaceous limestones	Shallow water evaporitic shelf
Arkansas, U.S.A.			
Stanley Shale[15]	Late Mississippian	Shales, siltstones, limestones	Deep water slope
Ireland			
Unnamed[16]	Mississippian	Limestones, dolomites	Shallow water shelf

[1] Barley et al. (1979); Dunlop and Buick (1981)
[2] Lowe and Knauth (1977)
[3] Reimer (1980)
[4] Heinrichs and Reimer (1977)
[5] Radhakrishna and Sreenivasaiya (1974)
[6] Deb et al. (1991)
[7] Willan and Coleman (1983); Hall et al. (1991)
[8] Wang and Li (1991)
[9] Jennings and Jilson (1986)
[10] Abbott et al. (1986)
[11] Stewart (1980)
[12] Krebs (1981)
[13] Hannak (1981)
[14] Dejonghe and Boulvain (1993)
[15] Morris (1974)
[16] Taylor and Andrew (1978)

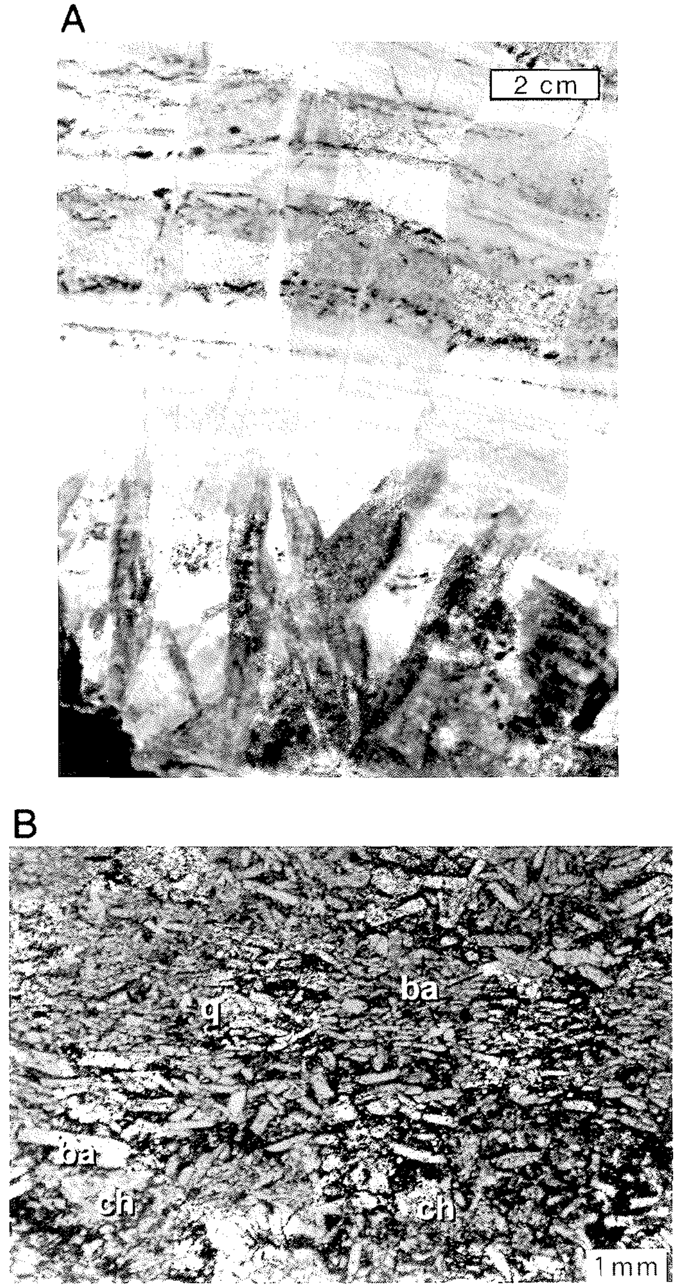

FIG. 2.—Field examples of Precambrian bedded barite. (A) Stratiform barite-chert horizon from North Pole deposit of Western Australia. Universal stage measurement of barite crystals show that they have interfacial angles of gypsum (from Lambert et al., 1978). (B) Detrital barite of the Archean Fig Tree Group, Swaziland, South Africa (from Heinrichs and Reimer, 1977).

gypsum (Lambert et al., 1978) (Fig. 2A) and that a portion of this sedimentary sequence was originally composed of evaporites. The high solubility of all common evaporite minerals relative to barite has allowed these barites to survive subsequent tectonism, metamorphism, and surface exposure. The Australian Archean barites appear to be the oldest remnants of evaporites in the geologic record (Lambert et al., 1978).

There are differences of opinion regarding the origin of barite in the ~3450 m.y. Onverwacht Group of South Africa. Petrographic and mineralogical analysis suggests an evaporite origin similar to that of the Australian barites (Lowe and Knauth, 1977; Lambert et al., 1978). Reimer (1980) advocates a volcanic source of the barium on the basis of close stratigraphic proximity to large volumes of volcanic rocks and minor amounts of associated sulfides. Detailed work on younger (~3200 m.y.) bedded barite in the overlying Fig Tree Group shows that these deposits are largely detrital with some diagenetic recrystallization rather than being pseudomorphs of evaporites (Heinrichs and Reimer, 1977; Reimer, 1980) (Fig. 2B). An obvious source of the detrital barite would, of course, be the older Onverwacht barite.

Archean bedded barite from central India is highly metamorphosed and occurs with a variety of Ba-bearing metamorphic minerals. As with the South African and Australian barites, no significant sulfide mineralization is noted. Whereas the Indian bedded barites are clearly synsedimentary in origin, and their exact depositional environment is difficult to interpret (Radhakrishna and Sreenivasaiya, 1974; Deb et al., 1991).

The Australian, South African, and Indian Archean bedded barite have all been studied isotopically. Assuming that the primary Rb-Sr signature of these barites has been retained, the Western Australian barite has the most primitive Sr signature of all the bedded barites (Table 2). Comparison of the $^{87}Sr/^{86}Sr$ composition of these barites with lunar and meteorite $^{87}Sr/^{86}Sr$ analyses have allowed constraints to be placed on the origin of the Earth and the Moon (McCulloch, 1994). South African and Indian Archean bedded barites are on average slightly more radiogenic than the Australian barite (Table 2), although both are consistent with mantle buffering of Archean seawater composition (Perry et al., 1971; Deb et al., 1991; Strauss, 1993).

Sulfur isotopic analysis of Archean bedded barite has been a critical piece of evidence for understanding the redox state and sulfate concentrations of Archean seawater. $\delta^{34}S$ compositions of the Australian, South African, and Indian bedded barites are all low relative to the minor amounts of coexisting sulfides (Table 2), which suggests that the biologic fractionation of sulfide sulfur observed throughout the post-Archean geologic record was not operative in the Archean ocean. Rather, the low sulfide-sulfate fractionation is attributed to inorganic oxidation of volcanic H_2S or SO_2 in an ocean with very small sulfate concentrations (Perry et al., 1971; Cameron, 1982; Schidlowski et al., 1983; Strauss, 1993).

