A geologic membrane-microbial metabolism mechanism for the origin of the sedimentary copper deposits in the Pastura district, Guadalupe County, New Mexico

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A GEOLOGIC MEMBRANE—MICROBIAL METABOLISM MECHANISM FOR THE ORIGIN OF THE SEDIMENTARY COPPER DEPOSITS IN THE PASTURA DISTRICT, GUADALUPE COUNTY, NEW MEXICO

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Abstract.—Examination of copper deposits in Pastura district shows that mineralization occurred at the sand/shale interface. Mineralization was greatest adjacent to the thinnest shales and decreased with increasing shale thickness, becoming non-existent adjacent to the thickest shales. This pattern of mineralization is consistent with geologic membrane effects that can occur in shales and clays in the subsurface. We propose a conceptual model invoking solute-sieving effects to help explain the observed mineralization in the copper deposits in the Pastura district. We suspect that the role of the membrane-functioning shales was to concentrate the copper and the dissolved nutrients necessary for metabolic-functioning of sulfate reducing bacteria in "layers of increased solute concentration," usually called the concentration polarization layer (CPL), adjacent to the shales. The sulfate-reducing bacteria, as a part of their metabolic process, produce H_2S, which precipitated the copper sulfides. Experimental studies have demonstrated that the CPL can range from several to more than 100 times that of background concentrations within the aquifer. Flux magnitude through shale is inversely proportional to its thickness and strongly affects CPL development. For any given solute, there is a threshold flux value that must be exceeded before rejected solute becomes unable to effectively back diffuse into the reservoir. Therefore, thick shales (with correspondingly low flux rates) typically do not form a CPL. This physical fact corresponds with the field observation that the sands adjacent to the thicker shales in the Pastura district are not mineralized. Our model explains why copper mineralization is localized in proximity to thin shale units and is not ubiquitous in the host rock.

INTRODUCTION

Becker (1892) appears to be the first to suggest the possibility of the natural concentration of metals by dialysis (membrane processes). A later paper by Brown (1971) also briefly suggested the possibility that sedimentary copper deposits may be formed by salt-sieving processes. Whitworth and DeRosa (1997) performed a series of clay membrane experiments in which they passed undersaturated copper carbonate, copper chloride, cobalt chloride, and lead chloride solutions through clay membranes. In each case, the solutions became sufficiently concentrated due to retardation of solute by the membrane to precipitate the mineral salts. These experiments offer solid experimental evidence that metals can be concentrated by geologic membrane-functioning materials.

The purpose of this paper is to suggest a geologic membrane-related mechanism for the origin of the copper deposits in the Pastura district, using field observations of copper mineral occurrence and stratigraphic unit thickness as a basis for our study. These field observations are 1) copper mineralization is always most extensive in those portions of sandstone adjacent to shale units, 2) sandstones adjacent to the thinnest shales exhibit greater mineralization, and 3) sandstones adjacent to the thickest shales contain only a trace or lack mineralization. Any model proposed to explain the distribution of copper mineralization in these deposits should also be able to explain the copper sulfide precipitation mechanism and, very importantly, why that mineralization is restricted instead of extending uniformly throughout the more permeable and laterally continuous sandstones.

Several sulfide precipitation mechanisms for sandstone-hosted copper occurrences have been proposed. Kirkham (1989) suggests that sulfide precipitation may be engendered by the mixing of groundwaters and ore-carrying brines. Garven and Freeze (1984) pointed out, however, that conditions which could lead to the mixing of two different fluids in the subsurface are rare. Eugster (1989) suggested that sulfide precipitation occurs at oxidation/reduction fronts within the strata. However, LaPointe (1989) points out that certain deposits have redox haloes surrounding them, which suggests the redox conditions may be related to mineralization, rather than the cause of mineralization. Most genetic models of sedimentary copper deposits, including ours, postulate that sulfide was produced as a product of bacterial reduction of sulfate (Hoy and Ohmoto, 1989). Our model explains why the postulated bacteriological-initiated redox conditions necessary for sulfide precipitation were confined to the locations at which mineralization occurs in the Pastura district.

