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EPIGENETIC ZONATION AND FLUID FLOW HISTORY OF
URANIUM-BEARING FLUVIAL AQUIFER SYSTEMS,
SOUTH TEXAS URANIUM PROVINCE

by

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ABSTRACT

The Oligo-Miocene fluvial uranium host aquifers of the South Texas uranium province were deposited principally as syndepositionally oxidized sands and muds. Early intrusion of reactive sulfide-enriched waters produced large intrastatal islands of epigenetic sulfidic alteration, which are characterized by isotopically heavy pyrite exhibiting unique replacement textures. The only available reservoir for such sulfidic waters is the deeply buried Mesozoic carbonate section that floors the thick, geopressed Tertiary basin fill. Thermobaric waters were expelled upward along major fault zones into shallow aquifers in response to a pressure head generated by compaction and dehydration processes in the abyssal ground-water regime. Vertical migration of gaseous hydrogen sulfide was of secondary importance. Repeated flushing of the shallow aquifers by oxidizing meteoric waters containing anomalous amounts of uranium, selenium, and molybdenum alternating with sulfidic thermobaric waters caused cyclic precipitation and oxidation of iron disulfide. Commercial uranium deposits formed along hydrologically active oxidation interfaces separating epigenetic sulfidic and epigenetic oxidation zones. Multiple epigenetic events are recorded in local imperfectly superimposed, multiple mineralization fronts, in regional and local geometric relationships between different alteration zones, and in the bulk matrix geochemistry and mineralogy of alteration zones. The extremely dynamic mineralization model described may be representative of processes active in many large, depositionally active basins.

INTRODUCTION

The coastal plain of Texas is an increasingly important producer of epigenetic sandstone uranium resources. The rapidly expanding data base generated by both exploration and mining has, within the past decade, led to development and refinement of exploration concepts that are, in some respects, unique to the province. Models initially applied were based on attributes of the well-studied epigenetic uranium deposits of the Wyoming Tertiary basins. The roll-front model and its implicit epigenetic oxidation-reduction zonation proved successful to a point, because Gulf Coast deposits do exhibit many features of their Wyoming counterparts. However, deeper exploration and more sophisticated description of known deposits reveal fundamental differences between the depositionally active Gulf Coastal Plain and the interior Tertiary basins. Interior basins have been depositionally moribund since the mid-Tertiary, and the total sediment pile above uranium-bearing aquifers is decreasing as older Tertiary strata continue to be eroded. In contrast, basinward stratigraphic equivalents of principal Gulf Coast fluvial uranium hosts, the Catahoula and Oakville Formations, have been buried deeper than 15,000 ft (4,500 m), and burial has continued throughout the late Tertiary and Quaternary. In addition, Gulf basin host sands overlie thick sequences of underconsolidated older Tertiary and Mesozoic sediments, which have not yet attained hydrostatic equilibrium with the surface. The result is a hydrologically active basin in which counterflow of geochemically different water masses has existed since deposition of the host fluvial systems and continues to exist.

The evolving, hydrochemical systems and the diverse fluid fluxes in such a dynamic basin have produced complex distributions and styles of epigenesis. Shallow uranium deposits that are most directly influenced by the active

meteoric ground-water regime typically closely resemble the roll-front type of mineralization (Eargle and others, 1975; McKnight, 1972). However, at depth, and in parts of shallow aquifers that have evolved flow systems greatly different from earlier systems, alteration and mineralization patterns and zonation reflect a complex interplay of water masses of different chemistries (Goldhaber and others, 1978; Goldhaber and others, 1979a; Galloway and Kaiser, 1980). Commonly used evidence for alteration front geometry is obscured. In particular, limonitic oxidation of iron may be masked by reintroduction of reducing, sulfidizing waters. Gabelman (1977) argued that such reducing waters were derived from deep, overpressured basinal muds and that they constituted the actual uranium-enriched ore-forming fluid. Subsequent data do not support the latter contention; nonetheless, Gabelman correctly pointed out the potential importance of the interaction of different water masses in the South Texas uranium province.

Objective

This report synthesizes published and new data on the hydrogeologic framework, paragenesis, and epigenetic zonation of uranium ore-producing parts of the coastal plain fluvial aquifers to interpret and document the history, nature, and economic significance of evolving fluid flow patterns in a compacting basin. Several specific questions are addressed:

1. What are the available ground-water reservoirs, and what are their chemical characteristics?
2. Is vertical movement of fluids, particularly those derived from considerable depth, confined to major structural features (Eargle and others, 1975; Goldhaber and others, 1978)?

3. Are vertically leaked fluids aqueous solutions, gases (as inferred by many authors including Eargle and Weeks [1961] and Klohn and Pickens [1970]), or some combination of both?

4. What characteristic epigenetic zonations are produced within the aquifer matrix during flushing by the various available fluids?

5. What pattern or patterns of successive fluid fluxes commonly result in or are associated with uranium mineralization?

This paper summarizes and reviews, in the context of each of these questions, the implications of the existing data base and thereby refines the generalized model for the origin of uranium deposits in Oligocene and younger fluvial depositional systems of the South Texas uranium province. Many elements of this model may apply to other mineral deposits in similar compacting, thick sedimentary basin fills.

Methodology

The Oakville Formation (Miocene) within Live Oak County (fig. 1) was selected as the focus of investigation. Two major, relatively well known Oakville-hosted uranium districts lie within the county along either margin of a major paleo-fluvial trend, the George West axis (Galloway and others, in press) (fig. 1). Characteristics of Oakville uranium deposits, particularly their structural and depositional settings, general geochemistry and paragenesis, and deposit geometries, appear to be typical of deposits in underlying Catahoula and overlying Goliad fluvial host systems.

Cuttings from petroleum test wells were examined, and observations were combined with generalized information based on uranium exploratory drilling to produce a regional alteration map of the lower Oakville sand sequence, which hosts most uranium deposits. Core samples and drill cuttings donated by mining

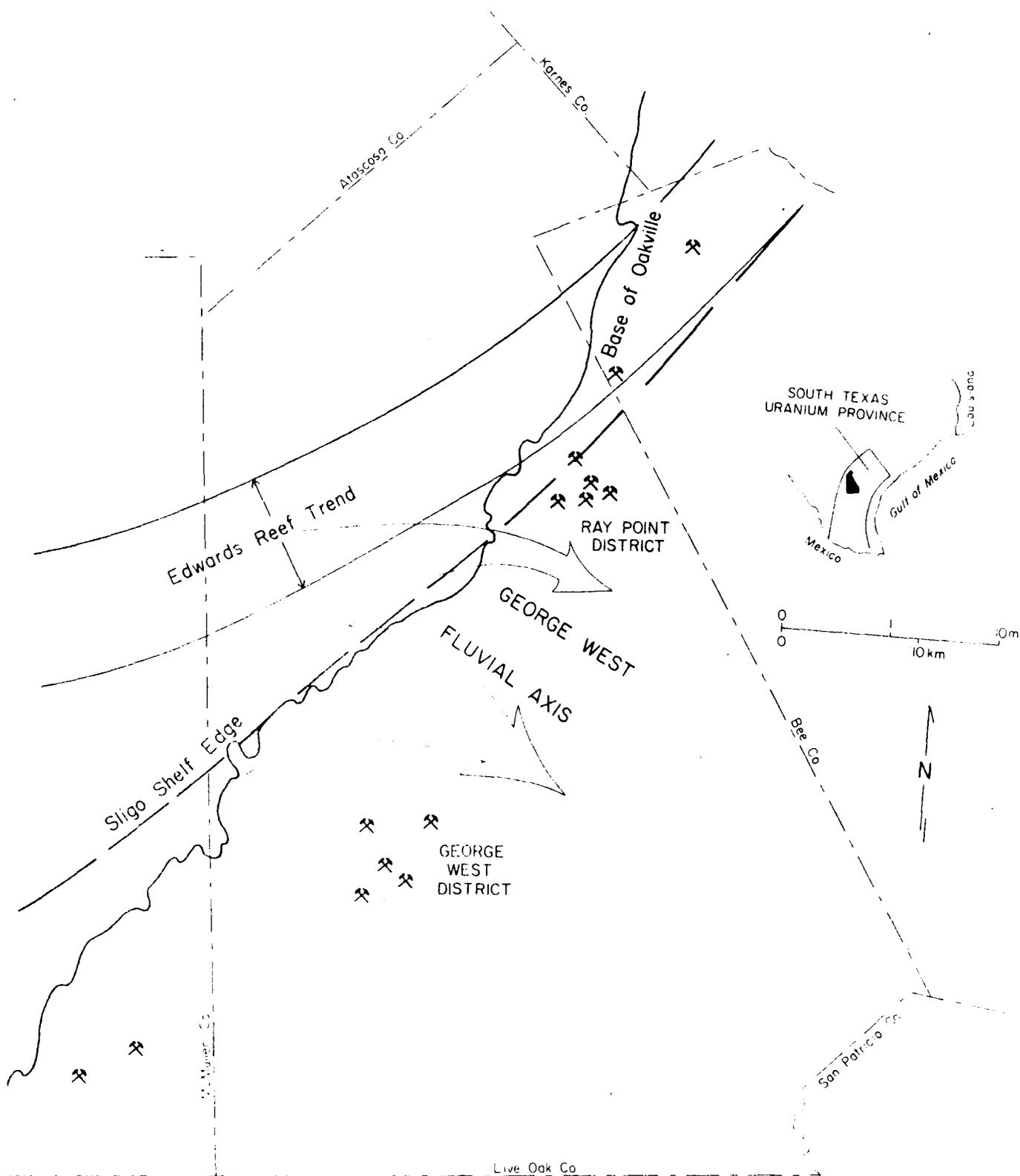


Figure 1. Location of the study area and position of the underlying Lower Cretaceous shelf margin.

companies were used for detailed geochemical and mineralogical description of epigenetic zones in and around mineralization fronts in both the George West and the Ray Point districts. Mineralogy of recognized zones was determined by conventional petrography, X-ray diffraction studies, and scanning electron microscope examination. Reflection microscopy of core samples from the George West district (Childs, in preparation) supplemented similar analyses for the Ray Point area by Goldhaber and others (1979a). Major constituents, including sulfate, carbonate, ferric iron and ferrous iron, were determined quantitatively by chemical analyses. Trace metals typically enriched within the deposits, including uranium, molybdenum, and selenium, were analyzed by spectrofluorometry. A suite of additional trace and major elements was determined quantitatively by inductively coupled plasma emission spectroscopy. Selected samples were subjected to carbon or sulfur stable isotopic analysis. All data have been tabulated and are on open file at the Bureau of Economic Geology.

The combined mineralogical and geochemical characterization of each zone, along with the spatial association of successive zones, provides a basis for reconstructing ground-water chemistry, flow direction, and origin of the waters responsible for altering the aquifer matrix. Data on the hydrodynamics and hydrochemistry of modern ground-water systems and reservoirs of the Texas Gulf Coast Basin were compiled and related to geometric and geochemical attributes of the various alteration zones.

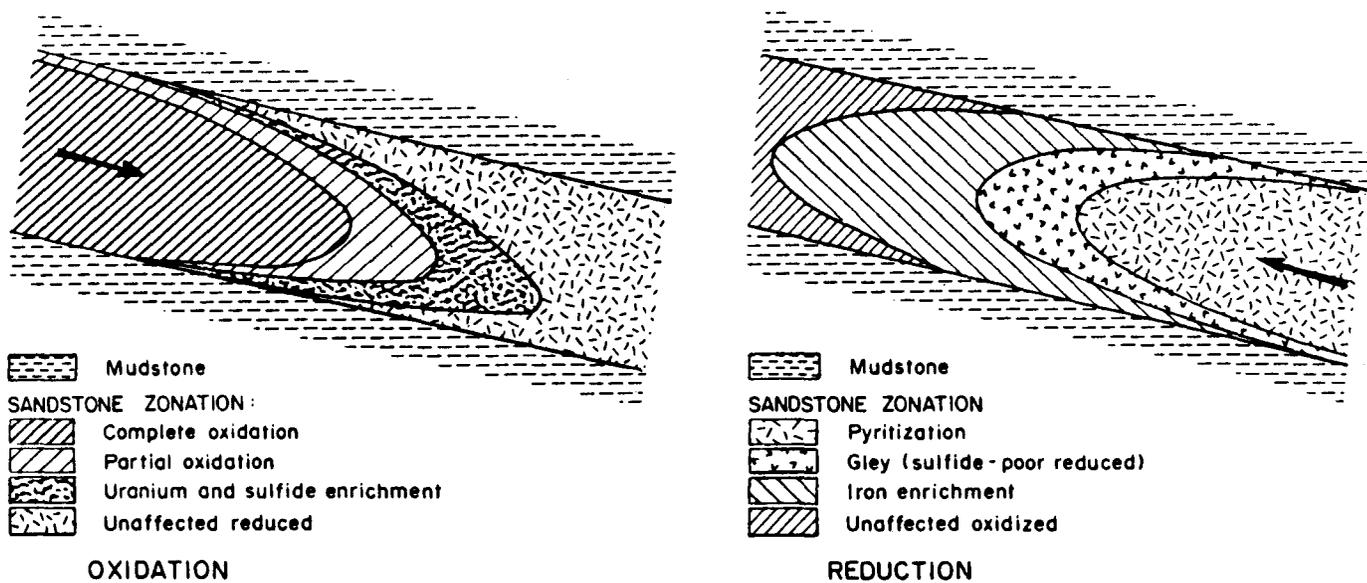
Finally, a paragenetic sequence based on zonal superposition and interpreted succession of diagenetic events was used to infer direction and historic evolution of ground-water fluxes through the mineralized parts of the shallow fluvial aquifers. Recognition of the epigenetic zones and reconstruction of their spatial and temporal relationships provide the basis for evaluating exploration results in geographic and stratigraphic frontiers in the South Texas

uranium province and illustrate a process model that may apply to many other hydrologically active depositional basins.