Proterozoic Barite

Examples of bedded barite from the Proterozoic are rare (Table 1). The lone example from the Early to Middle Proterozoic is the ~2000 m.y. bedded barite of the Aravalli Supergroup of central India. These bedded barites are associated with supracrustal quartzites, metavolcanics, and some carbonates but no known massive sulfides (Deb et al., 1991). The Late Proterozoic Dalradian Supergroup in Scotland has an exceptional number of bedded barite occurrences with a clear association to exhalative massive sulfide deposits as well as some barite deposits with only minor associated sulfides (Willan and Coleman, 1983; Hall et al., 1991). These deposits are found in

TABLE 2.— SUMMARY OF SELECTED $^{87}Sr/^{86}Sr$ and $\delta^{34}S$ DATA FOR BEDDED BARITE. VALUES REPORTED ARE MEAN + ONE STANDARD DEVIATION OF ALL ANALYSES REPORTED IN THE LITERATURE REFERENCE.

Location and geologic formation	$^{87}Sr/^{86}Sr$ (barite)	$^{87}Sr/^{86}Sr$ (seawater)[1]	$\delta^{34}S$ (‰)
Western Australia,			
Warrawoona Group (Early Archean)	.70053± 3 (n=4) [2]		3.6± 0.5 (n=18) [3]
	.70052 [4]		5.4±0.9 (n=2) [4]
South Africa			
Onverwacht Group (Early Archean)			3.0–6.9 (n=11) [5]
Fig Tree Group (Early Archean)	.7009-.7017 (n=8) [6]		3.8±0.4 (n=7) [3]
	.7014 [3]		3.4±0.3 (n=11) [6]
			4.1–8.4 [7]
			2.0–4.3 [8]
India			
Sagur Group (Early Archean)	.7018±7 (n=7) [9]		5.4±0.7 (n=12) [9]
			4.3+0.2 (n=6) [10]
Aravalli Supergroup (Middle Proterozoic)	.7234±3 (n=6) [9]		18.8±0.5 (n=16) [9]
Scotland			
Argyll Group (Late Proterozoic)	.7139±6 (n=6) [11]	.7071	36.5±2.0 (n=16) [11]
			32.3±2.7 (n=20)[12]
Southern China			
Qinling Region (Early Cambrian)	.7084±3 (n=7) [13]	.7095	22.9±0.8 (n=17) [14]
Jiangnan Region (Early Cambrian)	.7085+2 (n=5) [13]		34.9±2.2 (n=3) [14]
Western Canada			
Faro deposit (Late Cambrian)			25.2±1.2 (n=6) [15]
Grum deposit (Late Cambrian)			31.8±2.2 (n=10) [15]
DY deposit (Late Cambrian)			31.7±7.2 (n=13) [15]
Vulcan deposit (Late Silurian - Early Devonian)			43.5 (n=13) [16]
Jason deposit (Middle Devonian)	.7134±5 (n=10) [17]	.7077	24.4±1.2 (n=17) [18]
Lower Earn Group (Late Devonian)			27.0±3.4 (n=3) [19]
Nevada, U. S. A.			
East Northumberland Canyon (Late Devonian)	.7083 [20]	.7083	24.4±2.2 (n=10) [20]
Mountain Springs Deposit (Late Devonian)	.7097±8 (n=7) [21, 22]		
Argenta (Late Devonian)	.7107±8 (n=2) [21, 22]		29.1±13.6 (n=6) [24]
Miller (Late Devonian)	.7091 [23]		32.6±`8.7 (n=4) [24]
Queen Lode (Late Devonian?)	.70810 [21]		
Western Europe			
Meggen deposit (Middle Devonian)	.71072 [21]	.7077	23.1±2.0 (n=72) [25]
Ramselberg deposit (Middle Devonian)	.71100 [21]		22.7±3.1 (n=58) [26]
Chaudfontaine deposit (Late Devonian)	.7112±2 (n=11) [27]		28.0±1.5 (n=9) [27]
Arkansas, U. S. A.			
Fancy Hill deposit (Late Mississippian)	.7084±2 (n=2) [21]	.7082	
Millchem deposit (Late Mississippian)	.7085±2 (n=2) [21]		
Chamberlain deposit (Late Mississippian)	.7084±7 (n=7) [28]		
Italy (Mid-Late Triassic)	.70707±4 (n=4) [29]	0.7077	
Cuba (Jurassic)	.7120±6 (n=5) [21]		
Mexico (Early Cretaceous)	.7084±6 (n=8) [30]	0.7072	24.3±12.0 [30]
Paita (Holocene, Peru middle shelf)	.7104±3 (n=4) [31]		
Chiclayo Canyon (Holocene, Peru continental slope)	.7109±4 (n=6) [31]		

[1] Burke et al. (1982)
[2] McCulloch (1994); primary barite only
[3] Lambert et al. (1978)
[4] Strauss (1993)
[5] Reimer (1980)
[6] Perry et al. (1971)
[7] Reimer (1980); detrital barite
[8] Reimer (1980); diagenetic barite
[9] Deb et al. (1991)
[10] Hoering (1988)
[11] Hall et al. (1991)
[12] Willan and Coleman (1983)
[13] Wang and Chu (1994); excludes one value (0.713661) from Jiangnan area and another (0.716710) from Qinling area
[14] Wang and Li (1991); excludes analyses of concretionary barite
[15] Shanks et al. (1987); all samples described as baritic massive sulfides
[16] Mako and Shanks (1984); no reported standard deviations of data
[17] Turner (1986)
[18] Gardner and Hutcheon (1985)
[19] Cecile et al. (1983)
[20] Rye et al. (1978)
[21] Maynard et al. (1995)
[22] Barbieri and Masi (1983)
[23] Jewell, unpublished
[24] Mitchell (1980)
[25] Buschendorf et al. (1963)
[26] Anger et al. (1966)
[27] Dejonghe et al. (1989)
[28] Hulen (1978)
[29] Barbieri et al. (1984)
[30] Kesler and Jones (1981)
[31] Aquilina et al. (1997)

siliciclastic sedimentary sequences deposited during a period of extensional tectonics along a continental margin. In this sense, the Proterozoic Scottish deposits are similar to the well-studied Paleozoic barite of western Canada and western Europe. It is noteworthy that most large, well-known, Proterozoic sediment-hosted massive sulfide deposits (for example, Sullivan in British Columbia and the McArthur River area in northeastern Australia) are devoid of bedded barite (Gustafson and Williams, 1981).

$^{87}Sr/^{86}Sr$ analyses of the central Indian and Scottish Proterozoic bedded barites show clear continental affinities (Table 2) and probably reflect the circulation of hydrothermal fluids through continental crust. All Proterozoic bedded barites have $\delta^{34}S$ compositions that are heavier than Archean barite, which suggests that extensive biogenic fractionation and high sulfate oceans were common in the Proterozoic (Willan and Coleman, 1983; Hall et al., 1991; Deb et al., 1991) (Table 2).

Additional occurrences of Proterozoic bedded barite from southern Brazil (Cassedanne, 1989) and Zimbabwe (Thorpe, 1979) are poorly documented with respect to age, geologic setting, and genesis. The latter is particularly intriguing because of its similarities to the South African and Australian Archean bedded barites and its occurrence in rocks that could be anywhere from Late Archean to Middle Proterozoic in age.

