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# GEOCHEMISTRY AND PALEOCEANOGRAPHIC SETTING OF CENTRAL NEVADA BEDDED BARITES<sup>1</sup>

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## ABSTRACT

The bedded barite deposits of central Nevada are hosted by rocks of the Roberts Mountains allochthon and constitute the largest barite reserves in North America. Detailed geochemical studies of three barite deposits in the Devonian Slaven Chert indicate that rocks surrounding the barite have elevated concentrations of carbon and phosphorus relative to nonbarite-bearing rocks. Rare earth element data suggest that the barites were deposited in oxygenated seawater far from a spreading center. Ratios of Al, Ti, Fe, and Mn indicate that hydrothermal input to the sediment was minor relative to detrital input. The assembled data suggest a biogenic rather than a hydrothermal origin for the barite deposits. A model is proposed in which the barites were deposited at the O<sub>2</sub>-H<sub>2</sub>S transition of a coastal upwelling system in the Late Devonian ocean. This model is consistent with recent paleoceanographic analyses of rocks in the Roberts Mountains allochthon, and studies indicating that the Late Devonian marked the transition from an anoxic to an oxic deep ocean.

## INTRODUCTION

Bedded barite occurs in a variety of sedimentary rocks throughout the world. The barite generally occurs as stratiform bodies interbedded with fine-grained, siliciclastic sediments or chert. Some bedded barite is associated with sedimented-hosted Zn-Pb mineralization (Large 1983), although in many cases there is no associated base metal mineralization (Orris 1986).

Barite is also an abundant constituent (up to several weight percent) of modern deep sea sediments, particularly in the Pacific Ocean (Church 1979). Barium has long been known to mimic the behavior of nutrients (particularly Si) (Turekian and Johnson 1966) as well as other elements (e.g., Ra) (Chan et al. 1976, 1977) in seawater. This has led several workers to suggest that barite in oceanic sediments is the result of biogenic processes (Goldberg and Arrhenius 1958; Dymond 1981; Schmitz 1987). In some localities, a hydrothermal origin of barite is suggested, particularly for deposits near active spread-

ing centers (Arrhenius and Bonatti 1965; Bostrom et al. 1973).

The barite province of central Nevada consists of more than 100 individual bedded barite mines and prospects. These account for the highest barite production (2.5 million tons in 1981) and largest barite reserves (90 million tons) of any area in the United States (Papke 1984). All of the bedded barite deposits occur in siliceous sedimentary rocks of the Roberts Mountains allochthon. The allochthon consists predominantly of shale and chert with lesser amounts of siltstone, sandstone, limestone, and greenstone. Estimated ages of rocks of the Roberts Mountains allochthon are Cambrian to Late Devonian (Stewart 1980).

A few studies have been made of the entire Nevada barite province as well as specific deposits. Shawe et al. (1969) describe barite deposits from the central Toquima Range. Miller (1977) gives a geologic description and some sulfur isotope analyses of barite deposits from the northern Shoshone Range. Rye et al. (1978) conducted a stable isotope study of the Toquima Range barites. They demonstrated that the sulfate in the massive barites was derived from contemporaneous seawater (+25‰), although  $\delta^{34}\text{S}$  values were variable (+21 to +29‰). Nodular and concretionary barite had elevated  $\delta^{34}\text{S}$  values (+29 to +41‰), indicating that they formed in an environment that was closed with respect to sulfate. Papke (1984) provides a comprehensive survey of all barite mines and prospects in Nevada. Poole (1988) provides a discus-

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sion of the Nevada barite deposits within the context of Paleozoic rocks in the western United States Cordillera.

The present study was undertaken to establish a detailed geochemical characterization of barite-bearing strata and contemporaneous nonbarite-bearing strata within the Roberts Mountains allochthon. Specific goals include: (1) the description of individual barite deposits, (2) a comparison of the geochemistry of these rocks with similar ancient barite deposits, as well as modern and ancient deep sea sediments, and (3) placement of the barite deposits within the paleoceanographic setting of the allochthon.

*Barite in the Modern Ocean and Deep Sea Sediments.*—The deposition of barite in marine sediments has been considered in detail by several investigators. In coastal waters and estuaries, barium is desorbed from terrestrially derived clays when they mix with seawater. An example of this phenomenon is found in the Baltic Sea where barite micro-nodules occur in freshwater sediments permeated by seawater following the last glacial retreat (Suess 1980).

Results of sediment trap experiments from the Atlantic and Pacific Oceans indicate that barite is present as discrete particles 0.5–5.0  $\mu\text{m}$  in diameter (Dehairs et al. 1980). Controversy exists as to whether the barite is formed directly by siliceous phytoplankton and planktonic protozoa or whether it is precipitated by the release of sulfate in microenvironments of decaying organic matter. Recent detailed SEM/EDXRF work appears to favor the latter explanation (Bishop 1988).

High concentrations of barite have been found in deep sea sediments underlying several regions of the world ocean. Sediments of the eastern equatorial Pacific are particularly enriched in barium (up to several weight percent) (Goldberg and Arrhenius 1958). The barite content of cores from the Deep Sea Drilling Project in the Indian Ocean has been used to infer movement of the Indian plate beneath a highly productive equatorial upwelling zone (Schmitz 1987). The derivation of barite from submarine hydrothermal sources along the East Pacific Rise (Church 1979), the Gorda Ridge (Koski et al. 1988), Guaymas Basin (Koski et al. 1985; Peter and Scott 1988), as well as borderland locations such as coastal southern California (Cortecci

and Longinelli 1972; Lonsdale 1979), has been documented.

*Barite in the Sedimentary Record.*—In view of the diverse origin of modern, deep sea barite, it is not surprising that a variety of hypotheses have been proposed for the genesis of ancient barite deposits. Bedded barite in Archean rocks has commonly been interpreted as having an evaporite precursor (Badham and Stanworth 1977; Lambert et al. 1978). In Phanerozoic rocks, bedded barite is most common in the lower to middle Paleozoic with the Devonian being particularly well represented.

The association of stratiform barite with sediment-hosted massive sulfide deposits is well established. Notable examples include the Devonian Meggan and Rammelsberg deposits in Germany (Krebs 1981; Hannak 1981), the Mississippian Red Dog deposit in the Brooks Range of Alaska (Moore et al. 1986), and numerous deposits of Cambrian to Devonian age in the Selwyn basin of the Yukon (MacIntyre 1982; Mako and Shanks 1984; Lydon et al. 1985). In all of these deposits, barite occurs as a gangue mineral and/or a distal component of the polymetallic (generally Pb-Zn sulfide) mineralization. The massive sulfide deposits are believed to be the result of submarine exhalative activity associated with faults in active rift basins. The association of the massive sulfides and barite with organic-rich shales is taken as evidence that deposition occurred in basins with restricted oceanic circulation. The occurrence of barite in the distal portions of the deposits is attributed to mixing of hydrothermal solutions at an oxic-anoxic water interface.

This generalized exhalative model of barite deposition has been suggested as a mechanism for the formation of bedded and/or nodular barite occurrences which have no known association with polymetallic sulfides. Examples include barite nodules in the Appalachians (Nuelle and Shelton 1986), some of the stratiform barites in the Selwyn basin (Lydon et al. 1985), and the Nevada barites (Poole 1988). A variation of this hypothesis envisions barite precipitation from episodic dewatering of thick basinal sediments (Howard and Hanor 1987). Evidence for this hypothesis includes elevated concentrations of barium in modern subsurface brines such as those in the Gulf of Mexico. Yet another hy-

pothesis envisions barite being deposited from reduced fluids expelled from submarine carbonate aquifers (Morrow et al. 1978).

An alternative genetic model of bedded barite formation has evolved from the well known association of barium with the oceanic biological cycle. Shawe et al. (1969) pointed out a possible connection between barium-bearing phytoplankton and the bedded cherts and barites of East Northumberland Canyon, Nevada. This hypothesis received additional support from a study of the organic geochemistry of the fatty acids found in the central Nevada and Arkansas bedded barites (Miller et al. 1977). This study suggested that these barite deposits were formed by biological processes under anoxic conditions on the ocean floor. A similar conclusion was reached by Clark (1988) to explain the genesis of nodular barite in the Appalachian basin.

*Major, Minor, and Rare Earth Element Methodology.*—Geochemistry is a very useful tool for studying the origin of modern and ancient deep sea sediments. The amounts and ratios of various major, minor, and rare elements have been used to determine the percentages of detrital, hydrothermal, biogenic, and hydrogenous (i.e., derived directly from the water column) materials in modern deep sea sediments (Dymond et al. 1973; Bostrom et al. 1973; Bonatti 1975; Dymond 1981). Similar elemental ratios have also been used in the study of ancient deep sea sediments (Bonatti et al. 1976; Barrett 1981; Crerar et al. 1982; Pinto-Auso and Harper 1985), with the assumption that certain elements are not strongly mobilized during diagenesis and sub-aerial emergence of the rocks.