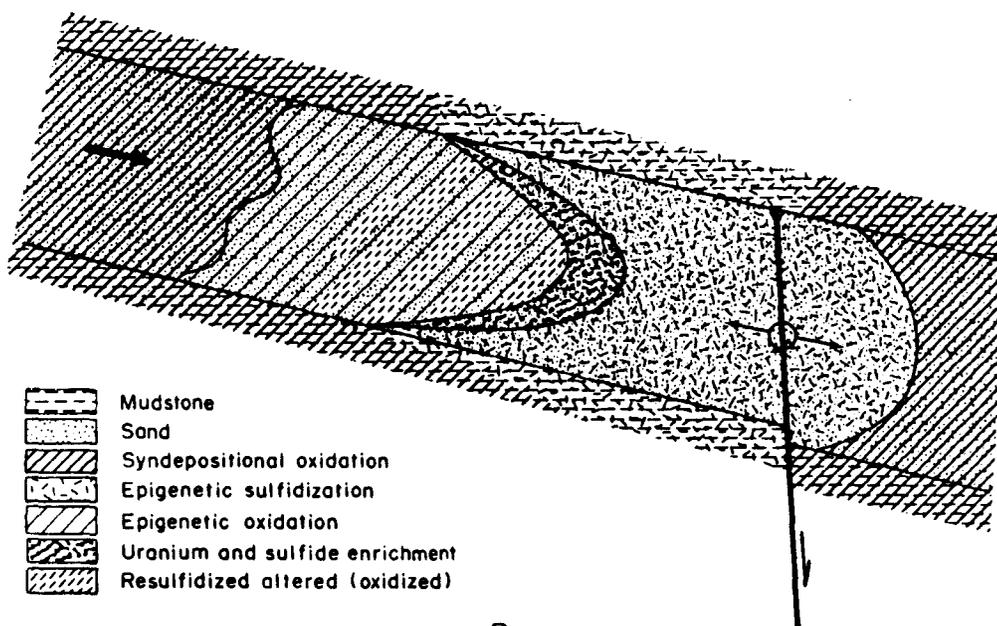
AQUIFER ALTERATION

The geochemistry, mineralogy, geometry, and internal zonation of both oxidizing and reducing alteration events that are preserved within the aquifer matrix record the successive flushing episodes by ground waters derived from different reservoirs. Shmariovich (1973) described and contrasted idealized epigenetic alteration patterns produced by the flux of sulfidic, reducing waters and by oxidizing waters through an aquifer (fig. 2A). Not all of the geochemical zones described by Shmariovich have been recognized in Oakville sediments of South Texas. Nevertheless, analogous epigenetic reduction and oxidation events are apparent (fig. 2B) and include syndepositional oxidation, epigenetic oxidation, and epigenetic sulfidization.

Syn depositional oxidation is characterized by alteration of iron phases to hematite. Presence of hematite implies either long-term, kinetically slow dehydration of original ferric oxyhydroxides formed by oxidation and hydrolysis of ferrous iron minerals in water-saturated media, or rapid dehydration due to periodic desiccation at warm temperatures (Langmuir, 1971). Indeed, features of many hematitic samples suggest paleosoil formation under subarid conditions (Galloway and others, in press). Hematitic alteration is commonly described as "primary oxidation" by geologists working in the South Texas uranium province. The implication that much of the Oakville is therefore a primary red-bed sequence is confirmed by core and sample examination. Fluvial deposits of both the underlying Catahoula Formation and the overlying Goliad Formation appear to have been similarly oxidized and dehydrated by syndepositional and earliest diagenetic processes.



A



B

Figure 2. Geochemical zonations produced by epigenetic oxidation and reduction of a shallow, meteoric aquifer. A. Idealized zones produced in a reduced aquifer by circulating oxidizing uranium-bearing meteoric water, and in an oxidized aquifer by intrusion of sulfide-bearing reducing ground water (modified from Shmariovich, 1973). B. Idealized geochemical zonation typical of mineralized parts of the Oakville aquifer of the South Texas uranium province.

Epigenetic oxidation is characterized by limonitic alteration of iron minerals. Presence of ferric oxyhydroxides indicates comparative youth relative to hematitic oxidation. Two variations are recognized. Phreatic oxidation occurs above the modern water table in shallowest, outcropping parts of the Oakville. More extensive tongues of limonitic alteration extend far below the water table into permeable sands.

Epigenetic sulfidization is recognized by the presence of well-crystallized to finely dispersed iron disulfide (primarily pyrite) and consequent gray color of the rock matrix. Reduction of the South Texas fluvial aquifers appears to be characterized by importation of additional sulfide. Gley (sulfide-deficient) alteration, though present, appears to be comparatively minor. Spatial distribution relative to mineralization fronts (fig. 2B) as well as detailed mineralogy of the sulfide phases, indicates that regional epigenetic sulfidization may be superimposed on both syndepositionally and epigenetically oxidized ground (Goldhaber and others, 1979a; Galloway and others, in press). The latter situation, which is a common attribute of many South Texas uranium deposits, is commonly called "rereduction."

Regional Alteration Patterns

The distribution of the three principal alteration zones within the highly mineralized lower Oakville sands of Live Oak County and vicinity is shown in figure 3. The Ray Point district lies within a pervasive zone of sulfidic reduction that extends more than 10 mi (16 km) downdip and at least 12 mi (20 km) updip within the underlying Catahoula tuffs and fine sands. A large tongue of epigenetic oxidation, approximately 20 by 10 mi (30 by 15 km) in extent, surrounds the elongate remnant of sulfidic section that hosts the George West deposits. Presence of limonitic alteration implies the earlier existence of

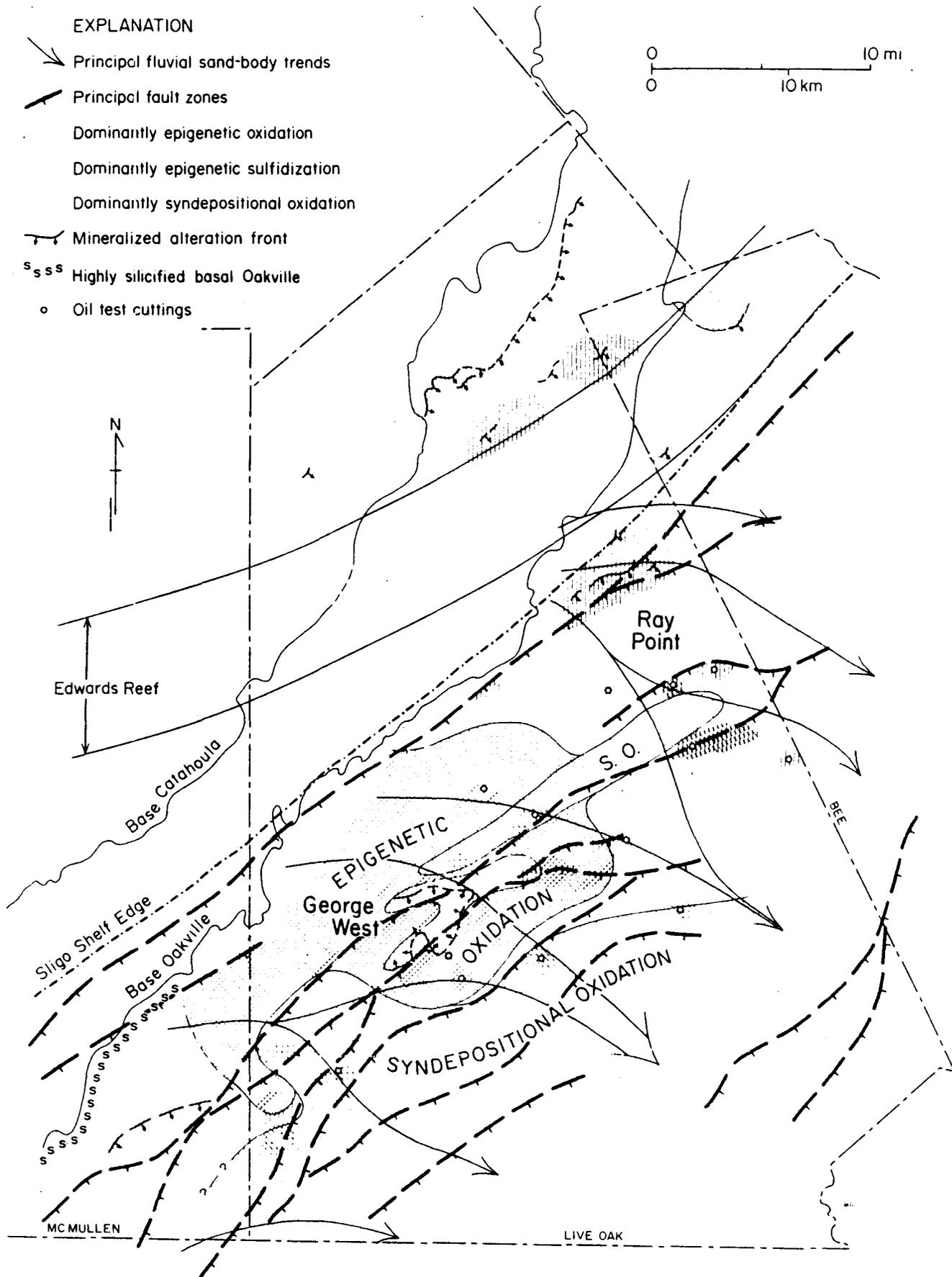


Figure 3

sulfidic sediment in this area as well. Downdip parts of the Oakville primarily exhibit hematitic, syndepositional alteration.

The strike-elongate trend of the alteration zones, as well as the close association of strong sulfidic reduction to major fault segments, supports the contention that the deep-seated fault zones have acted as loci of fluid movement into and through the shallow aquifers. Furthermore, careful comparison of changes in stratigraphic thickness across the two faults that intersect the two uranium districts reveals a similar history of displacement characterized by (1) initial rapid growth during deposition of early Eocene deltaic and fluvial strata, (2) quiescence during late Eocene deposition, and (3) modest reactivation beginning in Oligocene and most likely extending at least through Miocene time. Thus the faults that form the cores of epigenetically altered parts of the aquifer have a history of renewed activity that was contemporaneous with and subsequent to deposition of the Oakville fluvial system.

In contrast, alteration shows only moderate correlation with the dominantly dip-oriented fluvial facies trends shown in figure 3. The major tongue of epigenetic oxidation expands downdip generally along a major high-transmissivity channel belt.

Detailed Alteration Geometry and Zonation

The characteristics of alteration zonation in two major areas of Oakville uranium concentration, the Ray Point and the George West districts, have been examined in detail. Geometry of the principal mineralization fronts and areal

Figure 3. (left) Regional alteration zonation of lower Oakville sands, Live Oak County and adjacent areas. Possible related structural and stratigraphic features include major deep-seated fault zones, fluvial axes, and the Cretaceous shelf edges. Extensively sulfidized ground characterizes the northeastern part of the county and extends far updip into the older Catahoula section. In the central and southwestern part of the county, islands of sulfidic Oakville are surrounded by syndepositional epigenetic oxidation zones.

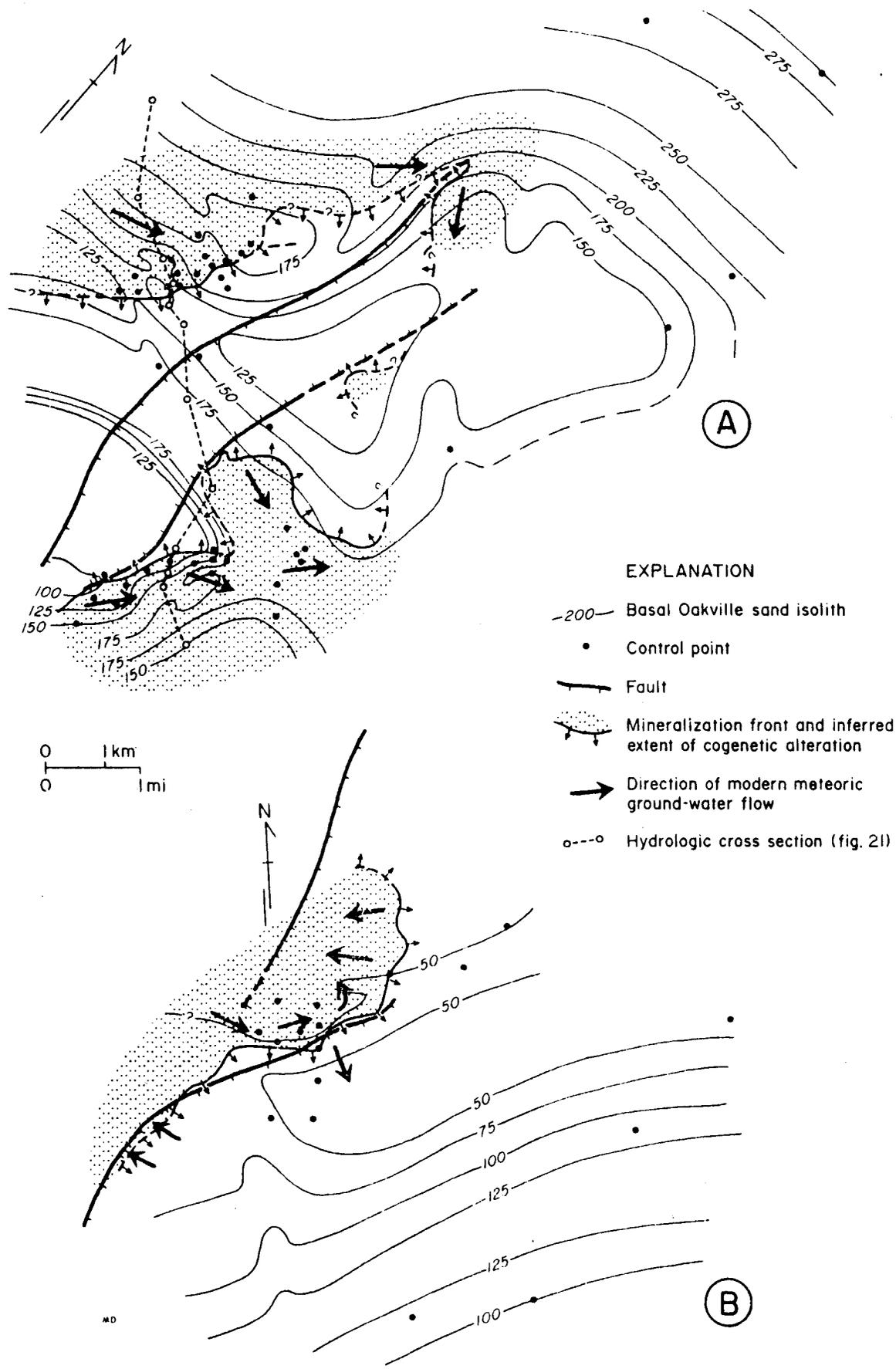


Figure 4

extent of cogenetic alteration tongues within the stratigraphic, structural, and modern hydrologic context are shown in figure 4. In both districts, mineralization fronts lie along the margins of highly transmissive, thick basal Oakville sand belts. Both the fronts and the host sand sequence show a general parallelism to faults that displace the Oakville section. The George West area is particularly interesting in that two major fronts appear to converge from both the updip and the downdip directions upon a narrow fault-defined graben (fig. 4A). This geometry can be explained only if (1) the fault acted as an efficient discharge boundary, or (2) development of the fronts was sequential and occurred under different ground-water flow conditions.