PALEOZOIC BEDDED BARITE

Paleozoic bedded barites constitute the most widespread and volumetrically significant amounts of barite in the geologic record. Major deposits are pre-Pennsylvanian in age and found throughout the world (Fig. 1). The preponderance of Paleozoic bedded barites occurs in black shale sequences with associated cherts and phosphorites as well as lesser amounts of volcanic rocks, limestones, and sandstones (Table 1). Significant amounts of barite occur with Paleozoic sedimentary rock-hosted massive sulfide deposits, although many large, economically important bedded barites are not associated with significant amounts of sulfide. Like Precambrian barite, the sulfur isotopic composition of Paleozoic barite has been effectively used to track open and closed ocean chemistry for selected periods of time (e.g., Goodfellow and Jonasson, 1984) and strontium isotopes have proven effective in documenting the source of barium in a variety of settings (e.g., Maynard et al., 1995). Paleozoic bedded barites have $\delta^{34}S$ signatures that are close to but not precisely the same as the Paleozoic evaporite curve (Fig. 3).

Southern China

Bedded barite deposits in southern China are among the largest barite reserves of the world. In spite of this, the Chinese deposits are among the most poorly documented of all barite provinces with respect to regional geologic setting and detailed studies of specific deposits.

Although Late Sinian (Late Proterozoic) rocks host concretionary barite and witherite, all of the major Chinese bedded barite deposits are found in Early Cambrian black shales and cherts of the Qinling and Jiangnan regions in the south-central portion of the country (Wang and Li, 1991). Barite deposits of the more southern Jiangnan area are believed to have formed on the interior of the Yangtze craton, while the Qinling deposits are found in the suture zone that formed between the Yangtze and Sino-Korean craton to the north during the early Paleozoic (Maynard and Okita, 1991). Exact age determinations and stratigraphic correlations of barite-bearing strata are lacking, although the massive barite beds appear to occur in stratigraphically higher intervals in deep water facies to the northeast (Wang and Li, 1991).

The Chinese barite deposits occur in massive beds, laminations, rosettes, and nodules and are apparently unique among major barite provinces of the world in being associated with major amounts of witherite ($BaCO_3$) and barytocalcite ($CaBa(CO_3)_2$). High concentrations of vanadium (up to 1% V_2O_5) have been documented in associated sedimentary rocks. Like many barite provinces, phosphatic concretions and organic carbon-rich shales (up to 16% total organic carbon) are commonly associated with the barite (Wang and Li, 1991). $^{87}Sr/^{86}Sr$ values from most of the Chinese deposits are very close to those of contemporaneous Cambrian seawater (Wang and Chu, 1994) (Table 2). However, single samples from the Sanjiang deposit of the Jiangnin area and Liulin deposit of the Qinling area are anomalously radiogenic. $\delta^{34}S$ values of the barite grade from relatively heavy (+35‰) in the platform settings to somewhat lighter values (+23‰) in the geosynclinal or continental margin deposits (Table 2). These observations are explained within the context of a euxinic interior basin that depleted seawater sulfate concentrations leading to relatively heavy sulfate that was then incorporated into the barite (Wang and Li, 1991).

Western Canada

Western Canada (the Yukon, Northwest Territories (NWT), and northern British Columbia) are host to a large number of economically important sedimentary rock-hosted massive sulfide (sedex) and barite deposits. These deposits are found in thick sequences of fine-grained siliciclastic rocks and chert deposited in an epicratonic rift basin that was active from the Cambrian through the Late Devonian (Table 1) and bounded to the east and west by carbonate platforms (Abbott et al., 1986).

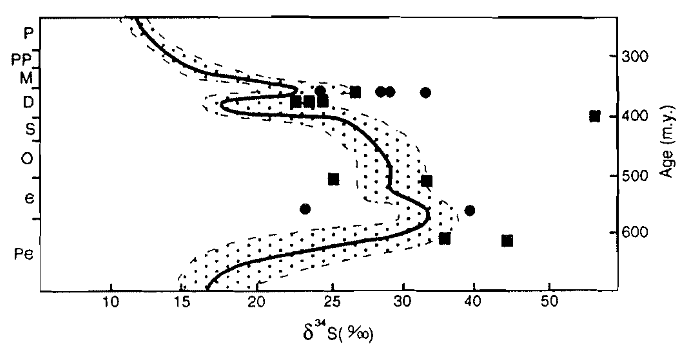

FIG. 3.—Mean values of $\delta^{34}S$ (‰) of Late Proterozoic through Paleozoic bedded barite from Table 2 plotted against the $\delta^{34}S$ curve of Claypool et al. (1980). Circles refer to barite-only deposits; squares refer to Pb-Zn-Ba deposits.

Along the Yukon-NWT boundary, this rift is known as the Selwyn Basin and to the southeast in British Columbia it is known as the Kechika Trough. The wide range of bedded barite and sulfide deposit ages in western Canada has allowed determination of secular changes of both sulfide and sulfate $\delta^{34}S$ values during the Middle Paleozoic. This work suggests that the Selwyn basin was anoxic, stratified, and hydrographically isolated from the open ocean during much of its existence (Cecile et al., 1983; Goodfellow and Jonasson, 1984).

Within the Selwyn Basin, three major districts of bedded barite and massive sulfide mineralization have been recognized (Carne and Cathro, 1982). The Anvil Camp on the western side of the basin hosts a number of important massive sulfide deposits at the contact of Cambrian noncalcareous metapelites of the Mount Nye Unit and calcareous metapelites of the Vangorda Unit (Jennings and Jilson, 1986). Barite mineralization appears to be minor, although a number of barite $\delta^{34}S$ analyses have been reported (Shanks et al., 1987) (Table 2). The Howards Pass Camp deposits along the Yukon-NWT boundary are hosted by Upper Ordovician-Lower Silurian carbonaceous shales and siltstones of the Road River Group and also have relatively small amounts of bedded barite (Carne and Cathro, 1982; Goodfellow et al., 1983). Deposits of massive sulfide and bedded barite are reported in the Upper Silurian to Lower Devonian portion of the Road River Formation south of the Howards Pass Camp (Mako and Shanks, 1984) (Fig. 4A). The MacMillan Pass Camp located immediately north of the Howards Pass Camp hosts several economically important sedex Pb-Zn-Ba deposits (Gardner and Hutcheon, 1985; Turner, 1986), as well as several bedded barite deposits with no associated sulfides (Lydon et al., 1985b). The number of "barite-only" deposits from the MacMillan Pass is greater than those of either the Anvil or Howards Pass areas. The massive sulfide and bedded barite deposits are found in Upper Devonian carbonaceous shales of the Lower Earn Group.