GEOLOGY OF THE DEPOSITS

Pastura District

The Pastura district is located in east-central New Mexico southwest of Santa Rosa (Fig. 1), and hosts mineralization in two different formations. The Pintada mine exploited copper mineralization from the Permian-age Grayburg-Queen Formation. The Guadalupe mine (also known as the Stauber mine) is hosted by the Triassic-age Santa Rosa Formation (Anderson, 1957). The beds at both deposits are relatively flat-lying and dip angles do not exceed 4°, although both deposits are found in structural depressions of uncertain origin; these structures appear to be associated with mineralization (McLemore and North, 1985). Previous studies concerning the geology of the district (Kelly, 1972) and nature of mineralization in are provided by Soulé (1956), Holmquist (1947), Sandusky and Kaufman (1972), and LaPointe (1974, 1976, 1979).

Pintada Mine

The Grayburg-Queen Formation hosts all of the mineralization in the Pintada mine (Fig. 1). The stratigraphic relationship of

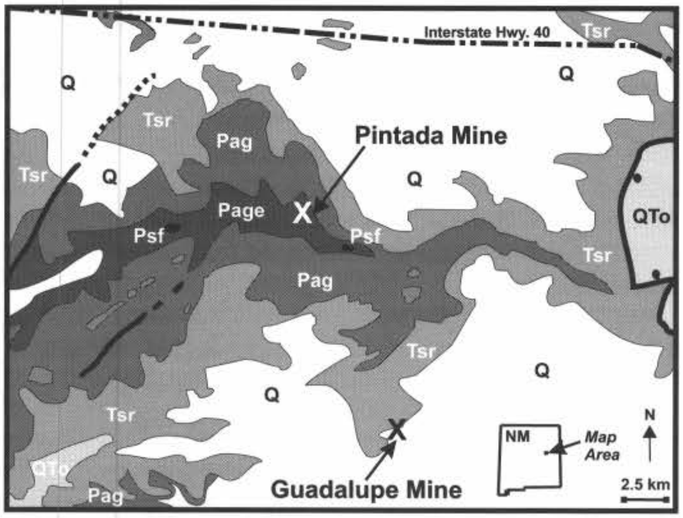

FIGURE 1. Location and generalized geologic map of the Pastura District. Symbols: Q – surficial deposits, QTo – older alluvium, Tsr – Santa Rosa Formation, Pag – upper Grayburg-Queen Formation, Page – lower Grayburg-Queen Formation, Psf – San Andres Formation. Map modified from Kelly, 1972.

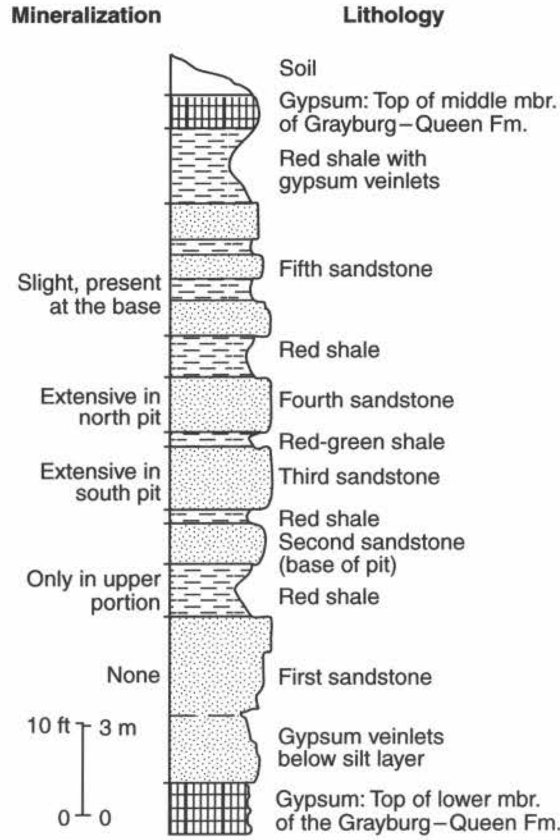

FIGURE 2. Stratigraphic column of the middle member, "lower sandstone unit," of the Grayburg-Queen Formation at the Pintada Mine in the Pastura District, New Mexico.

the basal contact of the Grayburg-Queen Formation and the San Andres Limestone (Permian) is obscure in the mine area although Kelly (1972) suggested a minor disconformity is present. The Santa Rosa Sandstone disconformably overlies the Grayburg-Queen Formation. Previous workers have divided the Grayburg-Queen Formation into three distinct units (Sandusky and Kaufman, 1972). The lower "gypsiferous" unit consists of massive gypsum which grades upward into the "lower sandstone" unit which hosts the mineralization. The "lower sandstone" consists of five separate, light gray to medium blue gray, fine to very fine-grained sandstone units separated from each other by thin green to red shale/siltstone interbeds (Fig. 2). The "upper sandstone", which contains no mineralization, is composed of fine grained, red-brown, thin bedded sandstones interbedded with thin layers of red-brown siltstone, mudstone, and shale. The contact between the two sandstone units is marked by a 0.3 meter gypsum layer at the top of the "lower sandstone" (Sandusky and Kaufman, 1972).