Al, Ti, Fe, Mn, P, C, and Ba are the major elements examined in this study. Al and Ti in marine sediments are largely derived from weathering of continental material, whereas Fe and Mn are deposited by seafloor hydrothermal vents (Bonatti 1975; Dymond 1981). P and C are deposited in sediments by biological processes. Both organic and inorganic C occur in deep sea sediments. The latter occurs as calcite, small amounts of which were found in <5% of the samples in this study; therefore only organic C analyses are presented here. As mentioned above, Ba can have a hydrothermal, biogenic or more rarely, a detrital source. Ratios of these characteristic major elements can be useful in es-

tablishing the provenance of a sediment. For instance, the  $Al/(Al + Fe + Mn)$  ratio is considered a good method of examining hydrothermal vs. detrital input because it is insensitive to biogenic input.

Ni, Co, U, and Th are the minor elements considered in this study. All of these elements are scavenged from seawater onto sediment particles that have a surface charge. High concentrations of these elements therefore represent a significant hydrogenous (precipitated from ambient seawater) component in a given sediment. The hydrogenous component is normally important when all other inputs are minor and indicates very low sedimentation rates. Pure hydrogenous sediments typically have  $Fe = Mn = (10-20) \times (Co + Ni + Cu)$  (Bonatti 1975; Crerar et al. 1982). Hydrogenous deposits also may contain up to 500 ppm Th (Bonatti 1975). Hydrothermal sediments generally have low concentrations of Th because they are deposited rapidly and therefore are not exposed to seawater for prolonged times.

Rare earth elements (REE) in deep sea sediments have been used to infer both sediment sources and depositional environment (Fleet 1984). The behavior of Ce is of particular interest because it exists in both soluble Ce(III) and insoluble Ce(IV) oxidation states. REE concentrations in river water and coastal seawater closely resemble crustal REE values. Seawater from the open ocean has a pronounced negative Ce-anomaly due to coprecipitation of Ce(IV) with oxyhydroxides and oxides of Fe in the nearshore environment (Fleet 1984). Seawater near mid-ocean ridges is extremely depleted in Ce due to the scavenging of Ce(IV) by hydrothermally produced Fe- and Mn-oxides (Klinkhammer et al. 1983).

Typical shales retain the REE signatures of the crustal rocks from which they were derived (Gromet et al. 1984; Fleet 1984). Biogenically formed chalks, limestones, and phosphorites often carry a signal from the ambient seawater (Wright et al. 1987; Liu et al. 1988). This effect appears to be particularly true for slowly growing deep sea authigenic minerals such as apatite. High sedimentation rates can attenuate this process, however, by changing the time the authigenic minerals are exposed to seawater (Wright et al. 1987).

These observations have been applied to a variety of ancient sediments. The lack of a Ce-anomaly in cherts formed in marginal or semi-enclosed seas contrasts with the negative Ce-anomaly of cherts from the deep ocean (Shumizu and Masada 1977; Rangin et al. 1981; Murray et al. 1990). Exposure of fossil apatite to anoxic water appears to result in a slightly negative to positive Ce-anomaly due to the higher solubility of Ce(III) ion (Wright et al. 1987). The change from basinwide anoxia to oxic conditions in the Atlantic Ocean has been documented with Ce-anomalies in marine carbonates (Liu et al. 1988). Sediments deposited near a midocean spreading center have depleted Ce concentrations due to the scavenging effect of Mn- and Fe-oxides in the vicinity of the hydrothermal vents (Fleet 1983; Murray et al. 1990).

#### REGIONAL GEOLOGIC SETTING OF THE NEVADA BARITE DEPOSITS

Rocks of the Roberts Mountains allochthon were thrust faulted at least 100 km eastward during the Late Devonian-Early Mississippian Antler orogeny (Roberts et al. 1958; Smith and Ketner 1968). The allochthon crops out over a large portion of Nevada from the Idaho border in the north to the California border in the southwestern portion of the state (fig. 1).

Although assignment of specific formations to the Roberts Mountains allochthon is a point of contention among some geologists, most agree that the Valmy Formation (Ordovician), Vinini Formation (Ordovician), Woodruff Formation (Devonian), and Slaven Chert (Devonian) were all involved in the thrusting. The Valmy consists of black chert, graptolitic shale, and minor quartzite and basalt. The Vinini has a similar lithology, although the amount of quartzite and greenstone is higher in the Valmy than in the Vinini (Stewart 1980). The Valmy occurs in the central and western portion of the allochthon and is considered to have a marine affinity while the Vinini is present in the eastern portion of the allochthon and has a more continental affinity (Murchev et al. 1983). Paleogeographic reconstructions consider the two formations stratigraphic equivalents of one another (Stewart and Poole 1974).

Although both the Vinini and Valmy For-

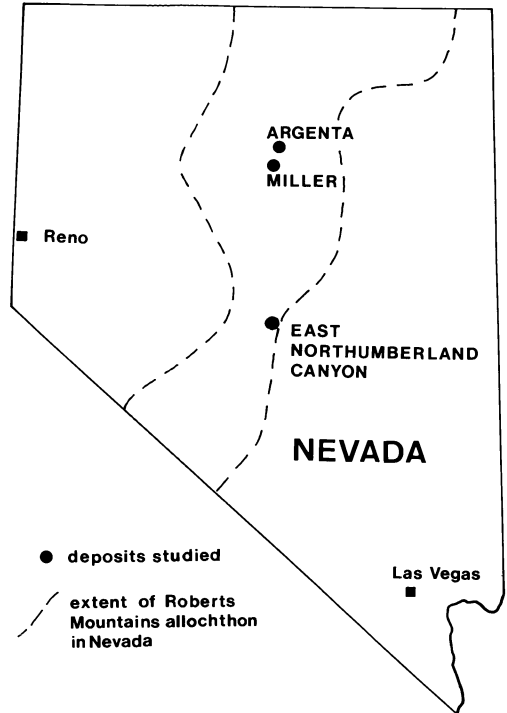


FIG. 1.—Location map of Nevada showing the outline of the Roberts Mountains allochthon and the bedded barite deposits studied in this paper.

mations contain fossils of Ordovician age, detailed mapping and sampling have yielded Devonian graptolites in rocks previously mapped as Valmy Formation (Stewart and McKee 1977), and a variety of Devonian fossils have been found in mismatched parts of the Vinini Formation of Elko County (Coats 1987). It is uncertain whether these rocks represent thrust slices of Devonian formations or are simply in depositional contact with the older Ordovician rocks.

The Devonian Woodruff Formation occurs in the central and eastern portions of the Roberts Mountains allochthon and consists primarily of black siliceous mudstone, siltstone, and chert with minor coarse siliciclastics, dolomite, and limestone. The Woodruff has higher concentrations of organic carbon and is interpreted to have been deposited on a continental shelf slope (Smith and Ketner 1975) or on a continental rise (Desborough et al. 1984).

The Devonian Slaven Chert outcrops extensively in the western portion of the allo-

chthon. The Slaven consists primarily of bedded chert with minor shale partings. Thick shale beds (up to 1 m) occur locally, as do very rare lenses of tan siltstone and limestone (Gilluly and Gates 1965). The micropaleontologic work of Wrucke and Jones (1978) demonstrates that the Slaven Chert includes some intercalated greenstone units.

The Slaven Chert and Woodruff Formation are considered correlative. The Slaven and Woodruff are believed to have been deposited in an inner arc-basic that existed from the Silurian through the Devonian (Poole et al. 1977).

Allochthonous rocks mapped as Vinini Formation or Slaven Chert host the vast majority of bedded barite deposits in Nevada (Papke 1984). In general, bedded barite deposits in the western portion of the allochthon occur in the Slaven, while those to the east occur in the Vinini.

Only those barite deposits hosted by rocks conclusively dated as Devonian were chosen for this study. Of these deposits, three were chosen for study on the basis of accessibility and degree of outcrop exposure. The Argenta and Miller barite deposits are located in the northern Shoshone Range, 14 and 5 km respectively, north of the type section of the Slaven Chert. The Famennian (Late Devonian) brachiopod *Dzieduszyckia* has been reported from various deposits in the northern Shoshone Range (Dube 1986; Poole 1988). The second group of deposits chosen for study are found in East Northumberland Canyon on the eastern flank of the Toquima Range in central Nevada (fig. 1). These deposits have been dated as Famennian on the basis of conodonts in a detrital limestone bed in the barite section as well as possible *Dzieduszyckia* fragments found in the barite (Poole and Sandberg 1975).