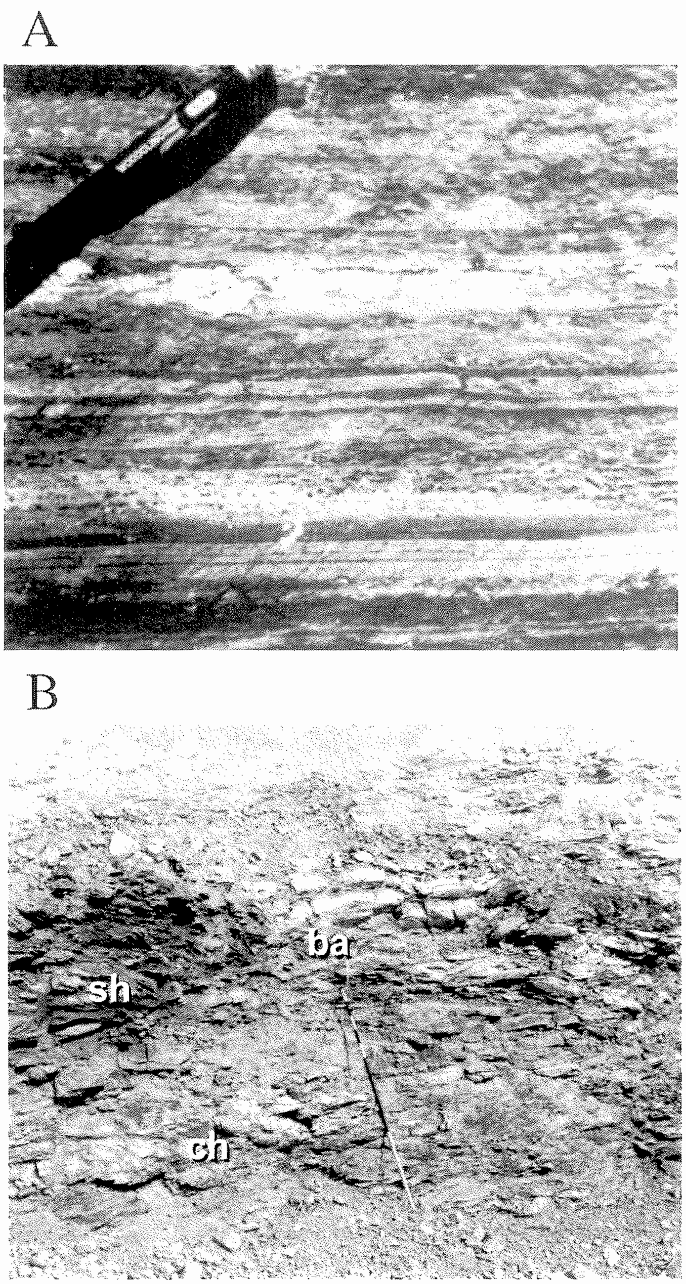

FIG. 4.—Field examples of Paleozoic bedded barite. (A) Laminated barite-chert from the base of the upper Earn Group (Late Devonian to Mississippian) near the Vulcan deposit, Northwest Territories, Canada (from Mako and Shanks, 1984). Note pencil for scale. (B) Sequence of deformed barite, chert, and organic-rich shales of the Slaven Chert (Late Devonian) in the Argenta mine of north central Nevada (from Jewell and Stallard, 1991). Jacob staff is 1.5-m long.

Bedded barite and shale hosted Pb-Zn-Ba deposits in the Kechika Trough of northeastern British Columbia are more spatially and temporally dispersed than those in the Selwyn basin. Deposits are found in host rocks that range in age from Ordovician through Devonian. Bedded barite deposits with no associated massive sulfides include the Ordovician Sika and the Devonian Kwadacha deposits (MacIntyre, 1982).

Research in the Selwyn Basin and Kechika Trough has emphasized an exhalative origin for the bedded barites (e.g., Large, 1983; Lydon et al., 1985a). In addition to association with massive sulfide mineralization, evidence of an exhalative origin of the bedded barite includes hydrothermal breccias, contemporaneous volcanism, and $^{87}Sr/^{86}Sr$ values, which indicate that the barite was derived from continental crust (Table 2). It is noteworthy that some of the bedded barites (particularly from the Devonian section) with no associated massive sulfide mineralization resemble other barite-only provinces of the world (China, Nevada, Arkansas) in terms of morphology and association with cherts and organic-rich shales (e.g., Mako and Shanks, 1984; Lydon et al., 1985a). It should be further noted that $^{87}Sr/^{86}Sr$ data have been reported for only one deposit (the Devonian Jason Pb-Zn deposit) (Table 2).

Alaska

Alaska has a number of bedded barite occurrences (Clark and Poole, 1989; Schmidt, 1997). Interestingly, shale-hosted stratiform deposits in Alaska appear to be either massive sulfide deposits with no barite or deposits composed only of barite (Schmidt, 1997). An exception is the Red Dog deposit in the western Brooks Range, a world class (77 million metric ton) Pb-Zn-Ba deposit with significant amounts of bedded barite hosted by Lower Mississippian to Permian black shales and chert. Genetic relationships of the barite to sulfide mineralization at Red Dog are similar to sedex deposits of western Canada and Germany (Moore et al., 1986).

Deposits composed only of bedded barite are hosted by Devonian through Triassic black shales, cherts, and minor amounts of limestones and fine-grained siliciclastic rocks. Most of these deposits are found in the western Brooks Range or in southwestern Alaska. Exact genetic relationships between the barite and various rocks types are poorly known due to lack of exposure or detailed geologic investigations. Reported $\delta^{34}S$ values of the barite range from 21‰ to 28‰ (Schmidt, 1997).

Nevada

Central Nevada contains some of the largest bedded barite deposits in the world. Barite is found in more than 100 individual mines and prospects that have reserves of approximately 90 million metric tons. An overview of the Nevada barite province can be found in Mitchell (1980) and Papke (1984).

Most of the central Nevada bedded barite is found in Ordovician through Late Devonian cherts and shales of the Roberts Mountain allochthon. These deep-water facies rocks were thrust over shallow-water facies rocks during the Late Devonian through Early Mississippian Antler Orogeny. Tectonic overprinting during the Mesozoic and Cenozoic has greatly complicated the host rocks of these barite deposits. The most common bedded barite bearing strata are the Ordovician Vinini Formation and the Late Devonian Slaven Chert (Papke, 1984). The general lithologic similarities and extreme structural complications of these two units make them difficult to distinguish in the field. Both are dominantly chert and shale, although the Vinini has higher amounts of coarse-grained siliciclastics (Stewart, 1980). Barite deposits in both formations are associated with cherts and organic-rich shales with lesser amounts of limestone and igneous rocks (Dubé, 1988; Graber and Chafetz, 1990; Jewell and Stallard, 1991) (Fig. 4B). Interestingly, all deposits that have been studied in detail and produced reliable paleontological data are Middle or Late Devonian in age. Sulfur isotopic data (Mitchell, 1980; Rye et al., 1978) show that massive bedded barite has a seawater sulfate source, while concretionary and rosette barite have relatively heavy sulfur ratios that are characteristic of a closed sulfur system. Analyses (Rye et al., 1978; Maynard et al., 1995) show that $^{87}Sr/^{86}Sr$ ratios of massive barites likewise are close to or slightly heavier than those of contemporaneous seawater (Table 2).

The relatively well-studied nature of the Nevada bedded barite has not yielded consensus about its origin. Structural complexity, poor stratigraphic control, and paucity of dateable fossils contribute to this situation. Ketner (1963) advocated diagenetic replacement of limestone on the basis of rare brachiopods found within some of the barite beds. Most subsequent workers have argued for a synsedimentary origin, with deposition by exhalative processes being a popular mechanism (e.g., Poole, 1988; Dubé, 1988). Shawe et al. (1969) and Jewell and Stallard (1991) argue for deposition by biological processes, citing a lack of significant associated volcanism and massive sulfides, analogs of barite deposition in the modern ocean, and major and minor geochemical systematics. Jewell (1994) details a model for the formation of a sulfate-reducing coastal upwelling system as a depositional mechanism for the Nevada bedded barite.