Three core traverses of mineralization fronts (fig. 5, A-C) illustrate typical cross-sectional geometries of the fronts and bounding alteration zones. Fronts approximate the well-known C-shaped roll in two cross sections (fig. 5, A and B) but display no nose in the third (fig. 5C). Geometry, combined with trace metal zonation across the front, defines the polarity of the front (Harshman, 1974; Galloway and Kaiser, 1980). In all three examples, the interior of the front represents cogenetically altered ground, and a vector component of flow of the mineralizing ground water crossed the front from left to right in the diagrams. Visual inspection of samples, however, readily shows that the altered interior is pyritic and reduced in all three examples. Only the two updip cores in the Ray Point traverse contain oxidized sediment. Pyrite-free oxidized interiors were also penetrated by several shallow cores from the George West district that do not lie on a traverse; they were sampled to supplement geochemical and mineralogical studies. Such resulfidization of

Figure 4. (left) Geologic framework, mineralization front geometry, interpreted cogenetic alteration (oxidation) pattern, and direction of modern ground-water flow in the George West (A) and Ray Point (B) districts. Note the subparallel sand isolith and fault trends and their close relationship to mineralization patterns. In contrast, modern ground-water flow shows little relation to mineralization front geometry and inferred polarity.

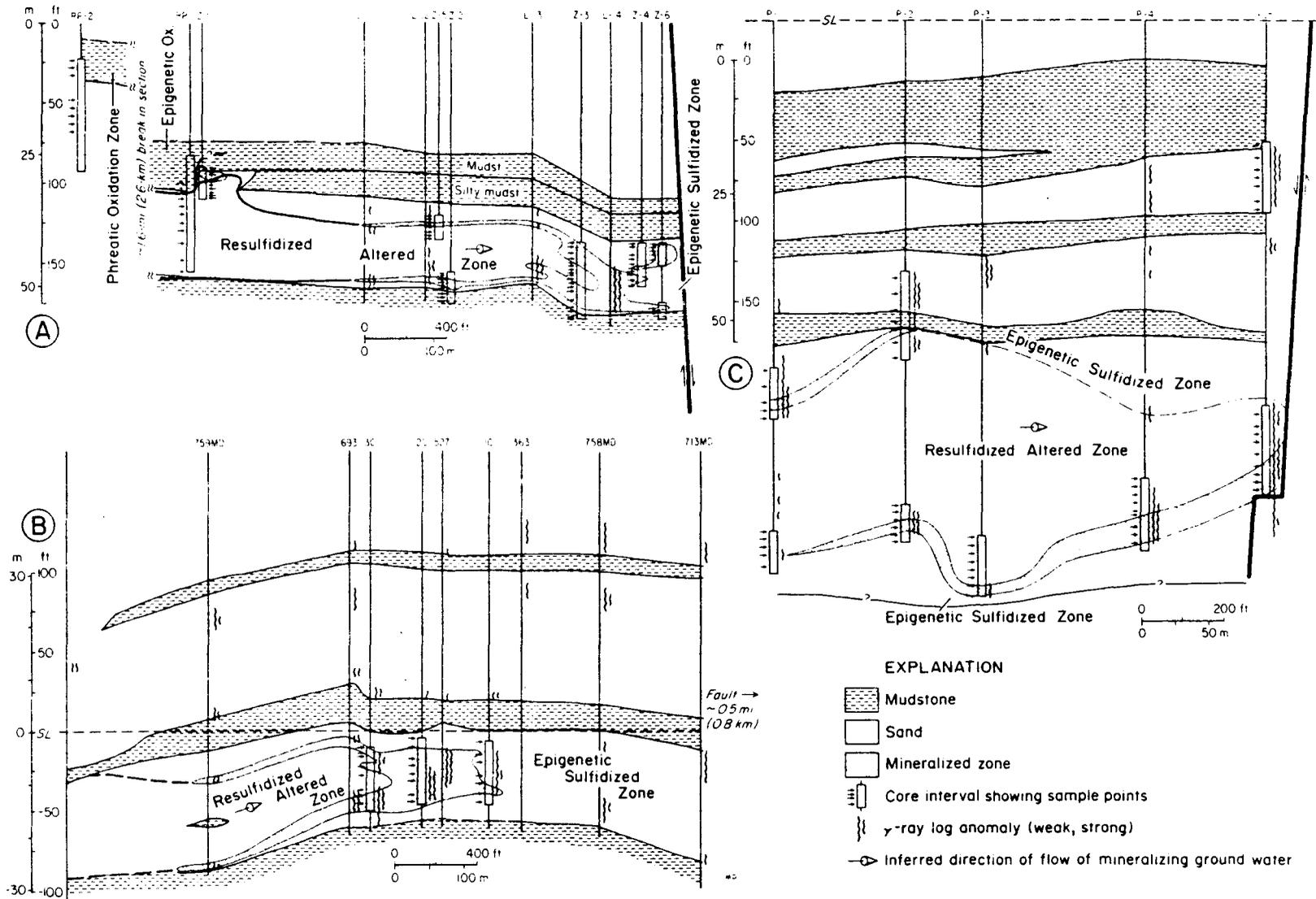


Figure 5. Cross-sectional geometry of mineralization fronts showing surrounding alteration zones and location of sampled core transects. A. Zamzow lease, Ray Point district. B. Updip front, George West district. C. Downdip front, George West district. All fronts show a roll-like geometry with modest to extensive modification typical of the South Texas province.

the oxidized upflow interior of a mineralization front in the Ray Point district has been described and documented by Goldhaber and others (1979a) and appears to be a common product of the fluid flow history that produced Oakville uranium deposits.

Geometric considerations can thus be used to further subdivide the sulfidic zone into epigenetic sulfidic barren (ESb) or mineralized (ESm) facies and re-sulfidized altered mineralized (RsAm) or barren (RsAb) facies. In combination with the syndepositional oxidation (SO) and epigenetic oxidation (EO) zones (including shallow phreatic oxidation [PO]), six potentially distinctive alteration facies characterize uranium host sequences within the Oakville fluvial system. Distribution of these zones is shown on the core traverses.

Geochemical and Mineralogical Characterization

Analyses of more than 260 samples provide the basis for a geochemical description of each recognized alteration facies.* Results are summarized in table 1. Where possible, constituents were related to mineral phases identifiable by petrographic or X-ray diffraction studies.

Syndepositional Oxidized Zone (SO): Uranium, molybdenum, and selenium concentrations are all very low. Iron occurs at background levels, almost entirely in the oxidized form and mostly as hematite. No heavy mineral separates of SO samples have been examined, but outcrop observations suggest the presence of detrital iron titanium oxide minerals. Carbonate content is low and consists primarily of detrital grains, reworked pedogenic nodules, and paleocaliche. Other trace metals occur at background levels typical of the entire sample suite.

*Raw analytical data are on open file at the Bureau of Economic Geology, The University of Texas at Austin.

Table 1. Geochemical characteristics of various alteration zones sampled in the George West and Ray Point districts. Listings show: average (range inclusive of 90 percent of all samples), number of samples analyzed. FeS₂, Fe₂O₃, CO₃⁼, SO₄⁼, and Fe in weight percent, all others in ppm.

G E O R G E W E S T D I S T R I C T						
	Syndeositional Oxidized Zone	Epigenetic Oxidized Zone	Wholly to Partly Resultidized Altered Zone		Epigenetic Sulfidized Zone	
			Mineralized	Barren	Mineralized	Barren
U ₃ O ₈	2(1-3), 11	10(2-14), 32	97(12-125), 28	3(1-10), 12	1170(8-12,000) 78	7(2-10), 31
Mo	4(2-9), 11	5(2-12), 32	5(2-22), 28	4(1-7), 12	63(5-310) 78	6(1-7), 31
Se	1(0.5-2), 11	13(1-8), 32	74(5-105), 28	2(1-6), 12	13(1-317), 78	1(0.2-6) 31
FeS ₂	0.12(0.03-0.2), 11	0.2(0.03-1.0), 32	1.6(0.3-4.0), 28	0.8(0.3-1.6), 12	1.9(0.5-4.8), 78	1.0(0.4-1.6), 31
Fe ₂ O ₃	2.7(1.4-3.9), 11	2.8(1.0-5.0), 32	1.4(0.4-4.2), 28	2.4(0.8-4.0), 12	1.4(0.5-4.0), 78	2.9(0.6-4.0), 31
CO ₃ ⁼	6(2-10), 11	5(1-15), 32	9(4-21), 28	7(4-15), 12	8(5-20), 78	10(5-22), 31
SO ₄ ⁼	0.13(0.06-0.33), 11	0.12(0.02-0.2), 32	0.14(0.02-0.89), 28	0.20(0.02-0.27), 12	0.20(0.04-2.0), 78	0.17(0.08-0.30), 31
Fe	2.1(1.3-3.1), 11	2.3(1-3.3), 26	2.2(0.5-4.7), 26	2.4(1.2-4.0), 12	2.0(0.5-4.5), 70	2.7(1-3.5), 31
Ti	0.24(0.12-0.36), 11	0.23(0.12-0.33), 26	0.15(0.06-0.35), 26	0.24(0.05-0.44), 12	0.19(0.08-0.34), 70	0.33(0.13-0.40), 31
Mn	0.030(0.018-0.045), 11	0.031(0.01-0.13), 26	0.047(0.013-0.15), 26	0.027(0.013-0.077), 12	0.032(0.01-0.09), 70	0.031(0.015-0.044), 31
Co	73(27-130), 11	64(40-110), 26	68(42-103), 14	62(24-165), 11	62(17-187), 56	36(20-80), 31
Cu	8(<5-20), 11	8(3-18), 32	7(2-11), 28	11(6-23), 12	11(3-38), 78	20(5-50), 31
Ni	17(<12.5-37), 11	28(9-110), 32	9(4-22), 28	92(4-699), 12	32(6-214), 78	30(6-80), 31
V	48(12-87), 11	57(<5-90), 26	44(<5-114), 14	49(5-107), 11	36(5-121), 56	61(17-90), 31
Zn	45(22-69), 11	53(24-70), 32	39(12-95), 28	54(13-100), 12	66(20-120), 56	70(30-100), 31
Sr	159(108-218), 11	155(116-200), 26	155(108-234), 14	180(130-288), 11	180(130-200), 56	203(120-280), 31
Zr	134(97-177), 11	129(75-200), 26	126(69-198), 14	116(69-154), 11	126(80-200), 56	160(100-210), 31