#### GEOLOGY OF THE NEVADA BARITE DEPOSITS

At the Miller, Argenta, and East Northumberland Canyon deposits, barite-bearing and nonbarite-bearing sections were examined in detail. At each deposit, efforts were made to locate stratigraphic sections not disrupted by faulting. The thickest measured section was 12 m, although in most localities, 6–7 m was the thickest, nonfaulted interval that could be located. The thickest measured barite bed was 5 m. At each measured sec-

tion, rocks were described and 10–20 gram samples were taken at 10 cm intervals. Chert, shale, barite, and minor amounts of siltstone and sandstone were the lithologies observed in this study. No volcanic rocks were seen in any measured sections of the Slaven Chert.

Morphology and concentration of barite in the Slaven Chert are varied. Economic deposits are typically in the form of massive sugary lenses with strike lengths of meters to tens of meters (fig. 2a, b). Subeconomic barite occurs as thin laminations, rosettes, and concretions in chert, shale, and siltstone (fig. 2c, d). Large, massive barite lenses are generally stratabound by the surrounding cherts. Thinner barite beds often show complex crosscutting structures and intergrown textures with the surrounding shales and cherts, indicating post-depositional remobilization of the barite. Lamination of the barite and chert occurs on scales as fine as 1 mm. Barite rosettes range in diameter from 2–30 mm and typically have a radiating, blade-like crystalline morphology.

Chert in the Slaven Chert occurs as irregular beds 1–5 cm thick and as nodules that pinch out over distances of 0.2–2 m. In general, chert in the barite-bearing sections has a more irregular morphology than chert in the nonbarite sections. Chert in the nonbarite sections is black gray to greenish white while chert in the barite-bearing sections is gray to black. The color difference reflects the amount of organic carbon in the cherts. All cherts are locally fractured and recemented by secondary silica.

Shale occurs as partings between the chert beds and as discrete intervals up to 1 m thick. The shale in barite-bearing sections is also darker than shale in nonbarite-bearing rocks.

Pyrite is a minor and very fine-grained component of all measured sections. The pyrite occurs in cherts and shales and more rarely in the bedded barites. Fe-oxides are common on fractured surfaces and chert bedding planes. In most mine benches, unfractured chert, barite, and shale beds are unaffected by supergene oxidation.

*Argenta deposit.*—The Argenta deposit is one of the five largest barite producers in Nevada. Open pit workings cover an area of 300 by 1000 m at the very northern end of the Shoshone Range (fig. 3a). Tertiary sediments and basaltic andesites crop out to east of the

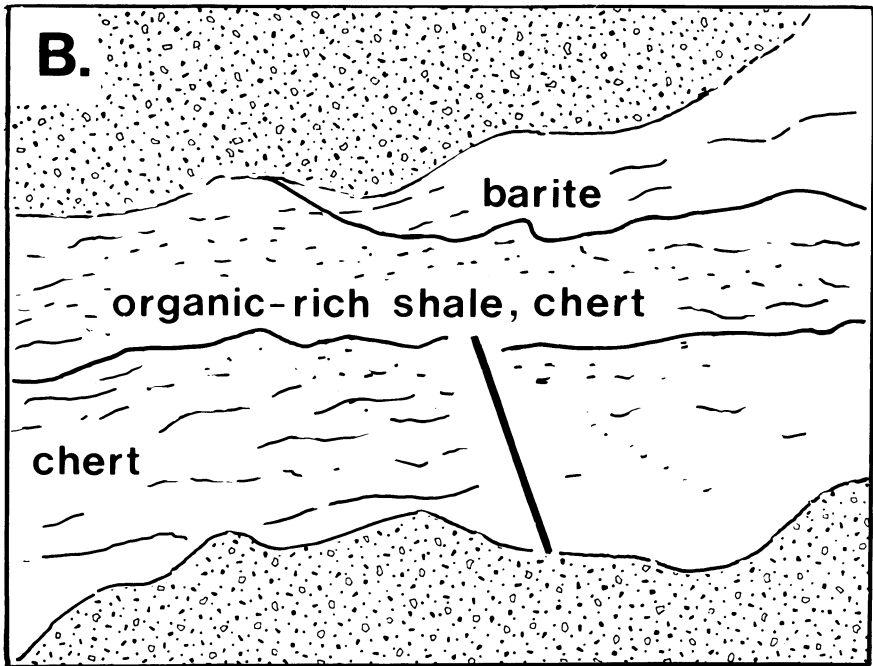
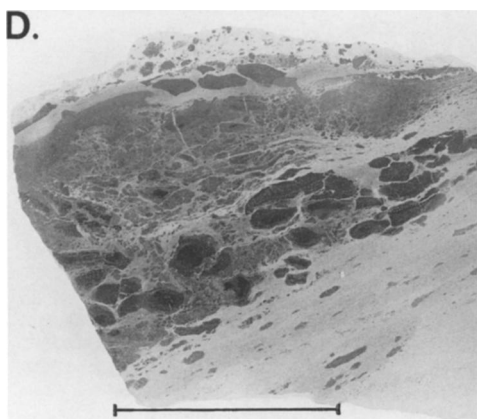
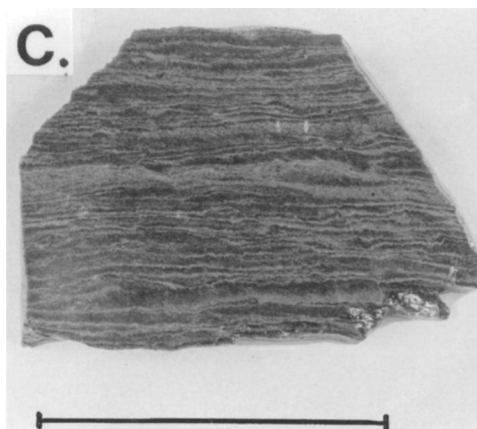


FIG. 2.—Photographs showing typical morphologies and textures of the bedded barite. (a) Exposure in the Argenta mine showing massive bedded barite and underlying organic-rich shales and cherts. Staff is 1.5 m. (b) Line drawing of (a). (c) Finely laminated barite-shale sequence, East Northumberland Canyon deposits. (d) Bedded chert with punky siltstone containing nodules of barite, East Northumberland Canyon deposits.



deposit, while the Valmy Formation is mapped to the west (Stewart and McKee 1977). The rocks are cut by numerous, low-angle faults. Folding is pervasive, although dips of individual beds are generally less than 45°.

Chert, barite, and minor shale constitute virtually the entire deposit. No siltstone, limestone, or greenstone was observed. The barite generally occurs as massive beds (up to 5 m thick), although locally there are minor spheroidal intergrowths with chert.

*Miller Deposit.*—The Miller deposit is located along the northwest flank of the Shoshone Range beneath a thin veneer of Quaternary alluvium. The mine is currently inactive, and the lower benches are flooded (fig. 3b). The deposit produced <1 million tons of barite from a pit 150 by 400 m wide. Folding and

faulting of the Slaven is very extensive along the exposed faces.

Lithologies in the Miller deposit are very similar to those of the Argenta deposit, although a greater abundance of organic-rich shale was observed locally. No limestone was observed in the Miller pit, although it has been reported in other descriptions of the deposit (Papke 1974, p. 86).

*East Northumberland Canyon Deposits.*—A variety of open pit mines, all of them currently inactive, are accessible on the north side of East Northumberland Canyon in the central Toquima Range. The East Northumberland Canyon deposits consist of five separate pits, which together have produced in excess of 1 million tons of barite (Papke 1984) (fig. 3c). In addition, several unmined, barite-bearing sections have been mapped on the south side of the canyon (Rye et al. 1978).

The Slaven Chert in the East Northumberland Canyon area is distinct from that exposed in the northern Shoshone Range. The East Northumberland Canyon (hereafter referred to as ENC) exposures contain a higher amount of siliciclastic sediment than the northern Shoshone Range (hereafter referred to as NSR) exposures. This siliciclastic sediment is a platy to massive, punky gray to orange siltstone, up to 5 m thick. In nonbarite-bearing sections, the punky siltstone often takes the form of flaggy, platy beds between the chert. The ENC exposures also contain abundant phosphatic nodules, which occur as grayish lensoidal concretions in black chert beds.

The ENC barite also has greater morphological variety than the NSR barite. Barite bed thickness ranges from 5 m down to millimeter-scale chert-barite laminations. Rosette barite is common as intergrowths in the chert and as discrete groups of radiating crystals in the massive siltstone. Concretionary barite also occurs as round to flattened spheroids in the siltstones.