Arkansas

The Arkansas bedded barite province is hosted by the Late Mississippian Stanley Shale and has been an important producer of barite for much of this century. The deposits are found in an east-west-trending syncline in the central part of the state; the principle zones of bedded barite occur at Chamberlin Creek in the east and Fancy Hill to the west. The Stanley Shale consists of organic-rich black shales interbedded with turbiditic siltstones and sandstones that were deposited on the southern edge of a continental margin that received sediment from the Appalachian Mountains to the north (Morris, 1974; Maynard and Okita, 1991). Devonian novaculite (metamorphosed chert), shales, and volcanic tuffs underlie the barite deposits. The barite occurs in a variety of morphologies, including rhythmic bands of shale, barite, and carbonate (Zimmerman and Amstutz, 1989).

The Arkansas bedded barites differ from the Nevada barites in having dominantly shale and siltstone host rocks, larger concentrations of carbonate, and trace amounts of anhydrite. A detailed trace element study of the Fancy Hill bedded barite deposit has also shown that the minor sulfide present was diagenetic with little input from hydrothermal sources (Howard and Hanor, 1987). $^{87}Sr/^{86}Sr$ analyses of the Arkansas barite are very close to those of contemporaneous seawater (Maynard et al., 1995) (Table 2).

Other Occurrences in North and South American

Lesser known Paleozoic bedded barite deposits have been noted in Sonora, Mexico (Poole, 1988; Clark and Poole, 1989), and northeastern Washington state (Mills et al., 1971). Neither area has massive sulfide deposits that can be directly related to the bedded barite. A small number of Paleozoic nodular and lensoid deposits have been described in west-central Argentina in a gray and black shale sequence of Ordovician age (Brodtkorb et al., 1982).

Western Europe

Well-documented bedded barite is associated with sedimentary rock-hosted Pb-Zn deposits in Germany (Meggen and Rammelsberg), Belgium (Chaudfontaine), and Ireland (Silvermines and a number of other deposits). Lesser known barite deposits occur throughout Europe. The German deposits have many of the same characteristics as the sedex deposits in western Canada, that is, a central core of massive stratabound Pb-Zn mineralization surrounded by an apron of bedded barite (Krebs, 1981; Hannak, 1981). Reported tonnages of barite at Meggen are much higher than at Rammelsberg (10 million tons versus 0.2 million tons) (Fuchs, 1989). Deposition of the

Meggen and Rammelsberg ore bodies also appears to have occurred in sediment-starved rift basins, although these basins were not nearly as large as the Selwyn and Kechika Basins in Canada. $\delta^{34}S$ analysis of these barite deposits indicate a seawater source for the sulfur and $^{87}Sr/^{86}Sr$ analyses suggest a continental source for the barium (Table 2).

The Chaudfontaine deposit is a relatively recent discovery in the Late Devonian shales and carbonates of western Belgium (Dejonghe, 1979). The deposit has a high percentage of bedded barite relative to Pb-Zn massive sulfides and the barite has a wide variety of crystal morphologies (Dejonghe, 1990) that appear to have grown in a semi-restricted evaporite basin (Dejonghe and Boulvain, 1993). The source of the sulfur was seawater, while other metals including barium have a continental source (Dejonghe et al., 1989) (Table 2).

Pb-Zn-Ba deposits are also associated with Carboniferous carbonate rocks in a variety of localities in Ireland (Morrisey et al., 1971; Coomer and Robinson, 1976; Taylor and Andrew, 1978). Stratiform bedded barite deposits have been described in Sardinia from Middle Cambrian dolomites (Barbieri et al., 1984b; Padalino et al., 1989) and in association with stratiform Pb-Zn mineralization in Devonian black shales, siltstones, and limestones in the Pyrenees of France (Lhegu et al., 1988). These deposits have relatively low tonnage and have not attracted extensive scientific scrutiny.

MESOZOIC TO MODERN BEDDED BARITE

Noteworthy bedded barite occurrences are relatively rare in Mesozoic and younger rocks. None have the large size and association with black shale sequences typical of Paleozoic bedded barites (Table 1). As discussed below, this may be attributed to the possibility that sulfate reducing ocean conditions were present during the Paleozoic that were not present during the Mesozoic.

A number of massive barite occurrences have been documented in deep sea drilling sites and on the seafloor of the modern ocean (Dean and Schrieber, 1977). Some of these deposits have been used as analogs for a variety of older bedded barite deposits (Torres et al., 1996).

Mesozoic Bedded Barite

Barite and a small amount of Pb-Zn mineralization is found in Middle to Late Triassic rocks of southern Italy (Barbieri et al., 1984a). $^{87}Sr/^{86}Sr$ analyses of this deposit suggest that the barite precipitated from seawater (Table 2). Early Jurassic dolomites host small bedded barite deposits in France whose paragenesis appears related to evaporite basins (Fuchs, 1989). A number of similar Early Jurassic barite deposits are found in evaporite sequences in central Argentina (Brodtkorb et al., 1989). Pb-Zn-Ba deposits from Jurassic sedimentary rocks in Cuba have been described by Maynard et al. (1995). $^{87}Sr/^{86}Sr$ data from these deposits suggest a continental source (Table 2). An early Cretaceous bedded barite deposit from the Atacama region of Chile occurs as mantos in a sequence of limestones and calcarenites that were extensively altered during subaerial diagenesis (Diaz, 1990). The geology and isotopic geochemistry of similar manto-type barite and celestite ($SrSO_4$) deposits are described in Middle Cretaceous limestones of northeastern Mexico (Kesler and Jones, 1981). Interestingly, this barite has $^{87}Sr/^{86}Sr$ that is distinctly more radiogenic than the celestite. $\delta^{34}S$ of the celestite is also lighter than that of the barite. Bedded barite from a Cretaceous chalk-chert sequence in the Judean Desert of Israel has an association with biologically produced sediments (cherts, phosphorites) that is similar to that of Paleozoic deposits (Bogoch and Shirav, 1978).

Bedded Barite on the Seafloor and from Deep-Sea Drilling Sites

Bedded barite associated with seafloor spreading on the modern ocean floor has been documented in a number of localities (Church, 1979; Lonsdale, 1979; Koski et. al., 1985, 1988; Peter and Scott, 1988). Other localities such as the California borderlands (Cortecci and Longinelli, 1972) and the Peru convergent margin (Aquilina et al., 1997) are not associated with seafloor spreading. The latter setting appears to be an example of fluid circulation through an accretionary prism.

Deep-sea drilling over the past several decades has led to the discovery of a number of bedded barite occurrences (Dean and Schrieber, 1977). Unfortunately, it is generally impossible to determine the morphology and areal extent of barite beds intersected by these cores. Nevertheless, analysis of the barite and associated pore fluids in deep-sea drilling sites holds the promise of providing considerable insight into how bedded barite may have formed in similar environments throughout the geologic record. A particularly interesting analysis of this sort is given by Torres et al. (1996) who model dissolution and reprecipitation of barite along diagenetic fronts where sulfate concentration of the pore fluids shows large gradients.