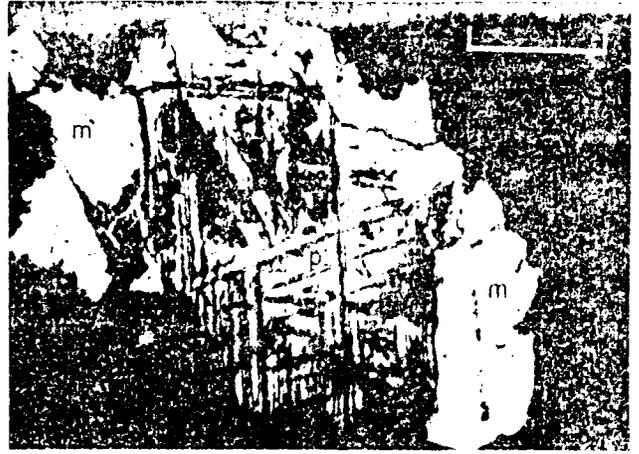
R A Y P O I N T D I S T R I C T						
	Phreatic Oxidized Zone	Epigenetic Oxidized Zone	Resultidized Altered Zone		Epigenetic Sulfidized Zone	
			Mineralized	Barren	Mineralized	Barren
U ₃ O ₈	2.5(2-3), 4	-	53(18-400), 22	5(4-6), 2	346(4-1300), 38	8(4-17), 3
Mo	3.5(2-5), 4	1.5(1-2), 2	18(1-6), 22	2(1-3), 3	110(9-500), 38	3(2-4), 3
Se	0.2(0.1-0.3), 5	0.4(0.2-0.6), 2	36(<1-60), 22	1.5(0.5-3), 3	20(0.1-34), 38	0.5(0.4-0.7), 3
FeS ₂	0.03(0.01-0.02), 5	0.25(0.2-0.3), 2	1.2(0.4-3.0), 22	0.5(0.5), 2	2.5(0.5-4.0), 38	2.0(1.7-2.0), 3
Fe ₂ O ₃	2.2(1-3), 5	3.7(3.4-4), 2	1.8(0.6-2.3), 5	1.1(1.1), 1	-	-
CO ₃ ⁼	6(1-11), 5	9.5(9-10), 2	10(3-18), 22	11(10-13), 3	10(3-17), 38	5(4-5), 3
SO ₄ ⁼	-	-	0.29(0.01-0.8), 22	-	0.18(0.02-1.0), 38	0.02(0.01-0.02), 3
Fe	-	-	1.3(0.5-3.2), 16	1.0(.73-1.3), 2	1.1(0.4-3.0), 36	3.2(2.7-3.4), 3
Ti	-	-	-	-	-	-
Mn	0.03(0.01-0.06), 4	-	0.035(0.03-0.06), 4	-	-	-
Co	-	-	-	-	-	-
Cu	-	-	6(2-18), 6	5(5), 1	9(5-10), 10	-
Ni	-	-	11(2-20), 6	15(15), 1	11(3-20), 10	-
V	-	-	-	-	-	-
Zn	-	-	48(16-130), 6	157(157), 1	48(16-72), 10	-
Sr	-	-	-	-	-	-
Zr	-	-	-	-	-	-

Epigenetic Sulfidic Zone (ESb and ESm): Concentration of uranium, molybdenum, and selenium ranges from very high within mineralized parts of the zone adjacent to the alteration front boundary to low background values (a few ppm) in areas distant from ore. Greatest values of total iron occur in barren sulfidic sediments (generally near faults); in contrast, mineralized samples appear to be slightly depleted in total iron. Iron disulfide content is high, typically exceeding 1 percent. Greatest abundances typify the mineralized part of the zone, with some samples containing more than 4 weight percent iron disulfide (table 1). Sulfide phases include both pyrite and marcasite that show a distinctive paragenetic sequence and specific morphologies (Goldhaber and others, 1979a; Childs, in preparation). Pyrite replacements of detrital iron-titanium oxide minerals form cores that are typically rimmed by marcasite (fig. 6, A and B). In addition, simple crystals or crystal clusters of pyrite are similarly rimmed by a later marcasite phase (fig. 6, C and D).

Ferric iron (expressed as Fe_2O_3) is also abundant, but depletion in the mineralized zone is indicated. Most significantly, sulfide isotopic analysis shows that resultant values represent the mixture of two end members; at Ray Point, marcasite contains extremely light sulfur ($= \delta^{34}\text{S}$ averaging nearly -55 permil), whereas the pyrite consists of heavy sulfide averaging between +10 and +20 permil (Goldhaber and others, 1979a). New data (Childs, in preparation; M. B. Goldhaber, personal communication, 1980) from the George West district confirm a similar trend. Carbonate content is moderate to high. Carbonate is locally enriched in or near the mineralized part of the sulfidic zone, forming a halo that mimics the roll-front geometry (Galloway and others, in press) (fig. 7). Excess carbonate commonly occurs in disseminated euhedral pore-filling calcite overgrowths on detrital carbonate grains (fig. 6, E and F). Average trace metals content shows little evidence for systematic enrichment,



A



B



C



D



E



F

Figure 6

but scattered, anomalously high values for vanadium, copper, nickel, and zinc may indicate some redistribution or concentration.

Epigenetic Oxidized Zone (EO): Uranium and selenium contents range from moderate to high, slightly exceeding comparable abundances in barren, epigenetically sulfidized ground (table 1). Molybdenum, in contrast, is depleted. Iron content is average and is dominated by ferric species, primarily limonite, which occurs as patchy grain coatings (fig. 8) and disseminations within matrix and rock fragments. Iron-titanium oxide phases are most likely absent, but few samples of epigenetically oxidized sand have been analyzed for heavy mineral content. Carbonate content is variable, but typically low. Trace metals show no evidence of concentration; averages are low to moderate.

Resulfidized Altered Zone (RsAb and RsAm): Uranium and selenium concentrations range from low to quite high depending on proximity to the mineralization front; thus barren and mineralized subzones are distinguished. Molybdenum content is low. Iron abundance is typical of the entire sample suite. Both ferrous and ferric phases are subequally abundant in the mineralized rim, whereas ferric iron dominates in the barren interior of the zone. Total iron disulfide content of resulfidized altered ground is significantly less than that of the epigenetic sulfidic zone (table 1, fig. 7A). Iron disulfide phases and textures are relatively simple. Single and clustered pyrite crystals and

Figure 6. (left) Characteristic diagenetic features of the epigenetic sulfidic zone. A. Partially sulfidized detrital iron-titanium oxide showing twin lamellae that are preserved within the replacement pyrite (p). Entire grain is coated by a marcasite rim (m). B. Completely replaced iron-titanium oxide grain preserving relict twin structure in pyrite core (p). Marcasite rim coats the grain (m). C. Core of authigenic cubic pyrite (p) coated by marcasite rim (m). D. Marcasite cluster with surficial coating of authigenic smectite. E. Euhedral calcite spar pore-filling cement (c) showing faint zoning produced by variable iron content (revealed by staining). F. Euhedral calcite spar cementing detrital sand grains. Scales given by bars in each photograph are as follows: A through C = 0.05 mm, D = 0.01 mm, E = 0.05 mm, F = 0.1 mm. Photos A through C are reflected-light photomicrographs of polished sections; E was photographed under plane polarized light; D and F are scanning electron photomicrographs.

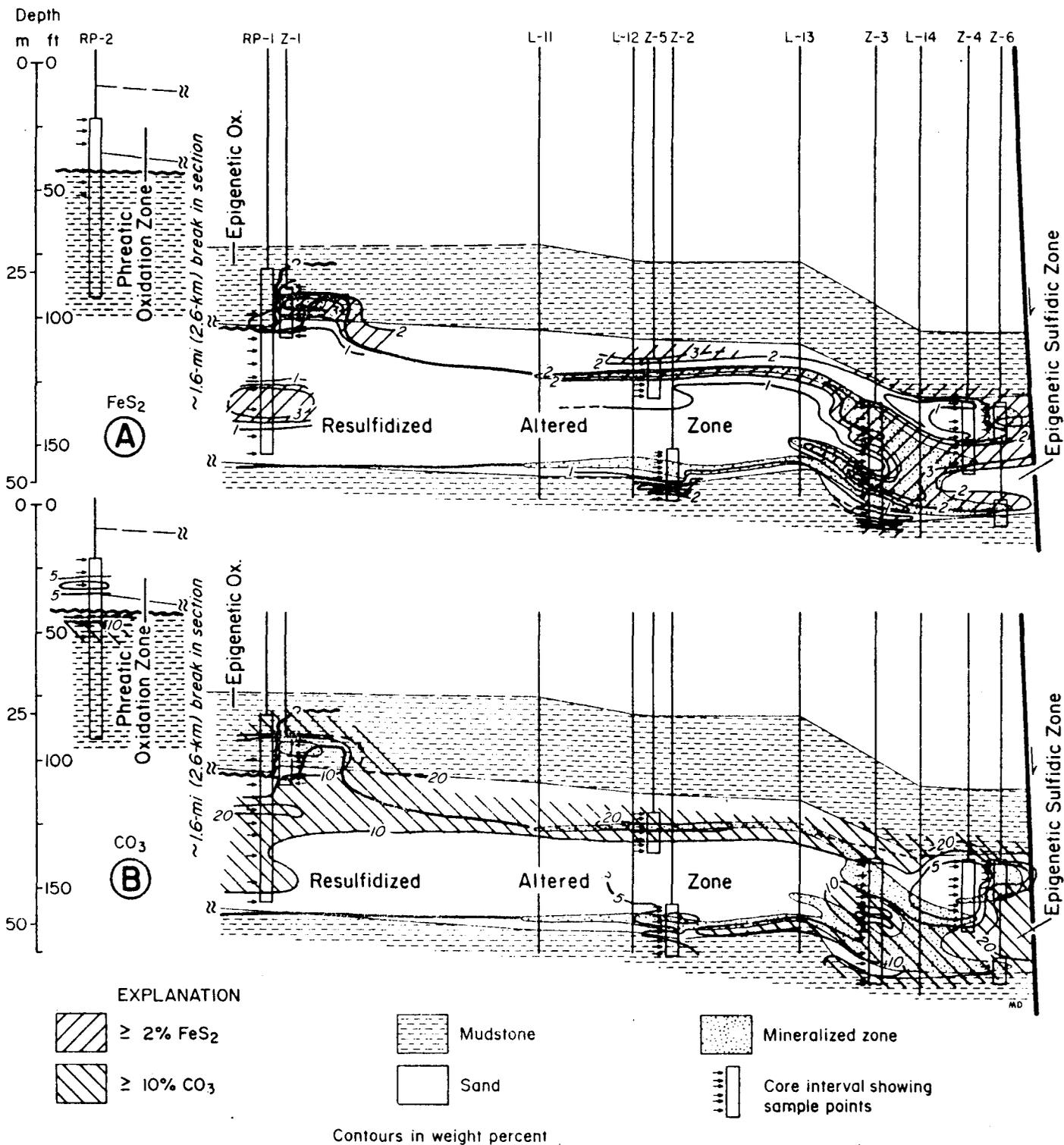


Figure 7. Geochemical zonation along the Ray Point front sample transect. A. Distribution of iron disulfide. Note enrichment typical of the mineralized boundary between the two sulfidic zones. B. Distribution of carbonate showing depletion within the resultidized altered zone. Such depletion is a relict of carbonate leaching associated with advance of the earlier epigenetic oxidation front.

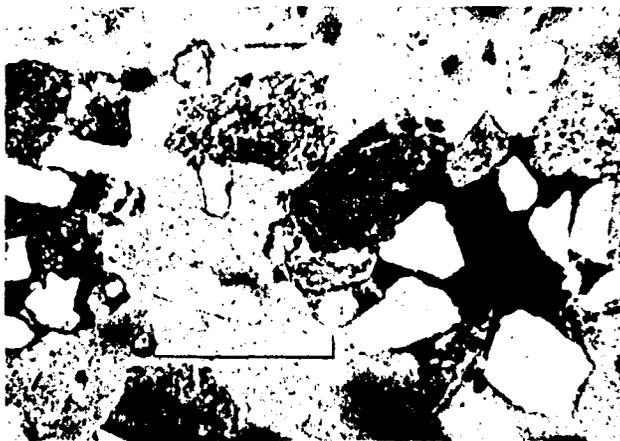
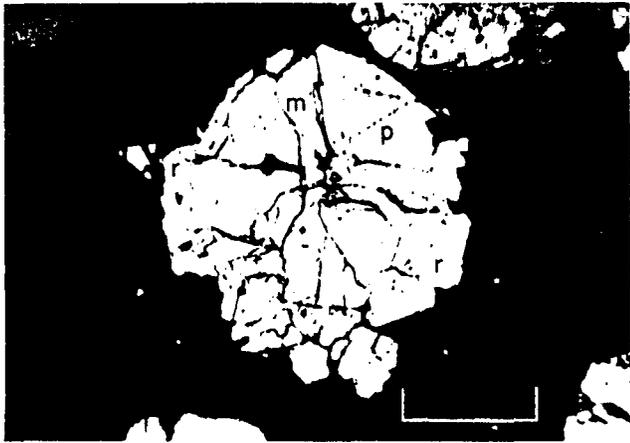


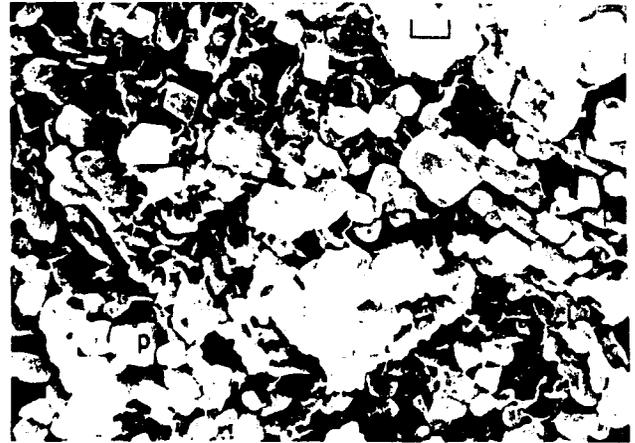
Figure 8. Limonite nest produced by epigenetic oxidation of iron disulfide grain. Plane polarized light; length of bar is 0.5 mm.

intergranular aggregates and pyrite-marcasite intergrowths occur (fig. 9, A-C). Textures indicating sulfide replacement of iron-titanium oxide minerals are notably absent. Sulfur of this zone is characteristically enriched in ^{34}S at both Ray Point and George West, with samples measuring as heavy as +28 permil (Goldhaber and others, 1979a; Childs, in preparation). Other trace metals show a few unusually high values (note especially nickel in table 1). Carbonate is depleted in much of the resulfidized altered tongue (fig. 7B), and particularly low values (less than 6 weight percent) indicate considerable leaching of both the preexisting intergranular calcite cement and the detrital limestone and caliche fragments that characterize Oakville sands (Galloway and others, in press). Such leaching is particularly evident near and within the mineralized subzone (fig. 7B) but may be highly localized and selective (fig. 9D).