#### GEOCHEMISTRY OF THE NEVADA BEDDED BARITE

At each of the Argenta, Miller, and East Northumberland Canyon deposits one well-exposed barite-bearing section was selected for detailed geochemical analysis. In addition, selected samples from six nonbarite-bearing sections were analyzed to provide a



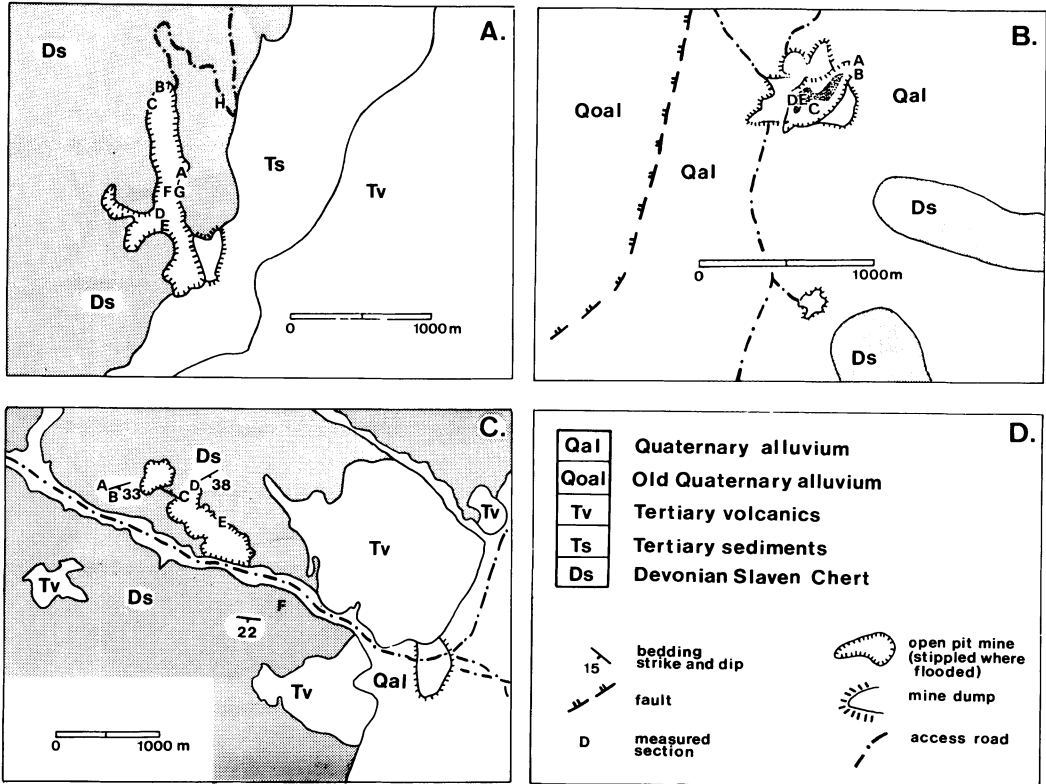


FIG. 3.—Simplified geologic maps of barite mines studied. (a) Argenta deposit (after Stewart and McKee 1977). Sections A, B, C, F, and G are barite-bearing and sections D, E, and H are nonbarite-bearing. (b) Miller deposit (after Stewart and McKee 1977). Sections A, B, and C are barite bearing and sections D, E are nonbarite-bearing. (c) East Northumberland Canyon deposits (after Rye et al. 1978). Sections C, D, E, and F are barite-bearing and sections A and B are nonbarite-bearing. (d) Map explanation.

geochemical baseline for the Slaven Chert at each locality.

A total of 95 samples (58 from barite-bearing sections, 37 from nonbarite-bearing sections) were analyzed. Each sample represents 10 cm of a measured section. Each 10–20 gram sample was split and ground to approximately 200 mesh. Organic carbon was determined with a LECO carbon analyzer. For samples that contained only minor barite, 500 mg of sample was progressively dissolved in hot HF, HClO<sub>4</sub>, and HCl. Samples that contained greater than 1% BaSO<sub>4</sub> were fused with LiBO<sub>2</sub> in graphite crucibles and then dissolved in 2:25 HNO<sub>3</sub>. The resulting solutions were analyzed by an inductively coupled plasma-optical emission spectrometer (ICP-OES) for Ti, Al, Fe, Mn, Ni, Co, P, and Ba. USGS standards AGV-1 and BCR-1 were run as internal checks. External checks were provided by XRF analysis of selected samples.

Elements with concentrations >1 wt % compared favorably with USGS standards and XRF analyses. ICP-OES results were somewhat below XRF results when elemental concentrations were <1 wt %. This may be attributable to matrix effects of Ba in the XRF analyses (Norrish and Hutton 1969).

All samples were dissolved and analyzed in duplicate. Reproducibility was generally 1–5% for Al, Fe, and P, 5–10% for Mn, Ba, and organic C, and 10–20% for Ti, Ni, and Co. Representative analyses from the measured sections are given in table 1. A complete list of all analyses can be found in Jewell (1989, Appendix C).

Rare earths of the cherts and shales associated with the bedded barites were determined by instrumental neutron activation analysis (INAA) Nuclear Activation Services, Ltd., Ann Arbor, Michigan. INAA was not attempted on the bedded barites due to compli-

TABLE 1  
ANALYTIC DATA OF SELECTED SLAVEN CHERT SAMPLES

Sample	Barite-bearing sections				Nonbarite-bearing sections		
	Arg-C -5.9	Mil-B -6.0	ENU-F -0.5	ENU-F -6.4	Arg-D -1.4	Mil-D -0.2	ENU-A -5.4
Al(%)	1.00	3.57	1.30	.30	2.58	5.29	4.13
Fe(%)	1.92	1.83	.47	.30	2.20	2.89	2.24
Ti(ppm)	380	1400	510	210	1280	2250	2100
Mn(ppm)	20	210	10		74	42	105
P(ppm)	2200	660	11800		450	340	578
Ba(%)	2.91	.29	.10	59.7	.17	.08	.15
Organic C(%)	.13	.81	2.22	.34	.08	.09	.84
Ni(ppm)	<5	13	50		42	17	136
Co(ppm)	<5	6	<5		8	5	13
La(ppm)	7.7	24.5	11.8		18.9	33.4	34.2
Ce(ppm)	14	41	7		27	56	59
Nd(ppm)	8	13	5		16	18	21

cations caused by Ba-133 in the procedure (Guichard et al. 1979).

*Major Elements.*—Al/(Al + Fe + Mn) is plotted against Ba concentrations for all samples analyzed in this study (fig. 4a). In general, Al/(Al + Fe + Mn) >0.5 is considered typical for pelagic sediments, while a ratio of <0.35 is considered indicative of significant hydrothermal input (Bostrom and Peterson 1969). Only two samples from the Nevada bedded barites have Al/(Al + Fe + Mn) <0.35, while the vast majority have Al/(Al + Fe + Mn) >0.5. This indicates that the detrital input to sediments that host the barite deposits is much greater than the hydrothermal input. The concentration of barium in NSR samples appears to have no particular correlation with the concentration of hydrothermal metals (fig. 4a), while the ENC samples show a slightly positive barium to metal correlation (fig. 4b). By contrast, samples from the Guaymas Basin and Gorda Ridge (both sediment-covered spreading centers with known massive sulfide occurrences) have locally high amounts of barite but Al/(Al + Fe + Mn) ratios generally <0.35 (fig. 4).

Mixing diagrams that use the elements Al, Mn, Fe, and Ti have been successfully used to show mixing ratios of hydrothermal and pelagic components in other ancient sediments (Barrett 1981; Pinto-Auso and Harper 1985). In general, hydrothermal sediments such as those from the Guaymas Basin and Gorda Ridge have extremely variable Fe contents (Fe/Ti 5–1000). Both the ENC and NSR

samples have a narrower Fe/Ti range (5–50). Considerable overlap exists in the Fe/Ti values of the ENC, NSR, Guaymas Basin, and Gorda Ridge samples (fig. 5a, b). Barite-bearing rocks have much more variable Fe/Ti ratios than nonbarite-bearing rocks.

Organic carbon analyses allow a clear distinction between barite- and nonbarite-bearing sections as well as differentiation between the ENC and NSR exposures of the Slaven Chert. ENC samples have organic carbon contents of 0.5–2.2 wt % while NSR samples never exceed 1.0 wt % (fig. 6). At both locations, barite-bearing sections have higher amounts of organic carbon than nonbarite bearing sections.

Phosphorous and organic carbon content of ENC and NSR samples have a positive correlation (fig. 7). Like organic carbon, phosphorous concentrations of barite-bearing samples are higher than that of nonbarite samples. ENC samples have very high phosphorous contents (up to 14% P<sub>2</sub>O<sub>5</sub>). The existence of Devonian phosphatic cherts in the central Toquima Range (including East Northumberland Canyon) has been noted previously by Coles and Snyder (1985) and Coles and Varga (1988). These authors consider the phosphatic rocks to result from coastal upwelling in a Tethyan-type ocean. The association of the bedded barite with this hypothesized upwelling is discussed in greater detail below.