THEORIES OF BEDDED BARITE GENESIS

The wide variety of bedded barite and associated lithologies has led to several theories of bedded barite genesis. For the purposes of this review, these are placed into three categories: diagenetic replacement, biologic precipitation, and exhalative. All three are supported to greater or lesser degrees by field relationships, geochemical data, and comparisons to modern analogs. Of the three categories, exhalative is perhaps the most diverse. In the present context, sedimentary exhalative (sedex) is meant to include all fluids expelled from the underlying sediment column. No distinction is made between fluids heated by magma, by circulation along a deep seated fault, or simply by geothermal gradients in an overpressured basin.

Diagenetic Replacement

Replacement of evaporite sequences by barite in some Archean bedded barite occurrences is well-documented on the basis of crystal morphologies of the barite and surrounding sedimentary associations (Lambert et al., 1978; Reimer, 1980).

Diagenetic replacement of limestone has also been suggested for Paleozoic bedded barite deposits of Nevada (Ketner, 1963), although the evidence is far less convincing because of the stratabound nature of the barite as well as the fact that limestone and barite are seldom found in close spatial proximity (Papke, 1984; Poole, 1988). Most subsequent researchers have adopted a synsedimentary mechanism for the Nevada as well as virtually all other Proterozoic through Paleozoic bedded barite deposits. In spite of the lack of evidence for the formation of bedded barite deposits by wholesale diagenetic replacement, there is considerable evidence that diagenesis is important on local scales (Papke, 1984). In fact, diagenetic reorganization of bedded barite would be a logical consequence of any early sediment diagenesis that included sulfate reduction. Sulfate reduction has been documented in organic-rich marine sediments associated with diagenetic barite deposits in the modern ocean (Torres et al., 1996). Diagenesis is also considered the primary genetic mechanism for bedded barites in the carbonate-hosted Mesozoic mantos deposits of Mexico (Kesler et al., 1981).

Exhalative

A sedimentary exhalative origin of bedded barite has been applied to virtually all deposits that have temporal and spatial associations with sediment-hosted massive sulfide deposits as well as to many bedded barites without these associations. This model evolved following the discovery from the 1960s through the 1980s of hydrothermal vents at seafloor spreading centers and continental margins. These discoveries led to a consensus that many ancient volcanic-hosted massive sulfide deposits were syngenetic rather than hydrothermal replacement deposits (Franklin et al., 1981). This exhalative model subsequently became a popular although by no means universally accepted model for sedimentary rock-hosted massive sulfide and bedded barite deposits throughout the geologic record (Gustafson and Williams, 1981). The most widely recognized modern analog for sedex deposits is the Guyamas Basin in the Gulf of California, where a large number of submarine hot springs and massive sulfide deposits have been documented in sedimentary basins near seafloor spreading zones (Koski et al., 1985; Peter and Scott, 1988). However, in many ancient sedex deposits a clear link with volcanism is lacking (Carne and Cathro, 1982; Large, 1983; Lydon et al., 1985a). For these deposits, the source of hydrothermal fluids is believed to be circulation along the normal faults of continental rift basins (Fig. 5). In this sense, no modern analog has been documented for sedex deposits, such as those of western Canada and Europe.

A variation of the sedex model that does have documented modern analogs involves excess sediment pore pressure rather than hydrothermal heating driving the exhalative processes. These seafloor discharges are characterized by relatively modest temperatures and tend to form in basins with relatively high sedimentation rates (for example, the Gulf of Mexico) or in those that are undergoing subduction (for example, the Peru margin). Fluids that precipitate barite along the Peru margin are reduced, contain high concentrations of dissolved barium, and have elevated $^{87}Sr/^{86}Sr$ values, which indicate derivation from a continental source (Aquilina et al., 1997). This form of the sedex deposition has been advocated for barite-only deposits in Arkansas (Howard and Hanor, 1987), although $^{87}Sr/^{86}Sr$ signatures would seem to indicate that the barium was derived from contemporaneous seawater rather than continental material (Maynard et al., 1995; Table 2).

Biological Precipitation

A biological origin for marine barite has been advocated since oceanographic surveys documented the association between marine biogoechemistry, elevated concentrations of barium in modern ocean sediments, and the occurrence of discrete barite particles in biogenic matter of the water column (Goldberg and Arhennius, 1958; Chow and Goldberg, 1960; Church, 1979; Dehairs et al., 1980). Barite formation has been documented in the microenvironments of organic particles falling through the water column (Bishop, 1988), which thereby accounts for the correlation between surface productivity and barite accumulation in the underlying sediments (Dymond et al., 1992). Seawater is the source of the barium as well as the $^{87}Sr/^{86}Sr$ signature of these particles (Martin et al., 1995). Barite accumulations of several weight percent are observed below zones of high biological productivity and low siliciclastic sedimentation rates (e.g., Dymond, 1981).

Biologically produced barite particles that fall into sulfate reducing waters of restricted basins of the modern ocean dissolve and enrich those waters in dissolved barium (Falkner et al., 1993). If sulfate-reduction were present in the open waters of ancient oceans, then the barite would dissolve and be reprecipitated as bedded barite in the ocean's oxic-anoxic transition zone (Fig. 6). Formation of massive bedded barite would require high surface productivity, significant water mass flux (that is, strong currents), and open ocean sulfate reduction to exist in the same locality (Jewell, 1994). In modern coastal upwelling zones such as the coast of Peru, these first two criteria are met while the third (sulfate reduction) has only been observed under rare circumstances (Dugdale et al., 1977). As discussed in more detail below,

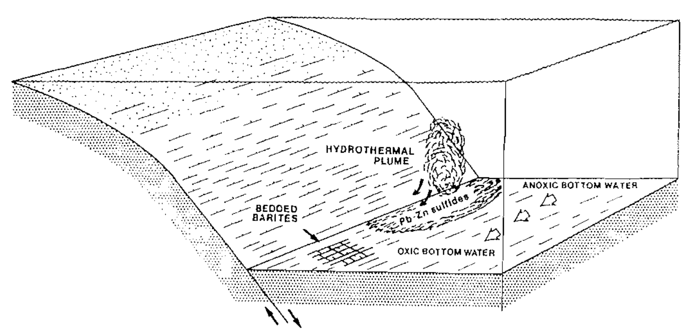

FIG. 5.—Diagram of sedimentary exhalative model of bedded barite deposition. Massive sulfide mineralization occurs near seafloor hydrothermal vents that are often associated with a major fault. Restricted circulation in the submarine basin promotes anoxic water, allowing dissolved barium to migrate to the site of bedded barite deposition at the O_2-H_2S transition zone.

open ocean sulfate reduction was probably more common in Paleozoic oceans (Berry and Wilder, 1978) and, in fact, could have been a natural consequence of the relatively large size of Middle to Early Paleozoic oceans (Jewell, 1995). Under these circumstances, bedded barite sedimentation rates could have been comparable to those of bedded chert (Jewell, 1994).