Additional Diagenetic Features: Silicate mineral phases also show significant diagenetic modification, including leaching of detrital grains of plagioclase feldspar and volcanic rock fragments and precipitation of smectite clays around detrital grains (fig. 9D). Clay minerals in particular provide a



A



B



C



D

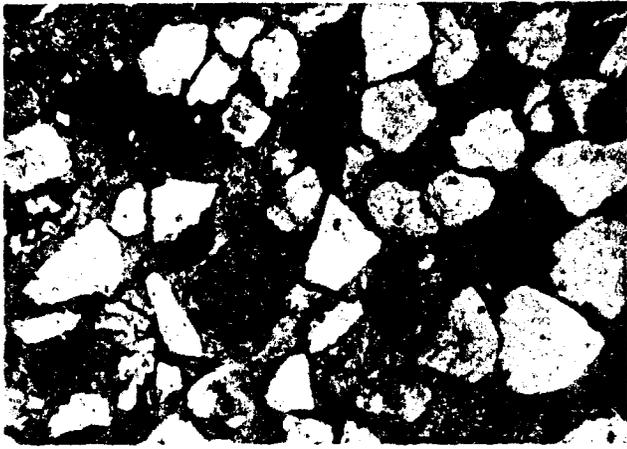
Figure 9. Diagenetic features characteristic of the resulfidized altered zone. A. Intergrown pyrite (p) and marcasite (m) grain with partial later stage rim (r). Note absence of relict detrital iron-titanium oxide core. Reflected light; length of bar is 0.05 mm. B. Scattered euhedral pyrite crystals (p) (in micritic matrix); length of bar is 1 μ . C. Detrital grain aggregates cemented by pyrite (p); length of bar is 0.25 mm. D. Partially etched euhedral calcite spar cement (s) and well-developed authigenic smectite. Note the localized effect of leaching in this sample. Length of bar is 1 μ .

highly reactive phase that has been shown to reflect the geochemical zonation of many uranium deposits. However, montmorillonite is the dominant clay mineral in all Oakville zones, and no pronounced zonation is evident. Traces of kaolinite are, however, more common within epigenetic sulfidic samples at Ray Point (Reynolds and others, 1980a; Galloway and others, in press).

In addition to general trends toward carbonate enrichment in and around the mineralized epigenetic sulfidic zone (fig. 7B), pore-filling and replacement calcite spar (fig. 10, A and B) occurs as local caps or pervasive masses within sand bodies adjacent to faults. Geologic relationships observed along various mineralization fronts suggest that the spar, which may completely occlude all macropore space, can precipitate both before and after ore formation. Isotopic analyses of carbonate-cemented samples, pure vein-filling calcite, and cement-free samples containing only detrital limestone and caliche fragments (table 2) indicate that the carbonate is highly enriched in ^{12}C . Extremely light carbon ($\delta^{13}\text{C}$ less than -30 permil), such as that characterizing the sparry pore and vein fills, is probably produced by oxidation of methane or other hydrocarbons in a regime of shallow ground-water circulation (Goldhaber and others, 1979b). In addition, thin, scattered pods of spar cement occur in many ore bodies and may exhibit moderately light carbon, perhaps reflecting early formation from oxidation of detrital plant debris.

Generalized Alteration Model

Integration of both regional and district alteration characteristics provides the basis for a generalized alteration model for the Oakville fluvial system (fig. 11). Geometry, spatial interrelationships, and diagenetic features establish a sequential paragenetic evolution involving (1) sulfidization of dominantly syndepositionally oxidized sediments along segments of major faults, and (2) partial epigenetic oxidation of the sulfidized sediment accompanied



A



B

Figure 10. Pervasive spar cement locally found in and around faulted parts of the Oakville aquifer. A. Complete cementation of sand by sparry calcite pore fill. Enlarged areas (r) indicate total replacement or recrystallization of detrital grains. Plane polarized light; length of bar is 0.25 mm. B. Blocky calcite pore fill leaving only microporosity along grain boundaries and within pedogenic and authigenic clay rimming detrital grains. Length of bar is 0.1 mm.

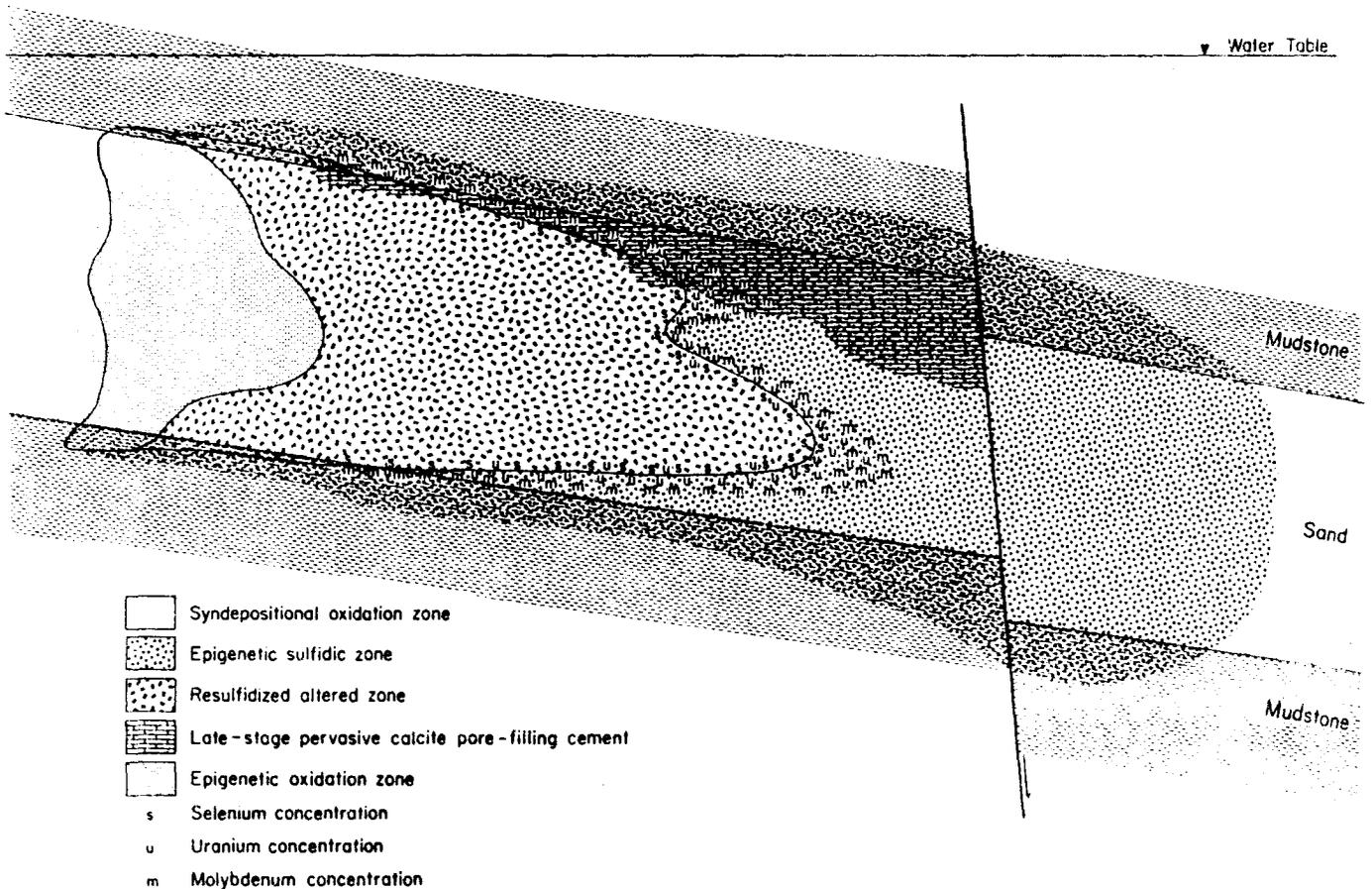


Figure 11. Generalized alteration zonation typical of the Oakville aquifer in the study area. Multiple epigenetic events produce a highly structured geochemical and mineralogic assemblage.

Table 2. Carbon isotope composition of selected Oakville samples
(PDB standard).

	<u>Lithology</u>	<u>^{13}C</u>	<u>Wt. % CO_3</u>
<u>Ray Point District (fault-related cementation and cap rock)</u>			
McL-2	Massive spar vein fill	-33.3	60
McL-5	Massive spar and iron disulfide vein fill	-20.4	60 (estimated)
McL-1	Highly spar-cemented sandstone	-14.9	--
F-1	Spar-cemented sandstone	-14.2	--
Z-3-157	Spar-cemented sandstone	-22.3	25
<u>George West District (Pervasive fault-related cementation)</u>			
GW-1-275	Spar-cemented sandstone	-19.8	27
GW-1-300	Friable sand	-9.9	12
GW-3-290	Spar-cemented sandstone	-21.0	23
GW-3-295	Spar-cemented sandstone	-21.0	23
<u>George West District (cementation not associated with fault)</u>			
P1-520	Spar-cemented sandstone	-7.4	25
P1-620	Spar-cemented sandstone	-19.8	20
P2-460	Friable sand	-6.9	4
P2-487	Friable sand	-7.8	9
P2-600	Friable sand	-8.4	5
P3-620	Friable sand	-6.8	5
P4-604	Leached, friable sand	-15.4	1
P4-625	Friable sand	-8.7	9

by metallogenesis, followed by (3) one or more events of additive resulfidization of all or much of the oxidized ground. Upflow margins of the sulfidic facies exhibit a renewed phase of oxidation that may occur above or below the existing water table. This latest oxidative phase may redistribute existing ore bodies if it encroaches on an existing mineralization front, but it is not characterized by large-scale concentration of uranium or associated metals along its active margin (Henry and others, 1980). In addition, pervasive calcite precipitation, which is also closely associated with fault segments and cuts across the zonal boundaries (fig. 11), may occur within the aquifer at any point in evolutionary development of the other alteration zones.

Specific alteration zones are defined by the oxidation state of contained iron and by textural features of the oxidized or reduced iron mineral phases present. To a lesser degree, abundance and morphology of calcite reflect the zonation. Uranium, molybdenum, and selenium, though principally concentrated at a major zonal boundary (fig. 11), also reflect the zones (Harshman, 1974). Other trace metals and elements show, at best, very poor correlation with alteration zonation.

Complex Zonal Structure

The general alteration model necessitates four discrete epigenetic alteration events--two episodes of sulfidization interrupted by oxidation and metallogenesis, all followed by renewed oxidative encroachment. It would not be surprising if some areas retained evidence for more than two cycles of sulfidic reduction and oxidation. Complex alteration phenomena and zone development are, in fact, recorded by a transect of well cutting samples across a major front in the George West district. The transect (fig. 12) illustrates (1) general mineralogical and geochemical patterns typical of principal alteration zones and their boundaries, (2) complexities that indicate multiple alteration of

separated by a poorly developed front (2) with a dominant upper wing (fig. 12). The lateral continuity and geometry of these individual fronts is documented by a series of parallel drill-hole cross sections along the strike of the mineralization front. In the down-dropped block, a large noselike ore body was penetrated (fig. 12, wells G1 through G3 and P1).

Anomalous values for molybdenum occur primarily downdip of the nose and wings of front 3. Significant selenium concentration occurs mostly updip of this front (fig. 12). However, the trace metal zones overlap and do not reflect a well-ordered pattern typical of most ore-bearing fronts (Galloway and others, in press). Detailed description of zonation is, of course, precluded by the use of drill cuttings. Significantly, analyses do not indicate uranium concentration along the boundary of the updip epigenetic oxidation tongue (E0), although anomalous molybdenum values do occur irregularly within oxidized ground (fig. 12, wells G18 and P4). Uranium concentration along this band of imperfectly superimposed mineralization fronts (approximately 0.5 mi or 0.8 km wide) does not attain ore grade or size. Where fronts merge along strike, however, tenor improves and minable deposits occur.

Copper is the only analyzed trace metal to show enrichment in individual alteration zones. Average copper content is highest in sulfidic ground near the fault (fig. 13), suggesting a genetic association with epigenetic sulfidization. Copper does not, however, show a direct correlation with sulfide or uranium content of individual samples.

Lateral and vertical distribution of iron phases within potential host strata not only defines the major alteration zones (fig. 14A) but also delineates the complex internal structure of the sulfidic zones, further supporting the presence of at least three successive mineralization fronts and associated resulfidized altered interiors (fig. 14B). Maximum sulfide content outlines the roll geometries of the three mineralization fronts. Although total iron content

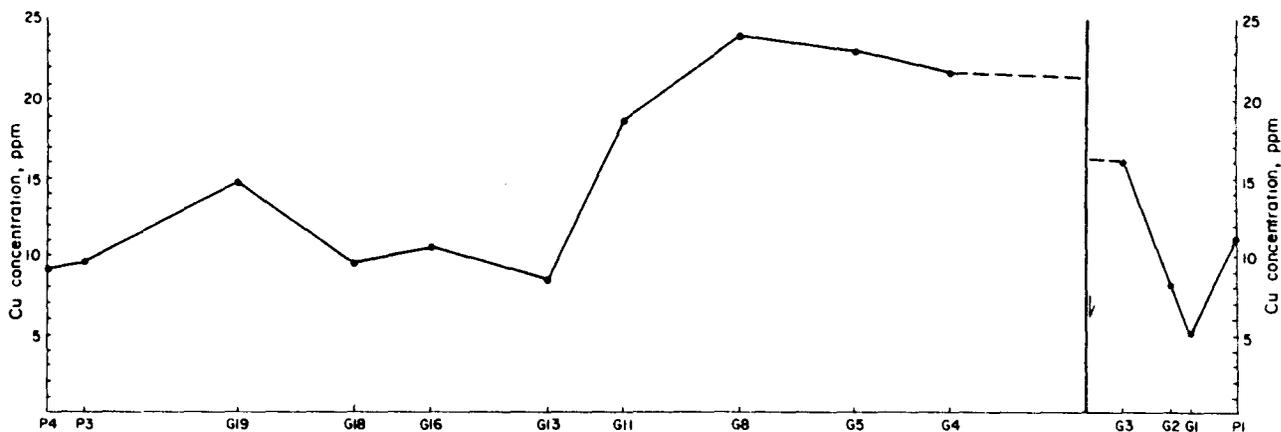


Figure 13. Distribution of copper within the drill cutting sample section averaged by well, although low, shows a marked increase in sulfidic zones near the fault. For well and sample positions, see figure 12.

remains relatively constant updip from the fault, weight percent of iron disulfide decreases systematically across successive resulfidized interiors of the three mineralization fronts (compare average values for wells G4, G11, and G16). Further, distributions of ferrous and ferric iron characteristic of the mineralized sand differ markedly between fault blocks.