*Minor Elements.*—Ni, Co, and Mn values for ENC and NSR samples plot within ranges

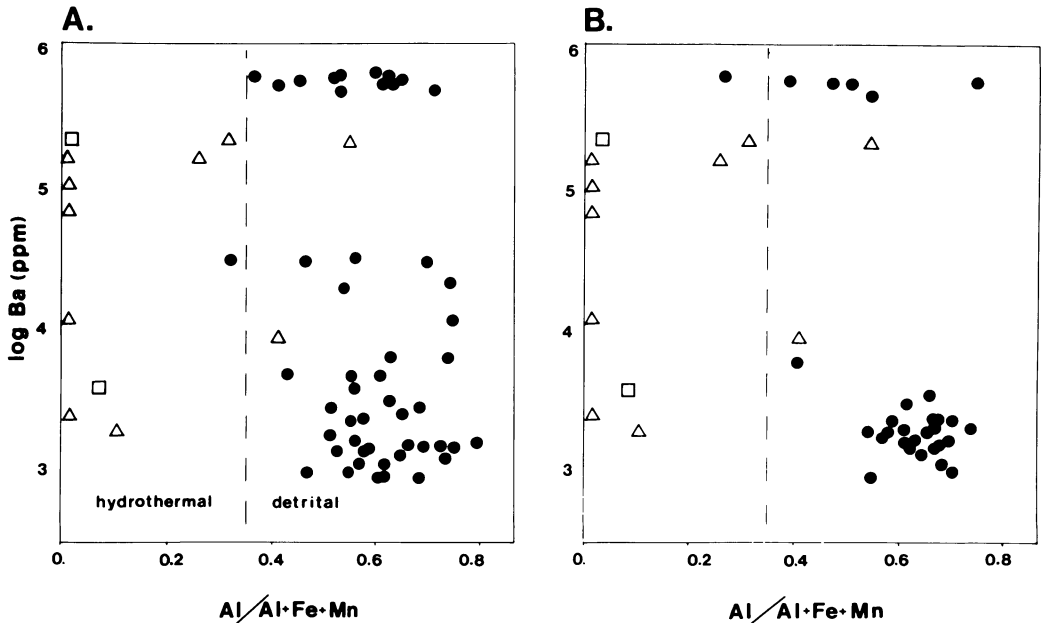


FIG. 4.—Plot of  $Al/(Al+Fe+Mn)$  metal ratios versus  $\log(Ba)$ . All concentrations are in ppm. Solid circles are data from the Slaven Chert, open triangles are data from the Guaymas Basin (Peter and Scott 1988) and open squares are data from the Gorda Ridge (Benninger and Koski 1987). (a) Northern Shoshone Range. (b) East Northumberland Canyon.

reported for various shale composites (Vine and Toutelot 1970; Turekian and Wedepohl 1961). Co concentration varies from 0 to 26 ppm at ENC, and from 0 to 21 ppm at NSR, while Ni varies from 0 to 250 ppm at ENC and 0 to 50 ppm at NSR. Mn concentrations are more variable, ranging from 10 to 100 ppm at ENC and 10 to 2000 ppm at NSR. The generally low values of Co and Ni in the Nevada barite province relative to Fe indicate that the hydrogenous component is quite small.

U concentration varies from 1.8 to 22 ppm and Th from 1.8 to 3.3 ppm. The concentrations of U and Th plot between the hydrothermal and pelagic sediment fields, as outlined by Bonatti (1975) for modern sediments (fig. 8).

**Rare Earth Elements.**—When normalized to the North American Shale Composite (NASC) (Gromet et al. 1984), the overall rare earth element (REE) pattern of the Slaven Chert samples are moderately but consistently depleted in Ce and enriched in Sm and Eu (fig. 9). Ce concentration is of particular interest due to its potential to predict both sediment provenance and redox state of the overlying water (Fleet 1984). In quantifying

the Ce-anomaly, we adopt the convention of Wright et al. (1987) whereby  $Ce^* = \log [3 Ce_n / (2La_n + Nd_n)]$ . With this convention the subscript “n” refers to NASC normalized concentrations. Positive  $Ce^*$  implies Ce-enrichment, and negative  $Ce^*$  implies Ce-depletion relative to the NASC.

A summary of computed  $Ce^*$  and total REE concentrations for the Slaven Chert samples in this study as well as those from other settings is given in table 2. Samples from nonbarite-bearing sections have a consistent, slightly negative  $Ce^*$  (–.034 to –.056 for ENC and –.030 to –.032 for NSR). These values are within the range of deep sea, pelagic sediment  $Ce^*$  values reported elsewhere (Wang et al. 1986; Murray et al. 1990). The slightly negative  $Ce^*$  appears to be caused by exposure to Ce-depleted seawater, although the effect appears to be very slight relative to the large negative  $Ce^*$  of seawater (de Baar et al. 1985).

$Ce^*$  of samples from barite-bearing sections are more variable than samples from nonbarite-bearing sections, although all have consistently negative  $Ce^*$  (–.155 to –.594 for ENC and –.008 to –.311 for NSR). The greater amount of Ce depletion is clearly re-

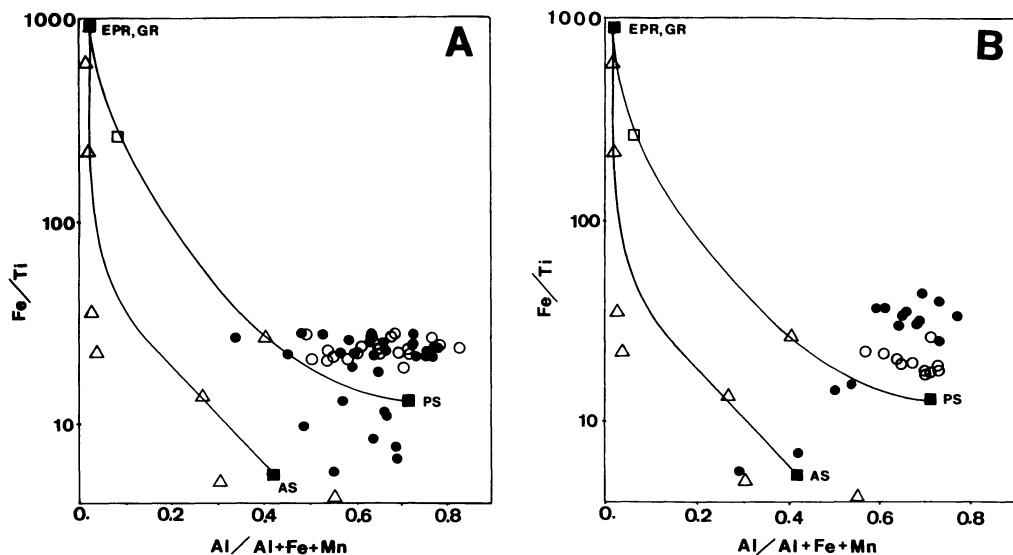


FIG. 5.—Plot of  $Al/(Al + Fe + Mn)$  metal ratios vs.  $Fe/Ti$ . (A) Northern Shoshone Range. (B) East Northumberland Canyon. These plots illustrate possible mixing relationships between metalliferous and detrital fractions of a given sediment. Plotted on both diagrams are average values for pelagic clays from the Atlantic and Pacific Oceans (AS and PS, respectively) and the East Pacific Rise sediments (EPR) (Barrett 1981) and Gorda Ridge sediments (Benninger and Koski 1987). Open circles are from nonbarite-bearing sections of the Slaven Chert, closed circles are from barite-bearing sections of the Slaven Chert, open triangles are data from the Guaymas Basin (Peter and Scott 1988) and open squares are data from the Gorda Ridge (Benninger and Koski 1987).

lated to the higher amount of phosphorous in these samples (fig. 10). As mentioned previously, authigenic minerals such as apatite are very effective at scavenging REE from seawater. The strongly negative  $Ce^*$  in phosphorous-rich samples would therefore be a reflection of  $Ce$ -depleted seawater (table 2).

The possibility that the  $Ce^*$  of apatite can be used to record the paleoredox conditions of seawater has been explored by a number of investigators. Using fish debris from various modern marine settings, Wright et al. (1987) suggest that  $Ce^*$  of approximately  $-0.10$  marks the boundary between oxic and anoxic settings. Although caution is expressed by McArthur and Walsh (1984) and Coles and Varga (1988) about the role of diagenesis and weathering, this threshold value for  $Ce^*$  seems to be in general agreement with other geological and geochemical criteria of anoxia (Elderfield and Pagett 1986; Wright et al. 1987; Coles and Varga 1988). Using the criteria of Wright et al. (1987), the phosphate-rich Slaven Chert samples appear to have been deposited in oxygenated seawater.