Associations with biologically produced sediments such as cherts and phosphorites and parallels with biogenic barite in the modern ocean were noted for the Northumberland Canyon bedded barite deposits of central Nevada (Shawe et al., 1969). A biological origin was later advocated for all of the Nevada deposits (Jewell and Stallard, 1991). The biological precipitation mechanism is appealing for barite-only provinces such as Nevada, China, and Arkansas because it explains the lack of massive sulfide deposits in the host rocks as well as why these three barite-only provinces have a dominantly seawater $^{87}Sr/^{86}Sr$ signature (Table 2).

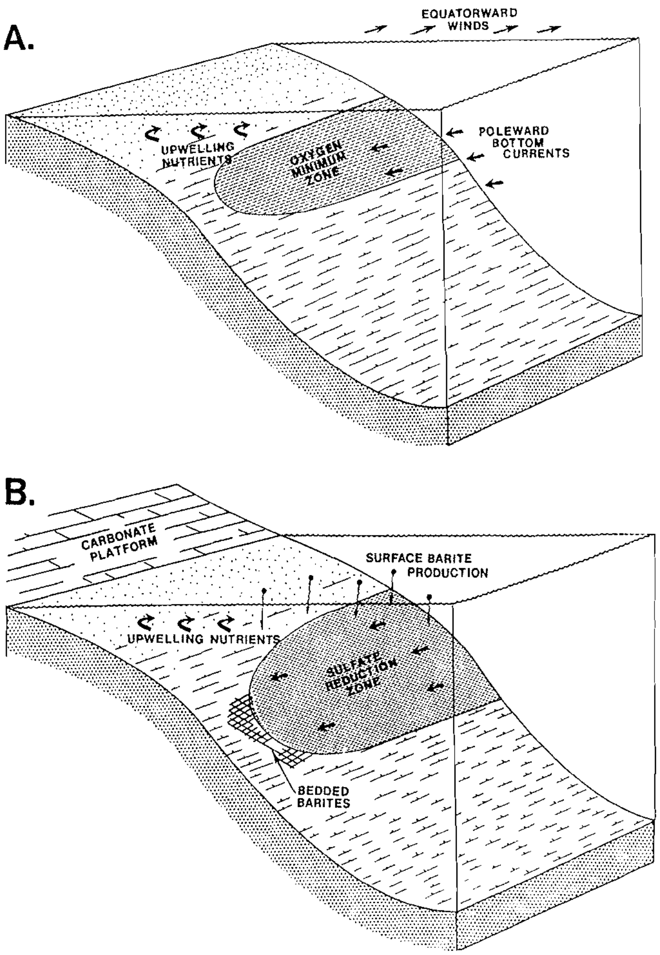

FIG. 6.—Diagrammatic representation of modern and ancient upwelling zones and their relationship to bedded barite formation. (A) Modern upwelling in which equatorward winds induce upwelling of nutrient-rich water. (B) Hypothesized Late Devonian upwelling zone. Disareobic or anoxic deep ocean causes water to be sulfidic below the photic zone. Biogenically produced barite particles settle into the H_2S-rich water. Barite is deposited at the O_2-H_2S boundary due to the interaction of barium-rich water with sulfate-rich water (from Jewell and Stallard, 1991).

DISCUSSION

Despite being a minor element in most crustal rocks, beds of essentially pure barite with thicknesses of tens of meters and strike lengths of several kilometers are found in selected sedimentary sequences throughout the world. Pure bedded barite represents an upgrade of ~1000 times over concentrations of elemental barium in average continental and marine sediments. What peculiar circumstances mobilized and transported large quantities of dissolved barium over long distances before it could react with sulfate to deposit beds of pure barite up to tens of meters thick at various times in the geologic record in a manner not observed in the modern ocean?

Sulfate reduction of seawater and concurrent dissolution of barium-bearing mineral phases is the most logical way of transporting elevated concentrations of barium to a suitable site of deposition. In seafloor hydrothermal and diagenetic systems, seawater is reduced and barium is leached during circulation of seawater through crustal rocks. H_2S-bearing fluids with elevated concentrations of dissolved barium discharge into oxygenated water to form barite-rich deposits near seafloor vents in the modern ocean (e.g., Koski et al., 1985; Peter and Scott, 1988; Aquilina et al., 1997). If similar discharges occurred in sulfate-reducing waters of ancient oceans, then the dissolved barium could migrate long distances from the exhalative source and produce the barite "apron," which is a common feature of sedex deposits (e.g., Large, 1983; Lydon et al., 1985a) (Fig. 5). In a similar fashion, if barite-bearing particles produced by biogenic processes in the upper portions of the water column entered sulfate-reducing water, they would dissolve and be reprecipitated at the edges of the sulfate-reducing zone (Fig. 6). Three critical questions thus emerge. (1) What conditions would lead to areally extensive sulfate reduction in ancient oceans given modern oceanographic conditions in which sulfate reduction is rare? (2) Why are massive bedded barite deposits most common in Early and Middle Paleozoic rocks? (3) How can a distinction be made between the sedimentary exhalative and biogenic models of barite formation?

In modern marine settings, sulfate reduction occurs when oxidation of organic matter exhausts the supply of oxygen and nitrate in the water column. This can occur as a result of physical limitations on the exchange of oxygenated water with the open ocean, high fluxes of organic matter, or some combination of these two factors. The most common sulfate reducing environments in the modern ocean involve settings where the exchange of water with the open ocean is restricted (for example, silled basins such as the Black Sea, Baltic Sea, and fjords). The sulfate-reducing waters of these basins have relatively high dissolved barium concentrations (Falkner et al., 1993). The Cariaco Trench is a fault-bounded graben off the coast of Venezuela that has restricted circulation and anoxic bottom waters (Richards, 1975). This setting may be a good modern analog for the ancient Selwyn, Meggen, and Rammelsberg basins, where active extensional tectonics might have produced seafloor hydrothermal circulation along normal faults as well as restricted the exchange of water with the open ocean.

Extensional tectonic basins and the subsequent restriction of water column circulation on a localized scale is a less appealing

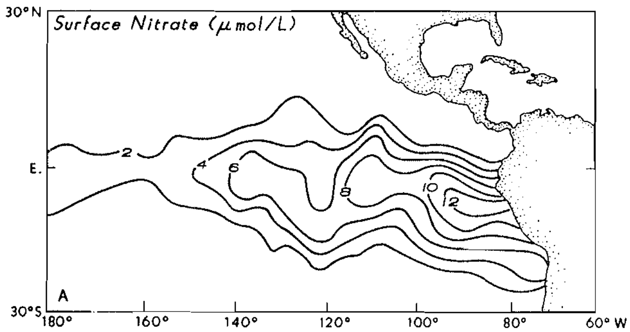

FIG. 7.—Surface nitrate concentrations (μmols/L) in the equatorial Pacific ocean (from Toggwieler et al., 1991)

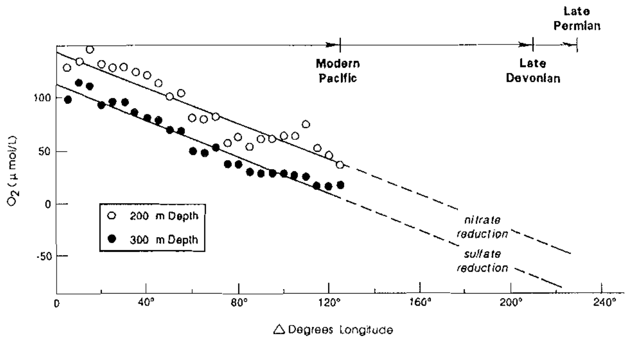

FIG. 8.—Oxygen concentrations as a function of ocean basin width (in changes in degrees of longitude in eastern direction for Pacific Ocean (data from Levitus, 1982). Dashed lines represent linear extrapolations of modern data to ocean widths which are believed to have existed in the Late Paleozoic. Negative oxygen concentrations refer to nitrate and sulfate reduction (from Jewell, 1995).