Mineralization at the Pintada mine is confined to the fine-grained quartz arenite units of the "lower sandstone". Chalcocite is the dominant primary sulfide mineral. Pyrite is present in small amounts and is irregularly distributed. Malachite and azurite are present and are commonly thought to have formed from *in situ* chalcocite oxidation due to subaerial exposure. Secondary carbonate minerals are found mainly on fractures, shale contacts and on surfaces of recently mined exposures although some appear to occupy original porosity. Organic material (hydrocarbon?) is found as wispy disseminations in some of the sandstones; importantly, the organic matter is not always mineralized.

Copper is most concentrated at the contact of the sandstones and the confining shale/siltstone units (Fig. 3.). At these contacts, mineralization is parallel to layering and can completely fill pores. Removed from the sandstone-shale contacts, the sandstone layers are characterized by wispy to disseminated mineralization, with the wispy mineralization apparently following primary bedding planes. Minor copper mineralization is observed in the silty units which separating the sandstones yet is absent in the clay-rich shales.

The amount of mineralization varies along the strike of the units as noted in the pit face (Fig 4). In the northern portion of this pit, mineralization is most well developed in the fourth sandstone unit (refer to Fig. 2). In the southern portion, the third sandstone is more intensely mineralized. The grade and thickness of copper mineralization in each sandstone unit also correlates inversely to the thickness of the bounding shale/siltstone such that copper grade and thickness are greater where confining shales are thinnest.

Guadalupe (Stauber) Mine

The Guadalupe mine was the largest copper producer in northeastern New Mexico (Anderson, 1957). Copper mineralization is confined to the lower member of the Santa Rosa Sandstone, which rests on an erosional unconformity on the Grayburg-Queen Formation (Kelly, 1972) in the mine area. In the vicinity of the mine, no other rocks cover the Santa Rosa Sandstone, which is also the case at the type section 27 km northeast from the mine (Kelly, 1972).

Mineralization at the Guadalupe mine is confined to a single sandstone layer characterized by a thickness varying from one to six meters that is confined by low permeability shale units.

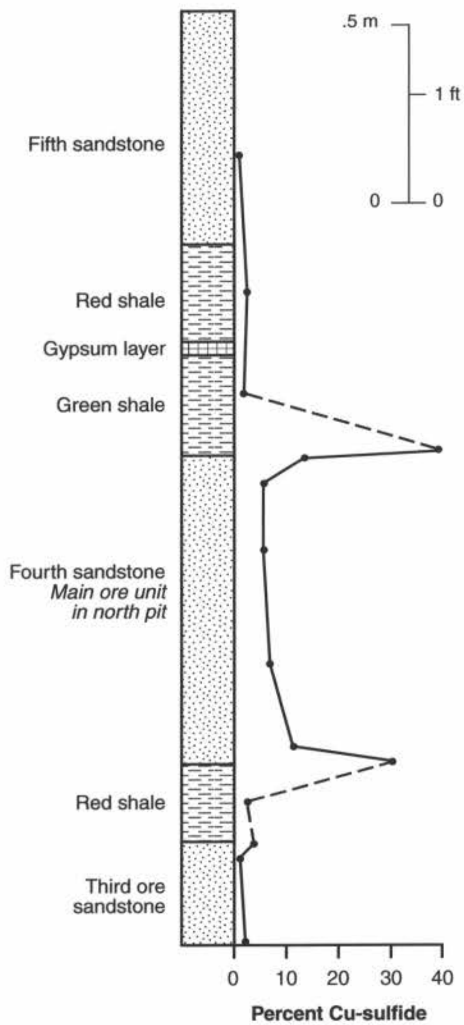

FIGURE 3. Variation in lithology and volume percent copper sulfide concentration at the Pintada Mine in the 4th sandstone unit in the north pit area. Dashed line indicates sampling was not continuous in that interval due to the friable nature of the rock.