In a detailed REE study of cherts and

shales from the Mesozoic Franciscan assemblage of northern California, Murray et al. (1990) show that sediments deposited within 500 km of an oceanic spreading ridge have a large, negative  $Ce^*$  ( $-0.5$  to  $-1.5$ ) and suggest that the large, negative  $Ce^*$  is the result of exposure to seawater whose  $Ce$  has been effectively scavenged by hydrothermally produced  $Mn$ - and  $Fe$ -oxides. Similar results are reported by Fleet (1984) and Ruhlin and Owen (1986). The lack of a  $Ce^*$  in this range for the Slaven Chert samples provides further evidence that hydrothermal processes did not contribute significantly to the formation of these sediments.

It is noteworthy that  $Ce^*$  values obtained from Devonian phosphatic cherts in the Roberts Mountains allochthon exposed to the north of East Northumberland Canyon (Coles and Varga 1988) have a slightly negative  $Ce^*$  ( $-0.071$ ). The association of phosphorites with a slightly negative  $Ce^*$  is clearly different from the ENC samples in this study (fig. 10). A possible interpretation is that the rocks analyzed by Coles and Varga were deposited in anoxic or disaerobic water, which would have a slightly negative  $Ce^*$ .

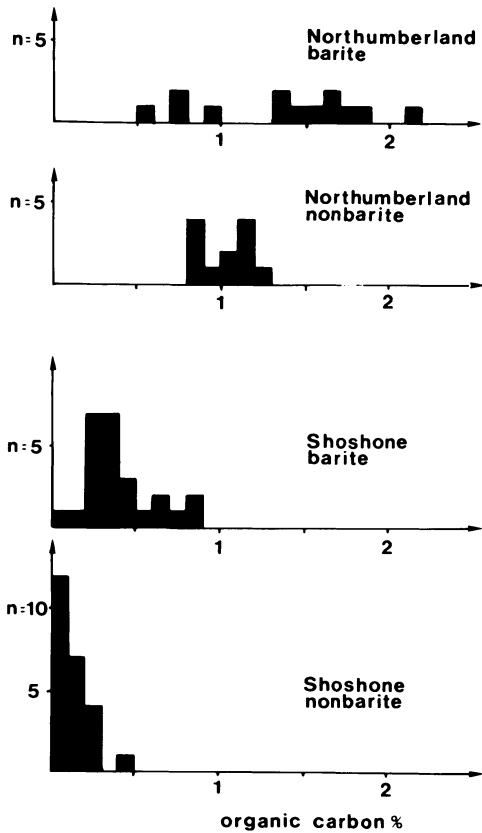


FIG. 6.—Histogram of organic carbon analyses of cherts and shales from the Northern Shoshone Range and East Northumberland Canyon deposits for both barite-bearing and nonbarite-bearing sections.

*Chemical Stratigraphy.*—Plots of individual measured sections allow detailed comparisons of the geochemical characteristics of massive barite beds and adjacent nonbarite-bearing beds. Examination of East Northumberland Canyon Section F (fig. 3c) is particularly enlightening because it is one of the thickest sections measured in this study (11.0 m) and it contains a single, massive barite lens. The Slaven Chert beneath the lens is enriched in phosphorous and organic carbon relative to overlying rock (fig. 11). Furthermore, barium concentrations below the lens appear to be somewhat higher than those above the lens.

#### GENESIS OF THE NEVADA BEDDED BARITE

*Models of Barite Genesis.*—Previous theories of bedded barite genesis can be roughly

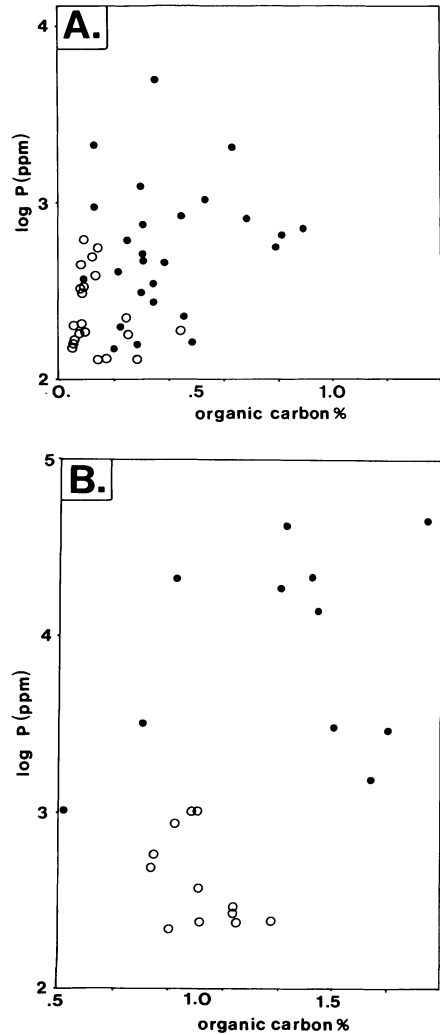


FIG. 7.—Organic carbon (weight percent) versus log(P) (ppm) of cherts and shales from the Nevada barite province. Open circles are samples from nonbarite-bearing sections and closed circles are from barite-bearing sections. (a) Northern Shoshone Range. (b) East Northumberland Canyon.

divided into the submarine exhalative theory (Morrow et al. 1978; Lyndon et al. 1985; Nuelle and Shelton 1986; Howard and Hanor 1987; Poole 1988) and biogenic theory (Shaw et al. 1969; Miller et al. 1977; Clark 1988). Examination of the analytic data presented above within the context of the regional geology of central Nevada and current oceanographic knowledge of the barium cycle allows a reasonably consistent genetic model of the central Nevada barite province to be derived.

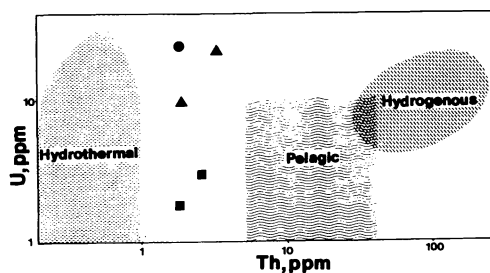


FIG. 8.—Th-U plot of central Nevada bedded barite samples. Squares are from the Northern Shoshone Range, triangles are from East Northumberland Canyon, and the circle is Cole and Varga's (1988) data from Devonian rocks to the north of East Northumberland Canyon. Also shown are typical fields for hydrothermal, pelagic, and hydrogenous sediments (Bonatti et al. 1976).

Geochemical evidence from both the barite and surrounding cherts and shales tends to favor the biogenic model of Nevada barite genesis. The bedded barites and nonbarite-bearing rocks have only minor amounts of the transition metals (e.g., Fe and Mn) generally associated with hydrothermal exhalative activity, and ratios of  $Al/(Al + Fe + Mn)$  indicate that the detrital sediment component predominates over the hydrothermal component. Further evidence of a biogenic origin is that barite-bearing sections contain significantly higher amounts of phosphorous and organic carbon than nonbarite-bearing sections. Elevated concentrations of these two elements is typically the result of high biological productivity.

Significant geological and geochemical dis-

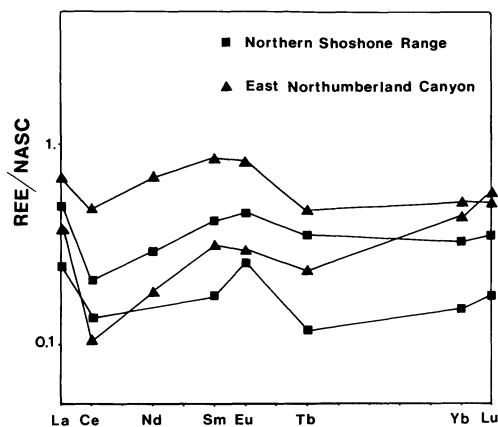


FIG. 9.—Rare earth element patterns for central Nevada bedded barite samples normalized to the North American Shale Composite (NASC) of Gromet et al. (1984).

tinctions can be made between the Northern Shoshone Range (NSR) deposits and the East Northumberland Canyon (ENC) deposits. ENC sections have more clastic sediment, organic carbon, phosphorous, as well as variable Ce-anomalies. These data suggest that the ENC sections were closer to a landmass than the NSR sections and that biological activity was particularly vigorous in the ENC area. This view is corroborated by the work of Coles and Snyder (1985) and Coles and Varga (1988) on rocks of the Roberts Mountains allochthon immediately north of East Northumberland Canyon. There, a paleoupwelling system adjacent to a landmass at  $<50^\circ$  latitude has been hypothesized.