Distribution of total carbonate reflects a similar zonation. Both oxidized zones are comparatively depleted of carbonate, as is the interior of each of the successive resulfidized altered tongues. Carbonate-rich halos or ribs outline the downdip margin of each mineralization front, and total average carbonate content increases toward the fault and into zones where epigenetic oxidation was less frequent (fig. 15A). Like that of iron, carbonate distribution within the host sand differs markedly on the downdropped side of the fault, suggesting a different flow history in structurally separated parts of the aquifer.

Development of multiple mineralization fronts and their associated alteration zones is reflected in trace element chemistry and mineralogy, and documents the hypothesis that fluid fluxes responsible for both oxidizing and sulfidizing conditions within the aquifer could recur. Water masses of radically different chemistry and origin have been able, at least locally, to repeatedly flush the

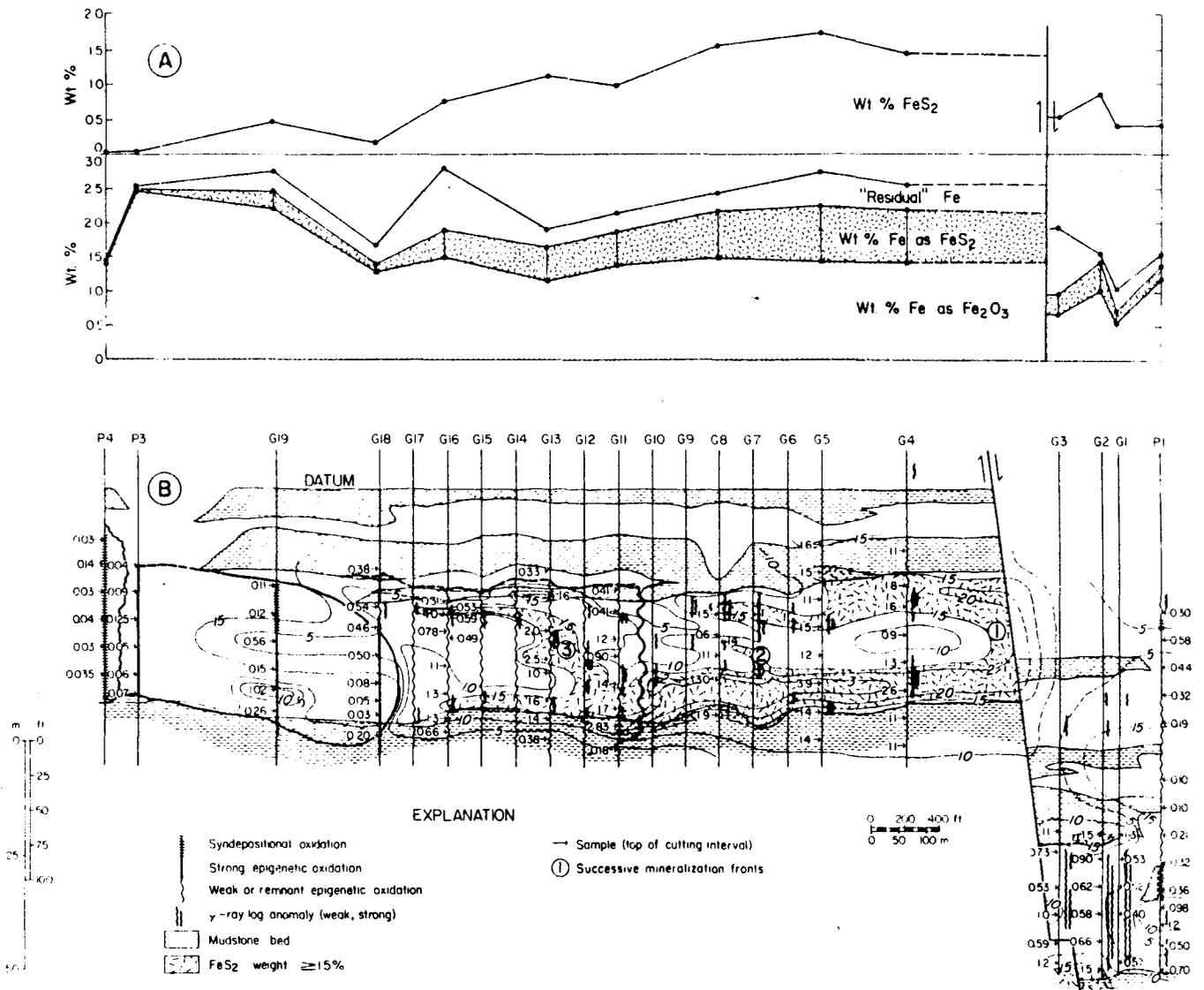


Figure 14. Distribution of iron phases across the complex front shown in figure 12. A. Average iron disulfide content of the sand body increases progressively toward the fault, indicating the additive character of sulfidization. Abundance of oxidized iron (expressed as weight percent Fe₂O₃) is somewhat higher within the epigenetically oxidized zone, then drops to a constant value within sulfidic zones. "Residual iron" reflects a consistent difference between total iron, as determined by inductively coupled plasma emission spectrometry, and treated sample separates designed to remove only sulfide or oxide iron phases. The difference may include iron in relatively insoluble sites not removed by the mineral-specific leaches. Note the contrast in iron content on different sides of the fault. B. Contoured distribution of iron disulfide outlines principal epigenetic zones and emphasizes the increased concentration of disulfide at mineralization fronts (labeled 1, 2, and 3). Greater concentrations of iron disulfide apparent at the base of the sand body are inconsistent with the intrusion of free gaseous hydrogen sulfide; rather, sulfide must have been uniformly distributed in solution in intruded, sulfidizing ground water.

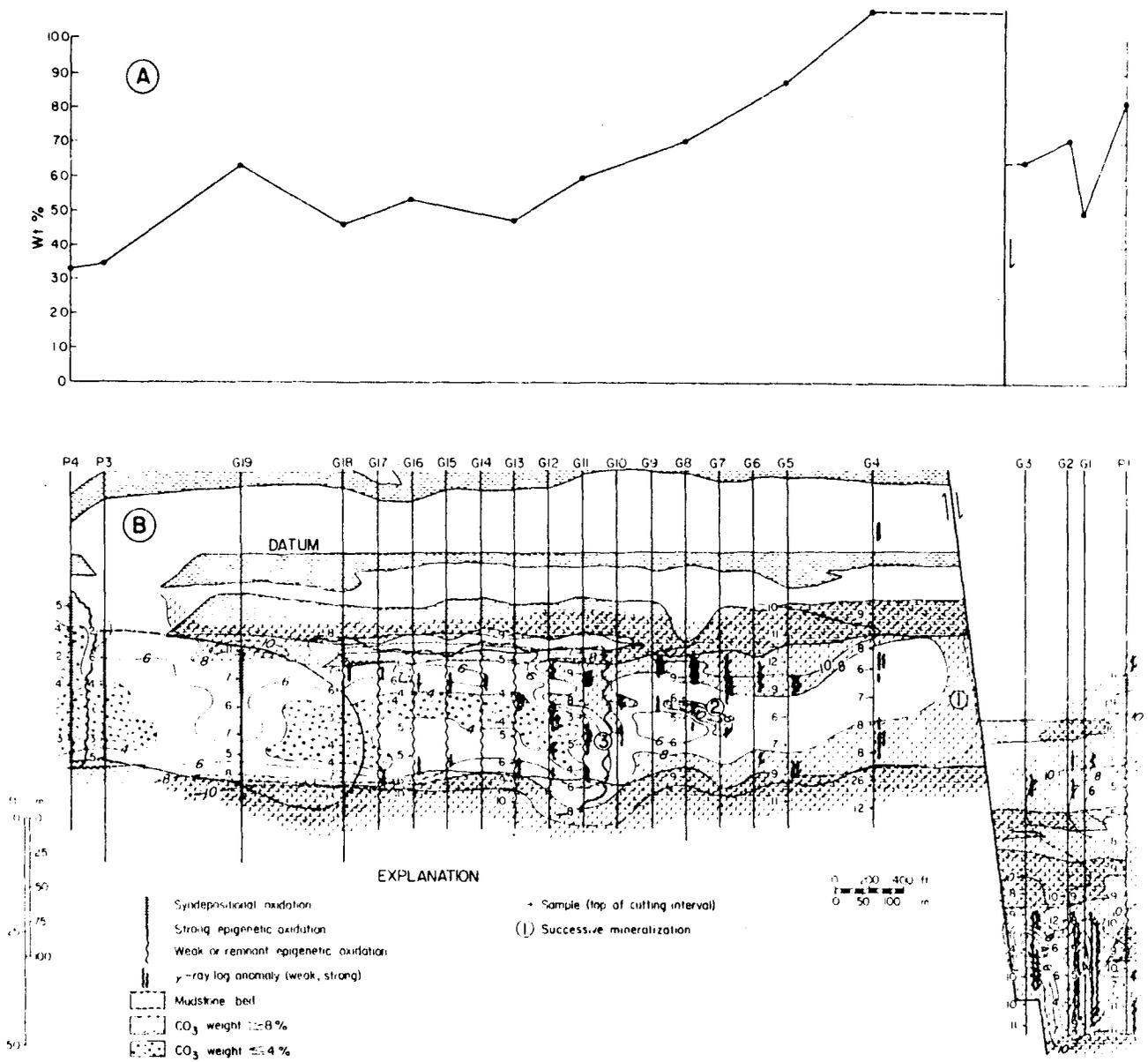


Figure 15. Distribution of calcite, expressed as weight percent CO₃, across the complex front shown in figure 12. A. Average carbonate content increases from oxidized through resultidized to sulfidized zones at the fault, but drops sharply across the fault. B. Two-dimensional distribution of carbonate reflects geometry of both the modern and the older, resultidized oxidation fronts. Carbonate content is greatest at the former noses of mineralization fronts (labeled 1, 2, and 3) and along the top and base of the sand body. Very low values (less than 4 percent) in oxidized and updip resultidized altered zones indicate significant leaching and removal of detrital and early-formed carbonate phases.

aquifer. Evidence of early flushing and sulfidization may be obscured or destroyed by later epigenetic oxidation, leaving only a single, preserved mineralization front along the boundary between oxidized and reduced ground. Multiple fronts, such as those evident in the drill cuttings transect, are preserved only where successive invasions of oxidizing water alter less and less of the sulfidic part of the aquifer.

Implications for Interpretation of Hydrologic History

Any interpretation of the flow history and source of ground waters that have permeated the uranium-bearing fluvial aquifers of the South Texas uranium province must explain the geochemistry and paragenesis of alteration, as well as the origin of the uranium ore itself.

1. Reduction of the hematitic aquifer matrix requires large-scale importation of highly reactive extrinsic sulfide (table 1). The reservoir for this sulfide must be isotopically enriched in ^{34}S . Furthermore, the sulfide must intrude the aquifer in a dissolved state rather than as gaseous hydrogen sulfide, as proposed by Eargle and Weeks (1961) and most subsequent authors; there is no evidence for its segregation as a gas cap, which should produce an increased abundance of iron disulfide in the upper part of sand bodies. On the contrary, sulfide content is commonly high at the base of the sand body in both ES and RSA zones (fig. 14B).

2. Migrating fluids do not introduce large amounts of metals other than uranium, molybdenum, selenium, and arsenic (table 1). Iron content shows no major, systematic variation in zonal abundance. Copper and zinc may be slightly concentrated in sulfidic zones.

3. Similarly, low values of uranium, molybdenum, and selenium in barren sulfidic zones do not support enrichment of these metals by the sulfidizing

waters. Uranium and selenium are, in fact, slightly more abundant in epigenetic oxidized samples, indicating their introduction by the oxidizing ground waters.

4. Sulfidic reduction is spatially associated with fault zones that are characterized by a period of rejuvenated activity during late Tertiary time.

5. Epigenetic oxidation requires importation of oxygen that reacts with iron sulfide to produce ferric oxyhydroxides. Most likely, oxygen is present in the ground waters as dissolved O_2 (Granger and Warren, 1978). By implication, E0 zones record the former existence of a sulfidic zone containing oxidizable pyrite or marcasite.

6. Advance of an epigenetic oxidation front into reduced sulfidic ground is characteristically a leaching event. Both sulfide and carbonate are removed from oxidized ground and partially reconcentrated as newly precipitated mineral phases as ground water flows into the reduced aquifer matrix (figs. 14B and 15B).

7. Geochemical reactions at zone boundaries are primarily Eh and pH dependent. Potentially reactive silicate phases, such as clay minerals, show little relation to zonal patterns.