Chalcocite is the main primary sulfide and has been replaced by supergene malachite and azurite. Mineralization shows greatest development at the base and top of the sandstone unit and weakly extends into the bounding shales for distances of up to twenty centimeters. Mineralization within the sandstone is a maximum of 4 m thick, although the majority of ore-grade copper is confined to the lower portions of the bed. The overlying shale is 12 m thick and the lower shale, described as plastic clay by Harley (1940), is 6 m thick. The lower shale unit is undulating with greatest development of mineralization in proximity to anticlinal structures in this lower shale. These structures are probably the result of soft sediment deformation or diagenetic compaction.

GEOLOGIC MEMBRANE PROCESSES

A semi-permeable membrane is defined as a material which will permit the passage of some molecules but not others (Noggle, 1984). As defined, such a membrane would be perfect, *i.e.*, it would absolutely preclude the passage of certain molecular species. Because such perfect membranes probably do not exist in nature (Fritz, 1986), a better working definition for a semi-permeable geological membrane would comprise any lithology that allows one solution component to pass through more easily than another.

Many studies have experimentally confirmed the ability of clays, which are a major component of shales, to act as semi-permeable membranes (Fritz and Whitworth, 1994). For example, Young and Low (1965) conducted experiments in which they passed saline solutions through actual discs of shale and siltstone, demonstrating that shales and siltstone are capable of acting as semi-permeable membranes. In addition to laboratory studies, many field studies have suggested the existence of geologic membranes. For example, the Milk River aquifer in western Canada has been cited as an example of a rock unit exhibiting membrane processes (Berry, 1960, Phillips, *et al.*, 1986). More recently, Neuzil (2000) presented field evidence of membrane-functioning shales.

Hyperfiltration (reverse osmosis) occurs when sufficient pressure is applied to the high-concentration membrane face to reverse the direction of water flow through the membrane. Under hyperfiltration conditions, both solute and water flow across the membrane from high to low solute concentration. Both osmosis and hyperfiltration can occur in the subsurface in conjunction with geologic membranes; however, osmotic processes are dissipative, meaning that they do not increase solute concentrations. Therefore, the role of osmosis in sediments is not considered in this paper.

We can use a simple diagram (Fig. 5) to describe what happens if groundwater is forced through a membrane-functioning lithology. Theoretically this situation begins with identical solute concentrations, c_i, on both sides of the membrane at time t = 0 (Fig. 5a). Because water passes more easily through the membrane than the solute, as time passes the solute begins to accumulate, c_o, at the high-pressure membrane face (Fig. 5b). The zone of increased concentration at the high-pressure membrane face is called the concentration polarization layer (CPL). As the CPL grows, ever more solute is available at the high-pressure membrane face to enter the membrane. Hence, membrane efficiency decreases and the effluent concentration tends to increase concurrently with growth of the CPL (Fritz and Marine, 1983). The concentration at the high-pressure membrane face continues to increase with time as does the width and amount of solute in the CPL (Fig. 5c). After a sufficient amount of time has passed, an equilibrium is reached (Fig. 5d) in which, if no precipitation is occurring within the CPL, the effluent concentration stabilizes at that of the original input concentration, c_i. However, if chemical reactions and/or mineral precipitation are occurring within the CPL, then the effluent concentration will always be less than the input concentration.

DISCUSSION

We will describe a geologic membrane-related model for the origin of the sedimentary-hosted copper deposits at the Pintada and Stauber mines. LaPoint (1974) discusses possible sources of copper in northern New Mexico, specifically the Pedernal uplift region. Specifically, these oxidized, copper-bearing solutions flowed along an aquifer bounded by confining shales. When groundwater passes

FIGURE 4. Photograph illustrating lithologic and mineralogic variation along strike at the Pintada Mine. Throughout the mine copper mineralization is most well developed where the bounding shale is the thinnest and least developed where the bounding shale is thickest. Note the variation in shale thickness from A to B on the photograph. Mineralization becomes higher grade and thickens in the area of B (shale thickness = 0.23 m) compared to A (shale thickness = 0.45 m)