TABLE 2

CERIUM ANOMALIES FROM THE SLAVEN CHERT AND SELECTED SETTINGS OF THE MODERN AND ANCIENT OCEAN

Location	Ce*	Number of analyses
East Northumberland Canyon (nonbarite sections)	-.034 to -.056	3
East Northumberland Canyon (barite sections)	-.155 to -.593	5
Northern Shoshone (nonbarite sections)	-.030 to -.032	2
Northern Shoshone (barite sections)	-.008 to -.311	6
Peru margin fish debris <sup>a</sup>	-.10 to -.50	7
Guaymas basin fish <sup>a</sup> debris	-.10 to .10	14
East Pacific rise sediments within 500 km of rise crest <sup>b</sup>	-.80 to -1.55	16

<sup>a</sup> Wright et al. 1987.

<sup>b</sup> Ruhlin and Owen 1986.

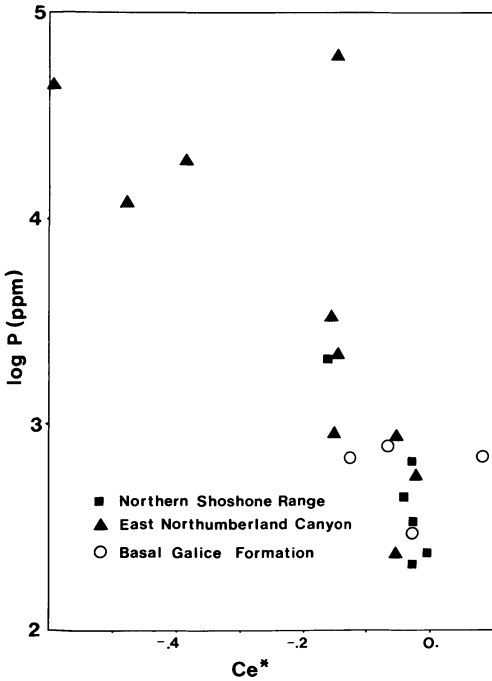


FIG. 10.—Cerium anomaly [ $Ce^* = \log 3Ce_n / (2La_n + Nd_n)$ ] (Wright et al. 1987) plotted against  $\log(P)$  concentration (ppm). The diagram shows that cerium depletion seems to be related to the amount of phosphorous in the rocks.

A modification of the biologic model for bedded barite formation proposed by Shawe et al. (1969) and others is hereby proposed for the central Nevada barites. In this model, a vigorous upwelling system similar to that envisioned by Coles and Varga (1988) existed over deep water adjacent to the Cordillera of the western United States. High biological productivity caused ocean water beneath the photic zone to become sulfidic. In this scenario, biologically produced barite settled into  $H_2S$ -rich water, which was undersaturated with respect to barite because of sulfate reduction. The barite particles produced in the photic zone were dissolved in the anoxic water. The lack of sulfate in deoxygenated waters allowed substantial quantities of barium ion to accumulate. At any point where the barium-rich water became oxygenated, barite saturation was achieved.

*Comparison of Modern and Devonian Upwelling Zones.*—Modern coastal upwelling zones occur along the eastern edges of ocean basins where equatorward winds cause the

offshore transport of surface water (Ekman transport) and the onshore transport of nutrient-rich deep water (fig. 12a). The upwelling of nutrient-rich water promotes high surface productivity. Organic matter sinking out of the photic zone consumes  $O_2$  and  $NO_3$ . The resulting "oxygen minimum zone" impinges on the continental shelf and slope between depths of 100 and 1000 m. The bottom currents in coastal upwelling settings are typically poleward (Smith 1981) (fig. 12a).

The scenario presented here for the Devonian ocean differs somewhat from modern upwelling zones such as the Peru-Chile continental margin. One of the primary differences is the manner in which sinking organic matter is oxidized. In the marine environment, organic carbon consumes oxidants in the order:  $O_2 \rightarrow NO_3 \rightarrow Mn(IV) \rightarrow Fe(III) \rightarrow SO_4$ . Since the amount of dissolved  $Mn(IV)$  and  $Fe(III)$  in the ocean is minimal, the primary oxidants are  $O_2$ ,  $NO_3$ , and  $SO_4$ . The free energy of  $O_2$  consumption and  $NO_3$  reduction are approximately equal but nearly five times that of  $SO_4$  reduction (Berner 1980, table 4.4). Thus in modern marine settings denitrification commences where  $O_2$  is low, but measurable (e.g., Cline and Richards 1972).  $SO_4$  reduction is rarely observed in modern upwelling zones and only occurs where  $O_2$  and  $NO_3$  are both absent (Dugdale et al. 1977).

Geological evidence suggests that the amount of oxygen in the early and mid-Paleozoic ocean may have been fundamentally different than the modern ocean. Field studies (primarily the abundance of black shales in relatively shallow marine settings) indicate that disaerobic or anoxic conditions were an oceanwide phenomenon during various periods of Paleozoic time (including the Late Devonian) (Berry and Wilder 1978). If a coastal upwelling system and associated high surface productivity developed in this type of ocean, the oxidants available to consume sinking organic matter would primarily have been  $NO_3$  and  $SO_4$  rather than  $O_2$  and  $NO_3$  as in the modern ocean. Under these conditions,  $SO_4$  reduction in the Devonian ocean would have been much more common than it is today (fig. 12b). As in the modern ocean, the beginning of sulfate reduction and  $H_2S$  production would begin when  $O_2$  and  $NO_3$  were totally exhausted. Barite precipitation would occur at this  $O_2/H_2S$  transition. Seawa-

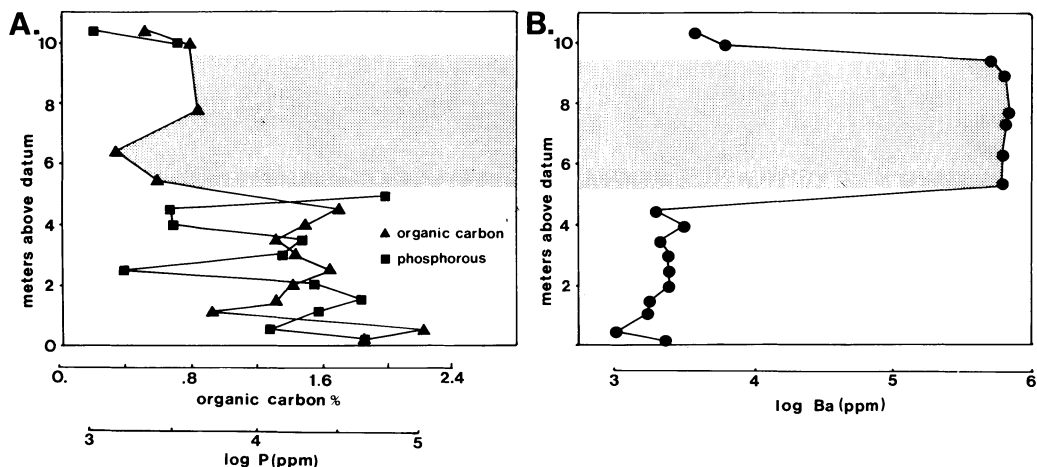


FIG. 11.—Chemical stratigraphy for Section F, East Northumberland Canyon deposit showing the relationship between organic carbon, phosphorous, and barium. Note the elevated concentrations of organic carbon and phosphorous below the massive barite bed relative to concentrations above the barite bed.

ter in the barite deposition zone would probably have oxygen in small but measurable amounts. The expected Ce-anomalies from this environment would be variable but slightly negative (table 2).

Claypool et al. (1980) have noted that some Late Devonian (Frasian to Famennian) evaporite deposits in North America are characterized by  $\delta^{34}\text{S}$  values much higher (up to +34‰) than  $\delta^{34}\text{S}$  from the rest of the world (approximately +24‰). The locally high  $\delta^{34}\text{S}$  values are attributed to the gradual ventilation of a deep anoxic or disaerobic ocean. These anoxic waters would be expected to have elevated  $\delta^{34}\text{S}$  concentrations due to fixation of lighter sulfur in the Late Devonian deep sea sediments. The progressive "leakage" of the  $\delta^{34}\text{S}$ -rich waters through upwelling zones adjacent to the North American coast would account for the anomalously high North American evaporite  $\delta^{34}\text{S}$  values. This hypothesis is consistent with the variable sulfur isotope values reported for the East Northumberland Canyon barites (Rye et al. 1978), as well as the mode of barite genesis proposed here.