8. Sulfidization and epigenetic oxidation are repetitive, competing events that record locally complex histories of ground-water flux.

9. Hydrocarbon gases may intrude the shallow aquifers at various times. Local oxidation of hydrocarbons produces highly indurated calcitic concretions and caps within sandstones.

HYDROGEOLOGY OF A COMPACTING BASIN

The complexity of alteration paragenesis within the Oakville aquifer demands successive interactions of geochemically different waters. Intuitively one would assume that two or more different sources, or reservoirs, have

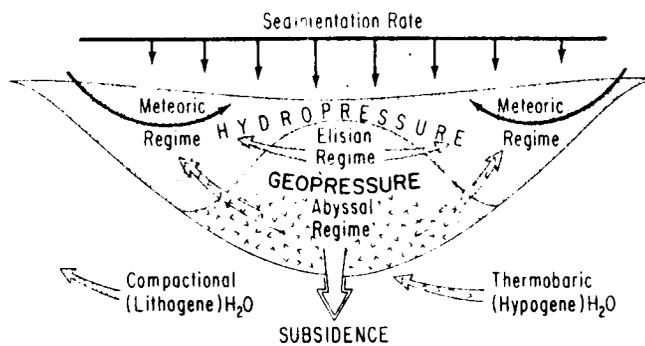


Figure 16. Ground-water regimes in a thick, compacting basin fill.

provided fluids that flushed the aquifer. A review of the hydrochemistry of major ground-water reservoirs or regimes of the northwestern Gulf Coast Basin is the starting point for interpreting fluid flow dynamics.

A general model for the ground-water regimes extant within a thick, compacting depositional basin includes three end members (fig. 16) (Kissin, 1978; Kreitler, 1979). (1) The meteoric regime surrounds the basin margin where surface waters infiltrate permeable strata, recharge aquifers, and move in response to regional, basinward-decreasing, gravitational head. (2) The elisian regime is characterized by upward and outward expulsion of contained pore waters, primarily from compressible, porous, fine-grained sediment, caused by compaction by lithostatic or tectonic stresses. Pressure head is thus the driving mechanism, and waters of this regime may be substantially overpressured if drainage efficiency is restricted by thick, low-permeability units. (3) The abyssal regime includes the deep core of the basin fill where permeability is severely reduced by compaction and cementation and large volumes of water are released by dehydration reactions of detrital mineral phases. Consequently, pressure and temperature are high, and fluids move in response to the pressure head.

Analogous fluid regimes exist within the northern Gulf Coast Basin, though the terminology cited above is rarely applied and boundaries between the regimes

are broad and indistinct. The terminology is useful for this discussion because it focuses attention on potentially important differences in waters found in the basin fill. A shallow meteoric regime extends to depths of 5,000 ft (1,500 m) or more, but is typically most active within the upper 2,000 ft (600 m) of the basin fill (fig. 17). Normal hydrostatic pressures persist to depths of 8,000 to 12,000 ft (2,500 to 3,700 m), although sediments continue to consolidate by both compaction and cementation. Expulsed pore waters constitute lithogene brines and are the dominant fluids within this elisian, or compactional, regime (fig. 17). With increasing depth, and commonly with decreasing sand content, drainage becomes highly restricted and expulsed fluids cannot readily escape; consequently, abnormal pressure, or geopressure, develops (Jones, 1975). Concomitantly, the thermal gradient increases, clay dehydration reactions accelerate, in situ fluid pressures approach lithostatic pressure, gas generation accelerates, and microfractures probably develop. This suite of events and reactions is typical of the abyssal regime (Bogomolov and others, 1978) and suggests that the deeply buried section lying well within the zone of so-called "hard" geopressure can be classified as "abyssal" (fig. 17) for the purposes of this discussion, although it is somewhat shallower and cooler than commonly implied by the term.

Hydrochemistry of Ground-Water Regimes

The three ground-water regimes provide potentially geochemically distinct reservoirs. The hydrochemistry of the meteoric regime is best known and documented. Compactional waters of the elisian regime, typical oil field brines in the Gulf Coast Basin, have also been subject to considerable routine geochemical analysis (Texas Water Development Board, 1972; White, 1965). Recent exploration for hot (300°F, 150°C) gas-charged, geopressured water and diagenetic studies in the Gulf Basin are beginning to reveal the hydrochemistry of deep

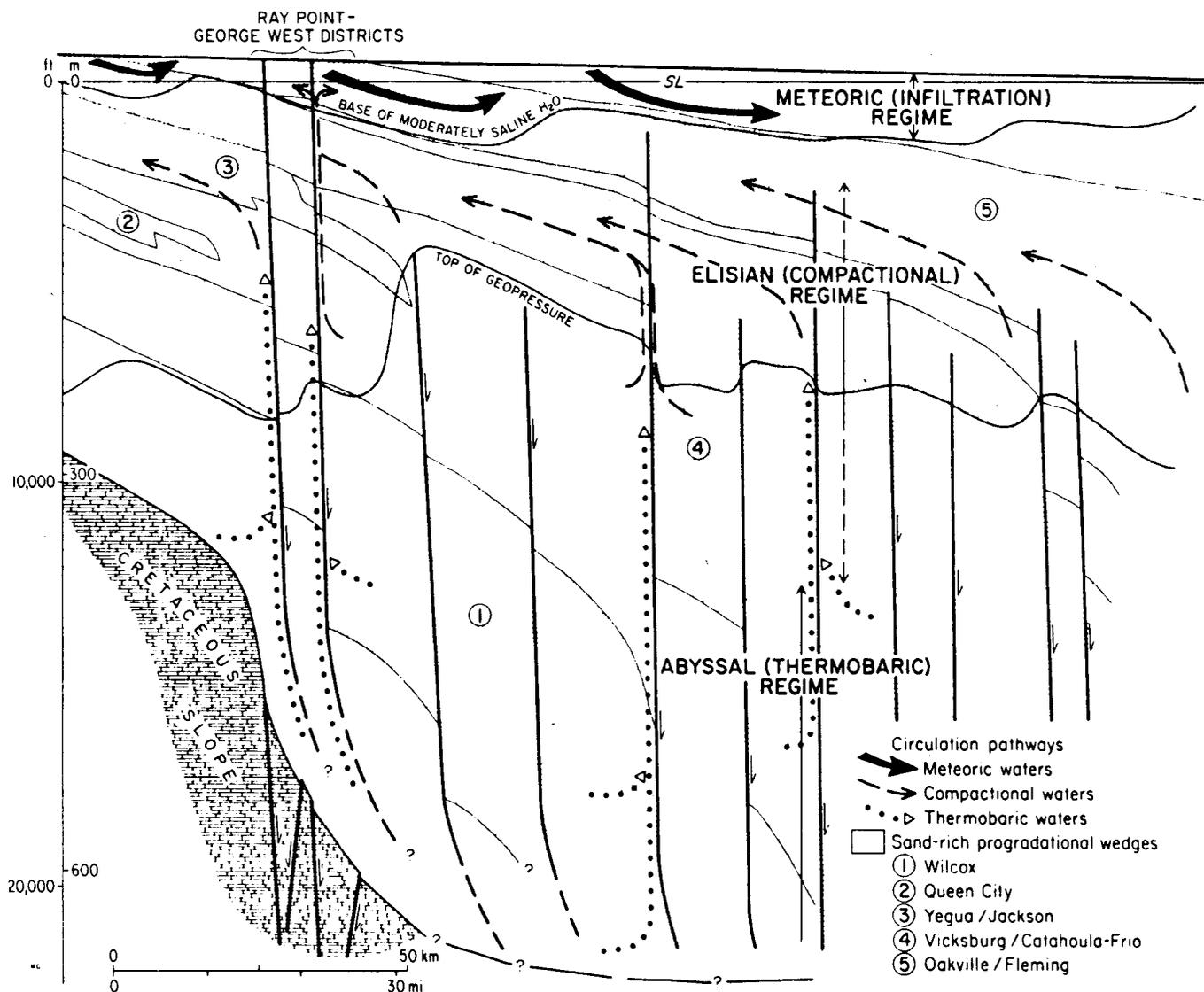


Figure 17. Ground-water regimes and circulation pathways within the offlapping Tertiary basin fill of the northwestern Gulf Coast Basin. Major growth fault zones developed within successive progradational cycles that extended the continental platform basinward of the Cretaceous shelf edge.

thermobaric fluids of a modified abyssal regime (Dorfman and Fisher, 1980; Prezbindowski, in preparation).

Abyssal Regime Fluids

Thermobaric fluids, including waters, solution gases, and free gases, occur within two significantly different types of basin fill. Cretaceous forereef slope and basinal carbonate and shale units form the stratigraphic under-

pinnings of the thick clastic Tertiary section (fig. 7). Lying at depths exceeding 20,000 ft (6,000 m), these faulted forereef deposits have been penetrated by the drill only along their updip margins inland of the major overlying Oakville uranium districts (fig. 1). Thick continental slope, prodelta, and down-faulted delta margin Paleocene and early Eocene mudstone and minor sandstone form the bulk of the overlying hot, geopressured regime.

Thermobaric waters are hot, moderately to highly saline, sodium chloride brines. Total dissolved solids content ranges from near 10,000 to more than 200,000 mg/L (Gustavson and Kreitler, 1977; Prezbindowski, in preparation). Greatest values occur in parts of the Coastal Plain characterized by salt diapirism; consequently, lower values typify deep brines in the South Texas uranium province. Very few systematic data on the trace element content of abyssal or near-abyssal brines are available. Reports in Dorfman and Fisher (1980) provide the most complete data available but reflect a sampling bias toward the central Gulf Coastal Plain, northeast of the uranium province. Dissolved uranium values from analyses of six downdip geopressured brines from Oligocene and Miocene reservoirs range from 0.003 to 0.03 g/L (T. Kraemer, personal communication, 1980). Although the Eh of these very deep waters has not been measured, they can be confidently inferred to be reducing relative to iron because of the presence of sulfide and common occurrence of pyrite in the host sediments. Data, though scanty, are summarized in table 3.

The abyssal regime is a major reservoir of gases; light hydrocarbons (principally methane), hydrogen sulfide, and carbon dioxide are actively generated by thermal degradation of organic debris at the temperatures characteristic of this zone (Hunt, 1979). High concentrations of hydrogen sulfide, which is extremely soluble in subsurface waters, occur primarily in carbonate reservoirs. In sand-shale sequences, abundantly available iron reacts with reduced sulfur species to form iron disulfide, thus removing sulfide from solution. Analyses of deep

Table 3. Geochemical characterization of principal ground-water regimes of the northwestern Gulf Coastal Basin. (mg/L unless otherwise noted).

	Meteoric	Elisian	Terrigenous	Abyssal	Carbonate
Depth range (generalized)	0-2,000 ft; 5,000+ max 0-600 m; 1,500+ max	2,000-12,000 ft ± 600-3,600 m ±	<12,000 ft ± <3,600 m ±		<20,000 ft <6,000 m
TDS	10 ² -10 ⁴	10 ⁴ -10 ⁵	10 ⁴ -10 ⁵		10 ⁵
Ca	10-10 ³	10 ² -10 ⁴	10 ² -10 ⁴		10 ⁴
HCO ₃	10 ² -10 ³	10 ²	10 ² -10 ³		n.d.
SiO ₂	10 -10 ²	10 -10 ²	10 -10 ²		n.d.
Fe	10 ⁻¹ to <10 ⁰	≤10	10 ⁻¹ -10		10 ³ -10 ⁴
Heavy metals (Cu, Zn, Pb, Ni)	<10 ⁻¹	<10 ⁰	<10 ⁻¹ -10		10-10 ² + (Zn; Pb)
Se, Mo, As	<10 ⁻²	≤10 ⁻²	<10 ⁻²		n.d.
U ₃ O ₈	≤10 ⁻¹	n.d.	≤10 ⁻⁵		n.d.
SO ₄	10 ¹ -10 ³	<10 ⁰ -10 ²	10 ⁰ -10 ²		10 -10 ²
H ₂ S, HS ⁻	≤10	<10	<10 ⁻² mol % in gases; ≤10 ⁰		10 ⁻² to 10 ⁻¹ mol % + in gases
Eh	+500 to -200 mV	Reducing	Reducing		Reducing
pH	6.8 - 8.2	5.5 - 7.5	4 - 6.5		n.d.

Data compiled from analyses in Galloway and others (in press), Dorfman and Fisher, eds. (1980), Prezbindowski (in preparation), Gustavson and Kreitler (1977), Kharaka and others (1977), and White (1965).

brines confirm these predictions. Hydrogen sulfide is a measurable constituent (0.2 to 0.04 mole percent) in gases produced from forereef Edwards Limestone reservoirs along the Wilcox fault trend (Moredock and Van Siclen, 1964). Hydrogen sulfide produced with deep Edwards hydrocarbons is isotopically enriched in ^{34}S , as is typical of deep, thermal sulfide (Goldhaber and others, 1979a). As predicted, hydrogen sulfide is rarely present in measurable quantities (less than 0.01 mole percent) in gases produced from Gulf Coast sand reservoirs, and typically measures less than 5 mg/L in produced waters (Kharaka and others, 1980). Carbon dioxide content of gases from both limestone and sandstone reservoirs of the abyssal regime averages several mole percent; methane is the dominant constituent. Both gases are highly soluble in brine.

Elisian Regime Fluids

Compactional fluids of the elisian regime include sodium chloride brines, hydrocarbon liquids, and gases. Waters do not vary greatly from their deeper Tertiary counterparts in overall composition (table 3) and are of the marine connate type (Kharaka and others, 1977).