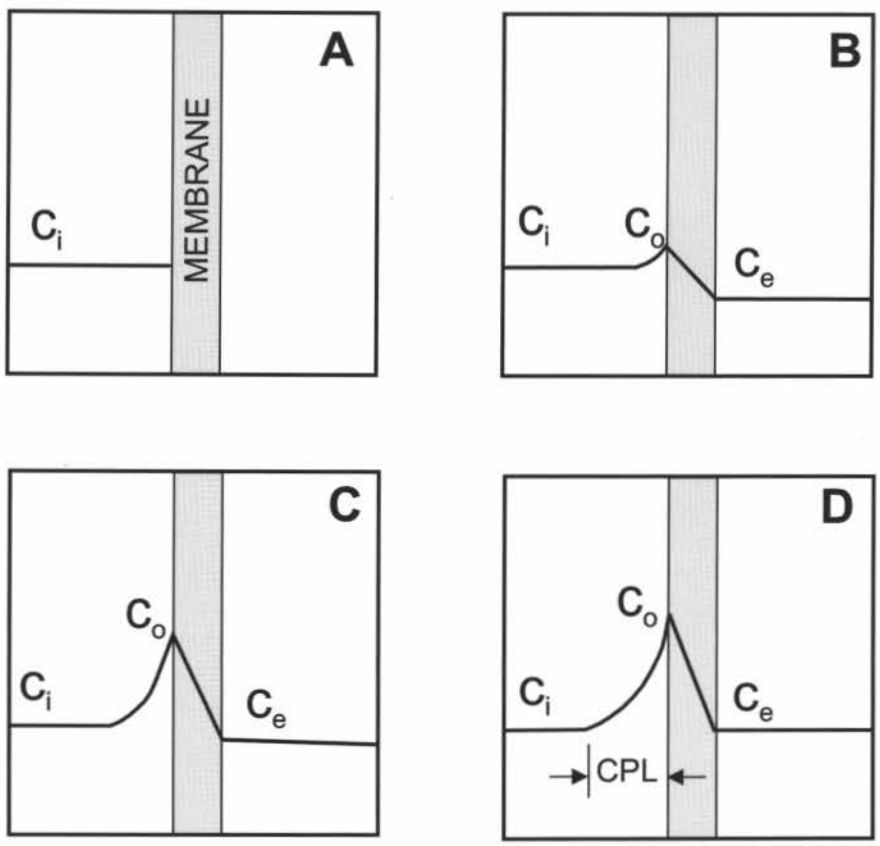

FIGURE 5. Conceptual development of the concentration polarization layer in a static cell. The initial conditions (A) are such that the solute is all on the high pressure side of the membrane and the pore fluids within the membrane contain no solute. Some time after solute flux through the membrane begins (B) the concentration at the high pressure membrane face C_0 increases because some of the solute is rejected by the membrane. Some solute also begins to pass through the membrane so that the effluent now contains some solute as well. Even later (C) C_0 has increased further as has the effluent concentration C_e. At steady state (D) the input concentration C_i is now equal to C_e and the value of C_o is constant. (Redrawn from Fritz and Marine, 1983).

through the shale-membrane, a portion of the solute is rejected, beginning a dynamic concentration of metals. This process continues as fluid flow occurs through a membrane-functioning unit. Solutes, while perhaps not always sufficiently concentrated to cause mineralization, are continually "swept" along the flow path.

If the volume flux of groundwater toward the membrane is sufficient to prevent the rejected solute from completely diffusing back into the aquifer, a CPL forms. Even though the component of flow parallel to the membrane interface will tend to diminish the CPL by dispersing a portion of the rejected solute back into the aquifer, groundwater flows are typically slow enough so that the CPL is not likely to be significantly diminished (Whitworth, 1998).

It is possible that metal concentrations within the CPL, near the membrane, would reach (super) saturation thus encouraging copper mineral precipitation in the sandstone adjacent to the bounding shale units. Notably, malachite and azurite are present in the copper deposits we examined; laboratory experiments (Whitworth and DeRosa, 1997) have demonstrated that copper carbonate can be precipitated by geologic membranes via the saturation of cupric copper and carbonate. Copper carbonate also forms from the weathering of copper sulfide minerals. Our observations indicate that no particular mechanism was solely responsible for the presence of copper carbonate mineralization in the Pastura district.