**Barite Sedimentation Rates.**—Surface productivity in present day upwelling areas such as the coast of Peru can reach  $1000 \text{ g C m}^{-2}/\text{yr}$  (Walsh 1975). Analysis of sediment trap material from the Pacific shows Ba:C (organic) ratios of approximately 1:4000 (by weight) (Dehairs et al. 1980). If biogenic bar-

ite were being produced in an upwelling zone, vertical Ba flux could be as high as  $0.25 \text{ g Ba m}^{-2}/\text{yr}$ . Barite precipitation at the  $\text{O}_2\text{-H}_2\text{S}$  interface would be enhanced by the fact that this interface would be relatively narrow (on the order of kilometers) relative to the overall width of the upwelling zone (on the order of hundreds of kilometers in modern settings such as the Peru-Chile margin). Assuming a steady state process whereby barite particle flux into the anoxic zone was approximately balanced by barite precipitation at the  $\text{O}_2\text{-H}_2\text{S}$  interface (fig. 12b), barite accumulation could be on the order of  $25 \text{ g Ba m}^{-2}/\text{yr}$  (approximately  $5 \text{ mm}/1000 \text{ yr}$ ). This sedimentation rate is within the range proposed for bedded cherts from various periods in the geologic record (Jenkyns and Winterer 1982).

The model of barite deposition outlined above implies intimate mixing of baritic sediment with the cherts and shales rather than formation of discrete, massive barite beds such as those observed in the field. The lens-like nature of the bedded barite might be due to several factors: (1) rapid fluctuation of the  $\text{O}_2\text{-H}_2\text{S}$  interface in the upwelling zone, (2) deposition of the dense barite in localized bathymetric depressions, or (3) post depositional thickening of the barite by diagenetic processes. This latter process has been clearly documented by Papke (1984) as well as being observed in this study.

**Depth of Barite Deposition.**—The im-



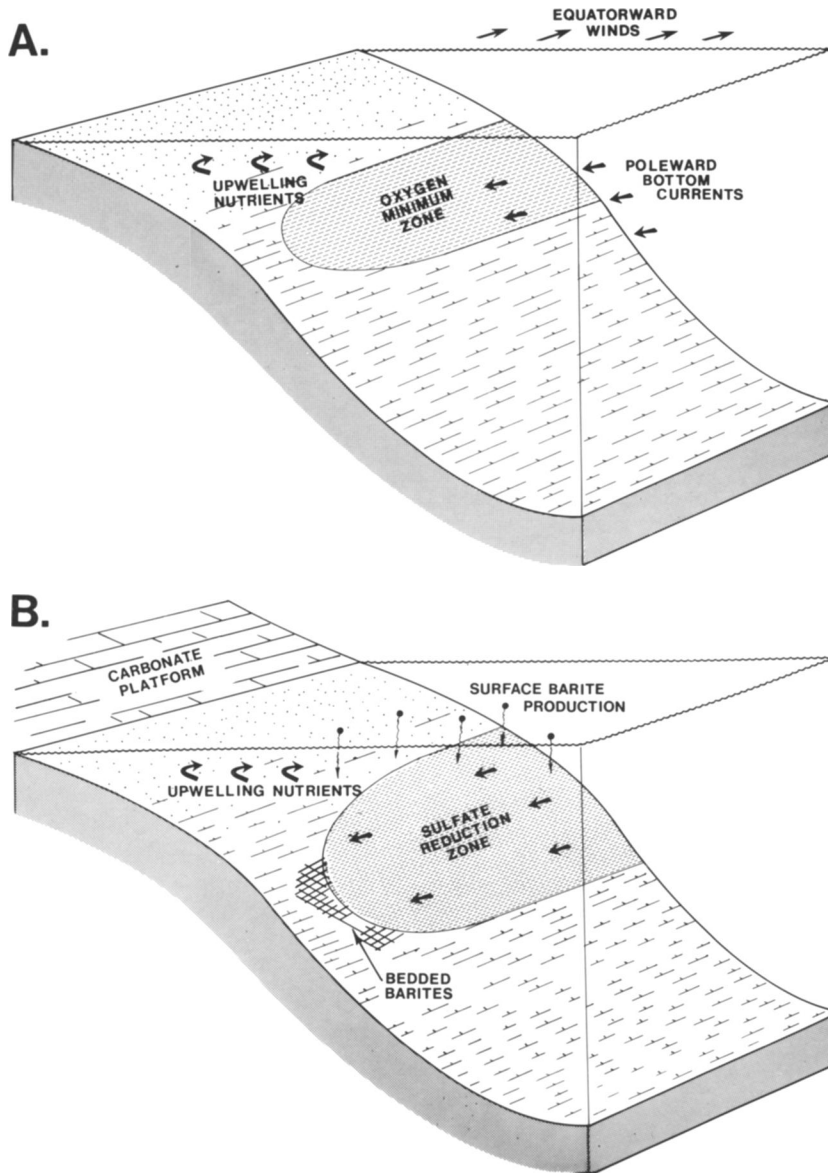


FIG. 12.—Diagrammatic representation of modern and ancient upwelling zones and their relationship to bedded barite formation. (a) Modern upwelling in which equatorward winds induce upwelling of nutrient-rich water. Bottom currents are poleward. (b) Hypothesized Devonian upwelling zone. Disaerobic or anoxic deep ocean causes water to be sulfidic below the photic zone. Biogenically produced barite particles settle into the  $\text{H}_2\text{S}$ -rich water. Bottom currents move the barium-rich water poleward. Barite is deposited at the  $\text{O}_2$ - $\text{H}_2\text{S}$  boundary due to the interaction of barium-rich water with sulfate-bearing seawater.

pingement of oxygen-minimum zones on continental rises in the modern ocean generally occurs between 100 and 1000 m depth. The deposition of most radiolarian cherts is typically considered to have occurred at water depths greater than 1000 m (Jenkyns and

Winterer 1982). However, some modern areas of vigorous upwelling (e.g., the Gulf of California) have radiolarites and diatoms accumulations in excess of 50% of the total sediment volume at water depths of less than 500 m (Calvert 1966). Also, as pointed out

by Coles and Varaga (1988), the predominant source of sediment for the Roberts Mountains allochthon was shelf carbonates to the east, so the amount of siliciclastic sediment relative to biogenic sediment was probably small. If this were true, significant amounts of bedded chert might accumulate at relatively shallow depths. Since field studies in modern upwelling areas show that bottom currents tend to move poleward, barite deposition would be expected on the lateral edges of the anoxic water zone.

#### CONCLUSIONS

The bedded barites in the Devonian Slaven Chert of central Nevada are associated with shales, cherts, and small amounts of siltstones of the Roberts Mountains allochthon. The two bedded barite areas examined in this study—the northern Shoshone Range (NSR) and East Northumberland Canyon (ENC)—have two distinctive depositional settings. The ENC locality has higher concentrations of siliciclastic sediment, phosphorous, and organic carbon than the NSR locality. The ENC deposits appear to have been formed somewhat closer to a continental sediment source than the NSR sediments in an area where biological productivity was relatively high. Neither the ENC or NSR barites are associated with volcanic rocks or mineralized breccias which might suggest the presence of a seafloor hydrothermal system.

Major and minor element concentrations in rocks associated with the bedded barites suggest that hydrothermal input to the sediments was much less than detrital input.  $Al/(Al + Fe + Mn)$  values are generally  $>0.5$ , a commonly accepted lower limit for sediment dominated by detrital input.  $Fe/Ti$  values also indicate that hydrothermal input was low relative to detrital input. At both ENC and NSR localities phosphorous and organic carbon concentrations of barite-bearing sections are higher than nonbarite-bearing sections, suggesting that biological activity was relatively high when the barite was being deposited. REE data shows consistently negative Ce-anomalies, suggesting that these rocks were exposed to oxygenated seawater.

A model consistent with available geological and geochemical data envisions the barite being deposited in sediments near the  $O_2-H_2S$

interface of an anoxic paleoupwelling zone. Barite fixed by biological activity in the photic zone would be fluxed to the underlying anoxic waters allowing the development of elevated barium concentrations. The large areal extent of the anoxic water zone relative to the  $O_2-H_2S$  interface would effectively concentrate the barite in narrow zones of deposition.

The coastal upwelling model of barite formation fits well with recently proposed paleogeographic reconstructions of the Roberts Mountains allochthon, as well as suggesting additional avenues of research. Coles and Snyder (1985) and Coles and Varga (1988) have suggested that the Slaven Chert was deposited beneath coastal upwelling systems at  $<50^\circ$  latitude. Interestingly, the upper Devonian phosphatic cherts analyzed by Coles and Varga have a slightly negative Ce-anomaly, elevated phosphate concentrations, and no reported bedded barite. These characteristics are consistent with deposition beneath the anoxic portion of the coastal upwelling system proposed in this study (fig. 12). These observations suggest that careful mapping of barite occurrences, phosphate concentrations, and Ce-geochemistry may be an effective tool in deciphering the paleobathymetry and paleogeography of these very curious sediments as well as other formations in the North American Cordillera.

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