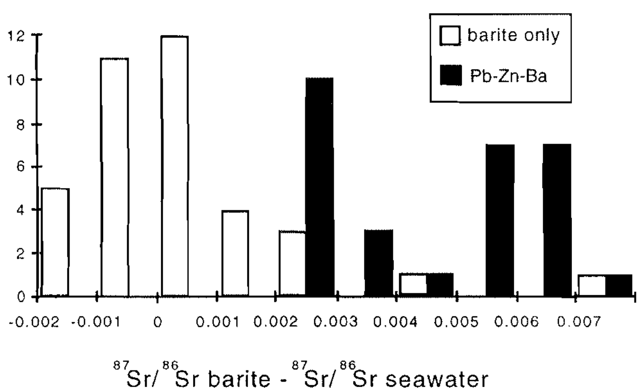

FIG. 9.—Histogram of measured $^{87}Sr/^{86}Sr$ of bedded barite relative to contemporaneous seawater $^{87}Sr/^{86}Sr$ values (modified from Maynard et al., 1995). Contemporaneous seawater values are from Burke et al. (1982). Barite-only data are from China, Nevada, and Arkansas and Pb-Zn-Ba values are from Scotland, Germany, Belgium, and western Canada (Table 2).

mechanism for the genesis of barite-only deposits such as those of Nevada and Arkansas. Although evidence of extensional tectonics has been found in some of these bedded barite deposits (e.g., Dubé, 1988), rift basins capable of restricting seawater circulation have not been systematically documented in the same fashion as the important sedex provinces of western Canada and Europe. Various arguments for widespread sulfate reduction in the open ocean during the Early and Middle Paleozoic have been put forward, however. Widespread evidence of anoxia on continental shelves suggests that the global ocean was oxygen deficient during the early Paleozoic (Berry and Wilde, 1978). Jewell (1995) outlined a mechanism whereby sulfate reduction was a commonplace feature of the equatorial regions of the very large ocean that existed concurrently with the large, closely spaced continents of the Middle Paleozoic through the Middle Mesozoic. Elevated concentrations of surface nutrients along the equatorial axis of the modern Pacific Ocean have long been noted (Fig. 7). This is a result of equatorial upwelling, which causes high surface productivity, in conjunction with the very strong, eastward-flowing equatorial undercurrent. Sinking organic matter is remineralized in the undercurrent and then recirculated to the surface in the equatorial upwelling system. The result is a "nutrient-trap" in which nutrients become enriched in an eastward direction (Fig. 7). Equatorial water at intermediate depths also shows pronounced oxygen depletion in an eastward direction, for example, near the South American coast, where it is close to anoxic (Fig. 8). Sulfate-reducing water has been observed during rare occasions in this area (e.g., Dugdale et al., 1977). The much larger size of the ocean during the Middle and Late Paleozoic would have enhanced this nutrient-trapping effect, thereby leading to widespread sulfate-reducing conditions in the equatorial ocean during this period (Fig. 8). These equatorial waters, in turn, would feed coastal upwelling at low latitudes along the west-facing portions of continents, further enhancing the possibility of sulfate reduction and the formation of bedded barite deposits (Fig. 6).

The biogenic model for bedded barite formation requires a seawater source of barium and strontium within the barite. This is supported by much of the data from China, Nevada, and Arkansas, which tend to have $^{87}Sr/^{86}Sr$ values close to that of contemporaneous seawater (Fig. 9, Table 2). It is also significant that paleogeographic reconstructions of these three localities plot very close to the paleoequator (Fig. 10), where the nutrient-trapping (and barium-enrichment) effect would have been greatest (Fig. 7).

In summary, understanding the genesis of bedded barite throughout the geologic record continues to be a useful and interesting avenue of research. Clear association of bedded barites with sedimentary exhalative deposits holds out the promise of finding new base metal deposits in the geographic vicinity. Likewise, a biologic origin of bedded barite allows the possibility of reconstructing productivity and redox conditions in ancient oceans. Several additional research possibilities are also possible to realize these potentials, including more detailed comparison of areas that contain both Pb-Zn-Ba and barite-only deposits (for example, Alaska and the Selwyn Basin) to understand specific differences between the two. In this regard, $^{87}Sr/^{86}Sr$ studies would be particularly useful in understanding sources of the barium (Fig. 9). More detailed descriptions of the morphology and form of barite occurrences on the modern ocean for which the genesis is clearly understood would also be useful for making meaningful comparisons with ancient deposits.

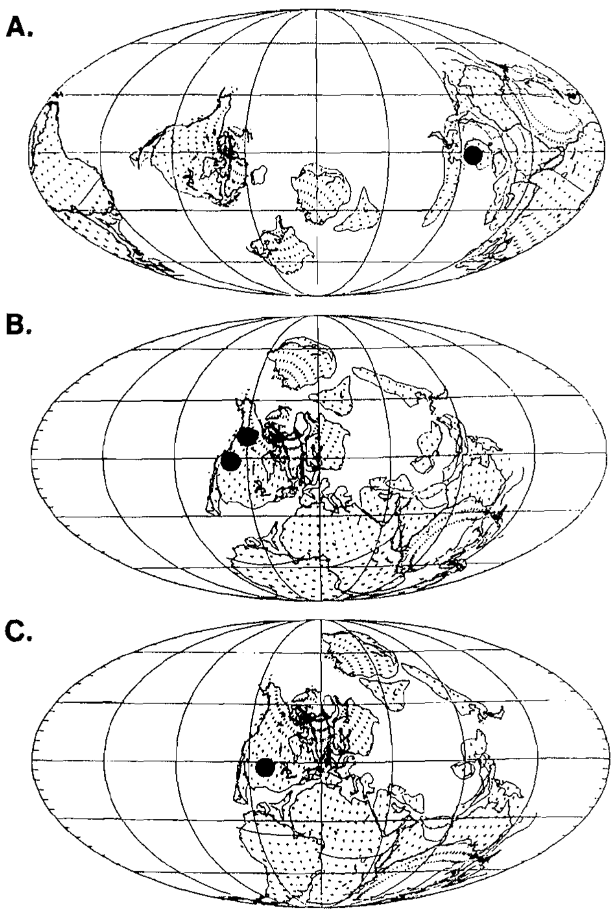

FIG. 10.—Paleogeographic distribution of important bedded barite provinces. (A) Central China (Early Cambrian). (B) Nevada and Selwyn Basin (Late Devonian). (C) Arkansas (Late Mississippian) (paleogeographic configurations from Scotese and McKerrow, 1990).

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