Most genetic models of sedimentary copper deposits, including ours, postulate that sulfide was produced by the bacterial reduction of sulfate (Hoy and Ohmoto, 1989). Certain anaerobic, sulfate-reducing bacteria (e.g. *Desulfovibro sp.*) exist at depth within groundwater systems and different varieties of bacteria can exist over a wide range of chemical and pressure conditions in the subsurface. For example, different varieties of bacteria can live in pH conditions of from 1 to 10, under fluid pressures of up to many hundreds of bars, and can survive temperatures of up to 75°C (Oppenheimer, 1963). Rose (1976) states that mineralization in red bed copper deposits seems to have occurred at temperatures of less than 75°C. Therefore, bacterial mediation of copper mineralization is not ruled out on the grounds of temperature. Furthermore, Rose (1976) reported that values of $\delta^{34}S$ in sulfides in these deposits range from -20 to -50‰ (Jensen, 1971) and are thus consistent with bacterial origin, although these values do not constitute proof of bacterial origin (Ohmoto, 1972). The lack of chalcocite twinning in these deposits indicates chalcocite precipitation temperatures were less than 115°C.

We suspect that the main role of the membrane-functioning shales in the formation of the copper deposits in the Pastura district is in concentrating both the dissolved copper and nutrients for use by sulfate reducing and other bacteria. Sulfate reducing bacteria are dependent on fermentative bacteria for the simple organic compounds their metabolism exploits (Chapelle, 1992). Organic matter is present in groundwater in colloidal form. In a study of colloids in groundwater at the Nevada Test Site, Kingston, *et al.* (1988) determined that organic colloids were present in the form of CH_2 and CH_3. We suggest that it is possible that one nutrient source for *Desulfovibro sp.* and the fermentative bacteria which supply their food source ultimately derive some, if not most, of their nutrients from groundwater colloids.

Hyperfiltration (to be technically correct in the case of colloidal materials—ultrafiltration) of groundwater colloids by geologic membranes would tend to concentrate a bacterial nutrient source within the CPL. Other dissolved nutrients such as phosphates and nitrates would also be concentrated in the CPL. This effect, occurring in a natural system, is similar to that described by Cheryan and Mehaia (1986) for membrane bioreactors, which use synthetic membranes to achieve microbial concentration for improving fermentation efficiencies in commercial fermentation processes.

In many sedimentary copper deposits, fossil wood and plant material have been a source of the carbon necessary for bacteriological metabolism or direct reduction/replacement, as evidenced by their mineralization. However, it is not always the presence of such organic material that causes sulfide precipitation. We observed unmineralized organic matter in the center of some of the sandstone strata in the Pastura district, while similar organic matter near the sandstone/shale boundary in the same unit were mineralized. This suggests that carbon may not be the limiting factor for bacterial growth and, therefore, generation of a sulfate-reducing environment at these deposits. Rather, we suggest that the limiting nutrient may be a solute, such as nitrogen or phosphorous, that was concentrated by the membrane-functioning shales. Because both nutrient and copper concentrations would be greatest at the membrane interface and diminishing with distance into the aquifer, mineralization related to microbial vigor and metals concentration in solution should be a maximum closest to the membrane. This is exactly the pattern of mineralization we observe in the Pastura district (Fig. 3).

When mass flux toward the membrane is insufficient to prevent the rejected solute from diffusing back into the aquifer, no CPL will form. Therefore, in cases in which flux toward and through the membrane is very low, one would expect no or only incipient and erratic copper mineralization at the membrane interface. Mineralization should only occur where the CPL develops to the extent that the solute concentration at the higher-pressure membrane face is greater than the solubility of a mineral species. This would explain why copper mineralization is not ubiquitous throughout the host rock and why mineralization favors the thinner shales where, for a given set of conditions, the solution flux through the shale is highest. In the Pintada and Guadalupe mines, the intensity of mineralization is inversely proportional to the thickness of the adjacent shale. We believe this occurs because volume flux through the shale is inversely proportional to shale thickness, as predicted by Darcy's law.

The concept of a "redox front" encountered at some distance downdip in the aquifer that encourages mineral precipitation, as is commonly proposed as a mineralization mechanism at many sedimentary copper deposits, does not appear to be reasonable in the Pastura district. We did not observe color changes, attributable to variable oxidation states of iron, cutting across sandstone bodies; instead, the more permeable sandstones tended to be gray, irrespective of mineralization, and the shales and less permeable silts and sands tend to be a reddish color. We suggest the color of the sediments may indeed be the result of redox phenomena, but not necessarily redox phenomena tied to mineralization.

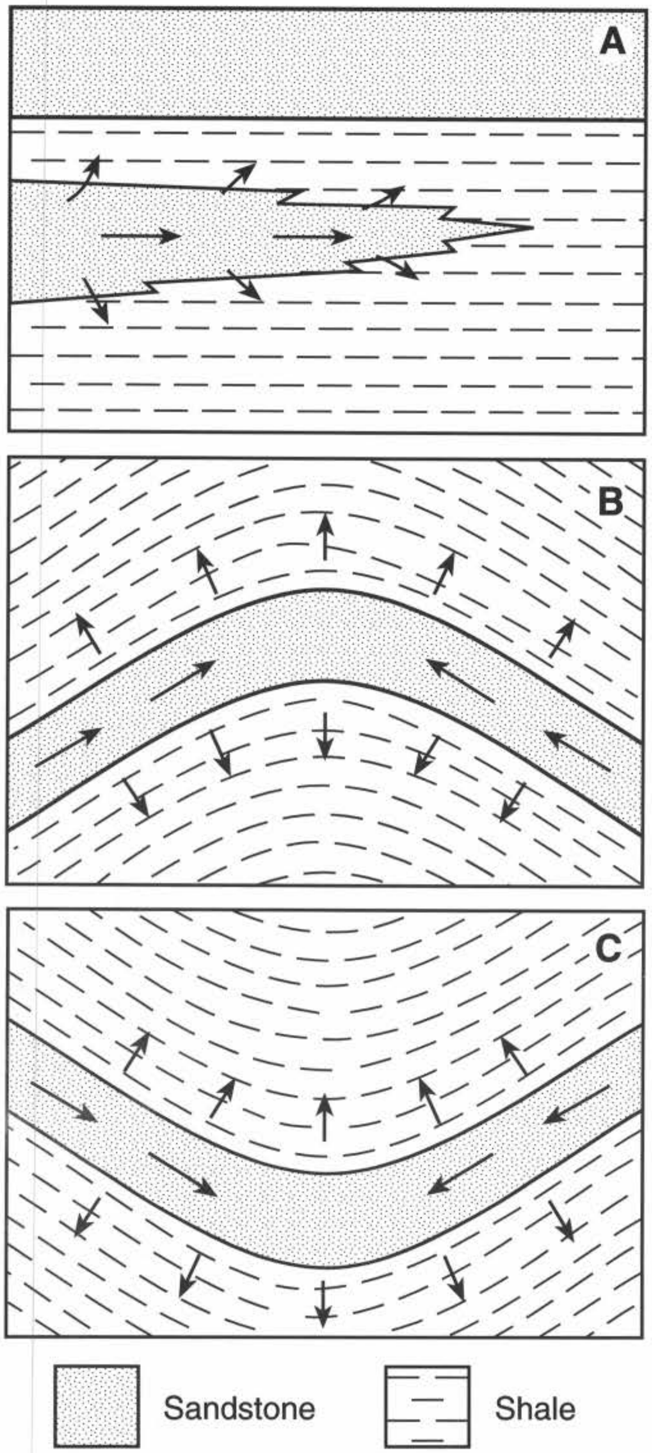

FIGURE 6. Conceptual diagram of focusing structures. A focusing structure is one which encourages flow through geologic membranes rather than through the aquifer. For example a facies change from sandstone to shale (A) may act as a focusing structure. Anticlines (B) and Synclines (C) may also direct flow through otherwise lower permeability rocks.

Fluid flow plays a major role in the formation of sedimentary copper deposits (and other similar deposits). Classically, groundwater scientists have typically considered fluid flow only within the aquifer based on the belief that fluid flow through confining beds is negligible (Freeze and Cherry, 1988). This approach does not adequately describe fluid flow in typical sedimentary depositional systems. Given a flow path of sufficient length, a facies change, pinch out, unconformity, fold, or fault will always be encountered.

When a facies change occurs in an aquifer, such that a permeability decrease is encountered, the effect is much like a partially closed valve on an open pipe. The valve, by reducing the cross-sectional area available for flow, effectively reduces the velocity of the fluid in the open pipe. So too does a permeability decrease slow the velocity of the fluid farther updip within the aquifer. Due to permeability decreases, some pinchouts, faults, unconformities, and folds have the capability to act as subsurface valves. The valve effect, then, by reducing flow velocity within the aquifer, results in a significantly lower flux than would be predicted by Darcy's Law using the hydraulic conductivity of the "good" aquifer matrix. As a result, the flux through surrounding shale membranes (aquitards) assumes a greater proportion of the flow. Thus, we expect subsurface flow through shales and other relatively low permeability rocks to be of significantly greater importance in most subsurface depositional systems than simple analysis using Darcy's Law would suggest.

Structures and stratigraphic transitions have been noted to aid in the development of larger ore deposits (Fig. 6). Hydrologic flow is focused by or along structures or stratigraphic facies changes, such as in synclines or basins, where fluid flow is directed toward the center of the structure. Because fluid flow occurring through a membrane-functioning unit results in some concentration of solutes, as fluid continues to flow through the membrane-functioning unit even greater solute concentration occurs until the solute concentration and bacterial activity leads to the precipitation of ore minerals. In the Pastura district, field observations suggest this mineralization was most likely to occur at such focusing structures. At Pastura, focusing structures are those stratigraphic sections where thinning in a membrane-functioning unit allows a significantly greater throughput of groundwater, thus concentrating or pooling most of the dissolved copper and microbial nutrients at a locus.

Features of fluid focusing are present at both the Guadalupe and Pintada mines. Mineralization is most well-developed in basinal or synclinal structures (Fig. 6B) yet is also focused in minor anticlines (Fig. 6C) where fluid flow is updip or is concentrated in a membrane structure which changes fluid flow characteristics. The latter situation is represented by more intense mineralization in proximity to the "humps" in the flooring shale described by Harley (1940) at the Guadalupe mine. At Pintada, mineralization is found in the center of a synclinal structure, a situation that encourages over-pressured, confined aquifers due to basin-edge recharge. In addition to a structural depression at the Guadalupe mine, stratigraphic pinchouts (Fig. 6A) may also have served as an additional mechanism to focus mineralization in the mine area (Holmquist, 1947). Stratigraphic pinchouts at the margins of basins are a particularly good place for the pooling of fluids and subsequent enhancement of the membrane effect. This feature is also noted at other deposits (Lange *et al.,* 1989) where minor structures or stratigraphic transitions within larger basins localize mineral deposition.

SUMMARY

Examination of two sedimentary copper deposits in the Pastura district shows that mineralization occurs in sandstones immediately adjacent to the confining shales. At each deposit, mineralization displays greatest development in copper concentrations and thickness adjacent to the thinnest shales and, conversely, with increasing shale thickness, becoming non-existent adjacent to the thickest shales. This pattern of mineralization is compatible with a geologic membrane-related process.

The fact that clays and shales can act as membranes has been firmly established by experimental and field observations. When solute is rejected by a shale membrane, and if flux through the membrane is sufficient to prevent effective back diffusion of the solute away from the membrane into an aquifer, a concentration polarization layer (CPL) is formed. Calculations demonstrate that, for reasonable hydrogeologic conditions, solute concentrations within the CPL can range from several to more than 100 times that of the background concentration within the aquifer (Whitworth, 1998). It is also reasonable to expect that shale membranes may also concentrate nutrients necessary for bacteriological metabolization of sulfate. Hence, we expect the CPL may be favorable for subsurface microbial activity with resulting H_2S production by sulfate-reducing bacteria producing sulfide mineral precipitation within the CPL.

Our mechanism also explains why copper mineralization is localized and not ubiquitous in the host rock. Because the magnitude of flux through a shale is inversely proportional to shale thickness, there is a threshold value of flux for any given solute through the membrane which must be exceeded before the solute rejected by the membrane becomes unable to effectively diffuse back into the reservoir. Therefore, one would expect that thick shales inhibit the formation of a CPL, while thinner shales would provide an environment appropriate for mature CPL development. Our observations indicate that the presence of a CPL is necessary for mineralization.

Finally, features of fluid focusing are present at both the Guadalupe and Pintada mines. At Pintada, mineralization is found in the center of a synclinal structure in an area of facies interfingering. In addition to a structural depression at the Guadalupe mine, a stratigraphic pinchout is also present and probably served as an additional mechanism to focus mineralization in the mine area. Stratigraphic pinchouts at the margins of basins are a particularly good place for "pooling" of fluids and subsequent enhancement of geologic membrane-microbial interactions, with related mineralization.

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