Concentration of hydrogen sulfide is low. Significant hydrogen sulfide generation from buried organic matter begins at temperatures above approximately 250°F (120°C) but increases substantially with further increases in temperature to a peak somewhere above 338°F (170°C) (Hunt, 1979) within the abyssal regime. Thus both waters and gases of the elisian zone are sweet; further, solubility of gases at the lower pressures decreases. Produced gases commonly contain 0.1 to 1 mole percent carbon dioxide. The hydrocarbon fraction includes abundant methane plus heavier fractions, distillate, and liquid petroleum. Most produced hydrocarbons of the Tertiary Gulf Coast Basin, and essentially all oil, are contained within the elisian zone.

Measured values of fluid pH commonly range between 6 and 8 (White, 1965; Kharaka and others, 1977), and the rock is dominantly reduced, containing iron disulfide or dispersed organic material, or both.

Meteoric Regime Fluids

The geochemistry of waters of the meteoric regime is the best known; Oakville waters (table 3) specifically have been extensively analyzed (Henry and others, 1980 and in press). Meteoric waters are typically fresh to brackish, mixed calcium-sodium bicarbonate-chloride types. Downflow from the outcrop recharge zone several geochemical gradients are apparent.

1. Bicarbonate increases moderately.
2. Chloride and total dissolved solids content increase markedly.
3. The sodium to calcium ratio increases as the absolute amount of calcium decreases.
4. Generally pH increases gradually from about 7 to 8 (fig. 18).
5. Eh decreases typically abruptly (fig. 18) producing three regional Eh plateaus centered around +400, +50, and -100 mV (fig. 19). Dissolved oxygen decreases to below detection limits within the intermediate plateau (fig. 18).
6. Dissolved sulfide (measured as H₂S) remains below detection limits or locally may increase to a few mg/L (fig. 18). Ground-water sulfide in the Ray Point district is isotopically light, with $\delta^{34}\text{S}$ ranging between -35 and -60 permil, as would be expected from either bacterial or inorganic reduction of ground-water sulfate (Goldhaber and others, 1979a).

Content of trace metals is typically low to very low, except near ore deposits. Background uranium, molybdenum, and selenium values are generally less than 5 ppb, 10 ppb, and 1 ppb, respectively. Uranium and selenium are most mobile in shallow oxidizing waters; molybdenum is mobile throughout the range of Eh and pH conditions typical of modern Oakville meteoric ground waters (fig. 18).

OAKVILLE AQUIFER-CENTRAL TEXAS PROFILE

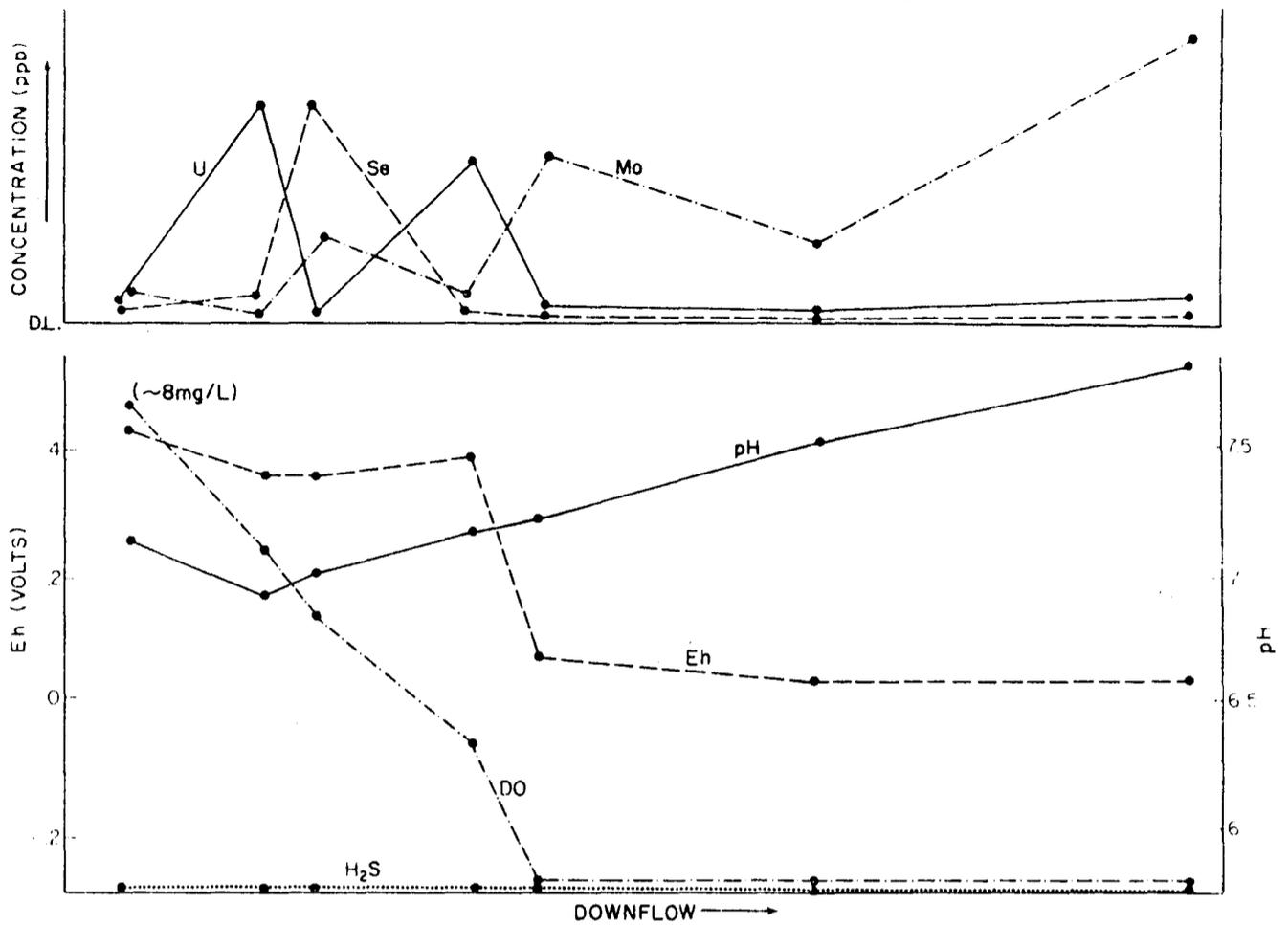


Figure 18. Typical downflow geochemical evolution of meteoric ground water. From data in Henry and others (in press).

Hydrocarbon gases have been encountered by shallow drilling, indicating the probable presence of local pockets or caps of methane within shallow aquifer sand bodies.

Regime Interactions

The four described fluid regimes in the Texas Coastal Plain contain water masses that exhibit some geochemical differences pertinent to interpretation of alteration phenomena. (1) Only the meteoric regime contains large volumes of oxidizing water. Abyssal and elisian waters are uniformly reducing as evidenced

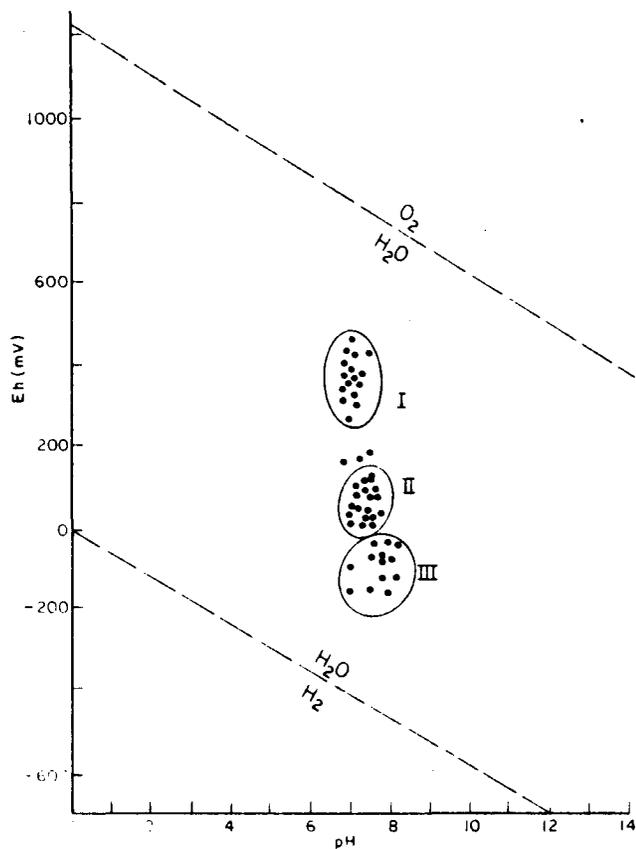


Figure 19. Plateaus of Eh characteristic of the meteoric ground-water regime of the Oakville aquifer. Modified from Henry and others (in press), figure 50.

by presence of soluble sulfide, ammonia, and methane. (2) Circumstantial as well as some analytical data indicate that only deepest fluids of the abyssal regime, primarily those contained in Mesozoic carbonates, contain significant volumes of hydrogen sulfide in both gaseous and dissolved forms. (3) None of the water masses is highly enriched in uranium or other trace metals commonly found in or around uranium mineralization fronts.

Of the three regimes, the meteoric system is by far the most dynamic. Local segments of the Oakville and underlying Catahoula aquifers do exhibit anomalous compositions and concentrations of dissolved solids that are interpreted to indicate active or recent discharge of deeper brines into the meteoric circulation system, commonly along fault zones (Galloway and Kaiser, 1980; Galloway

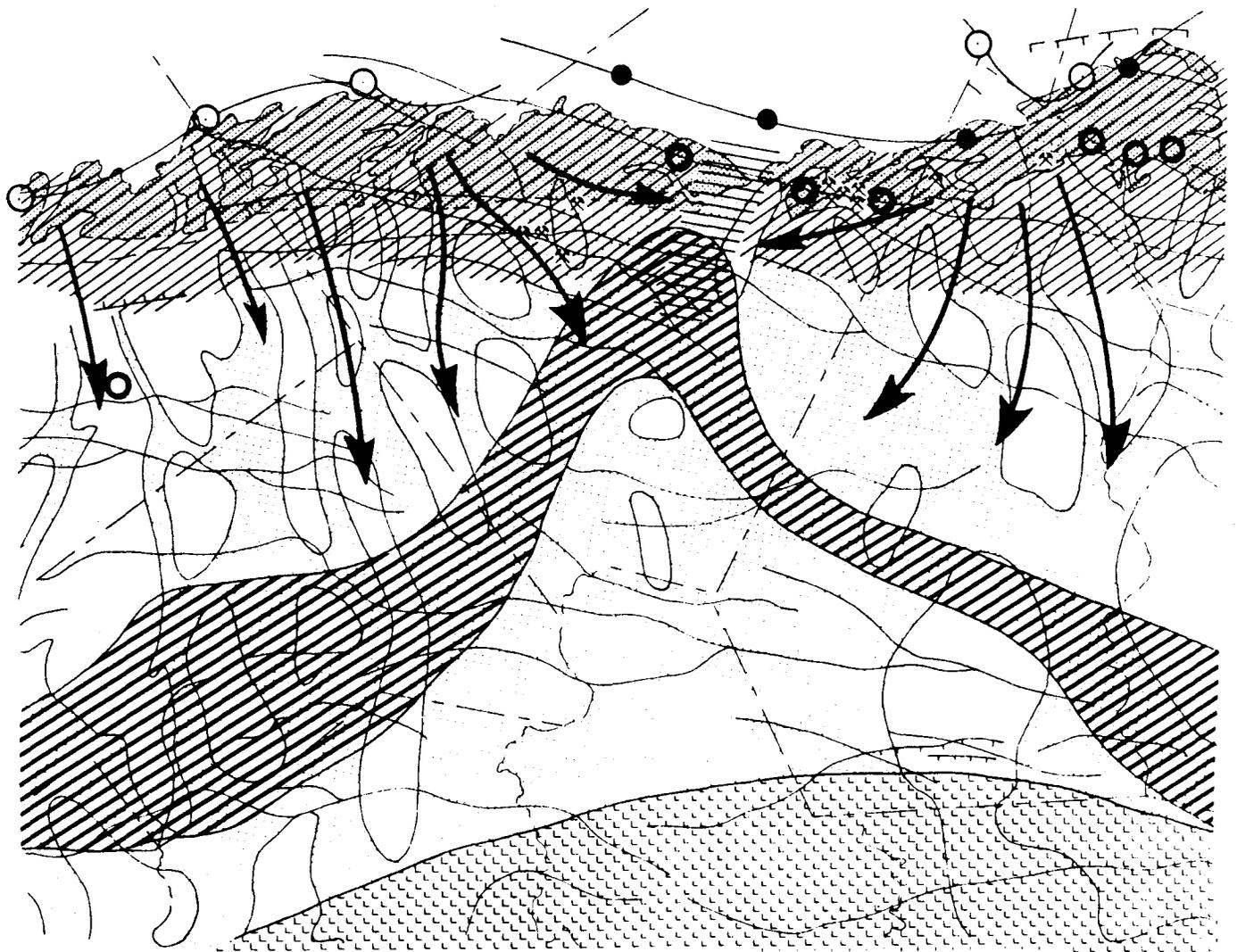
and others, in press). The deep-seated growth faults provide the most obvious vertical conduits for localized upward discharge of both deep compactional and thermobaric fluids (fig. 17). Geophysical data suggest that the deep slope and basinal limestone substrate is broken by faulting (C. Winker, personal communication, 1980; Wooten and Dunaway, 1977). Within normally pressured sand-rich parts of the elisian regime, compaction waters can also move updip relatively freely within deltaic and fluvial sand bodies producing broad, diffuse mixing zones where they encounter the active meteoric regime.

DYNAMICS OF ORE GENESIS

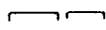
Rigorous reconstruction of evolving fluid flow dynamics must integrate the record of geochemical changes preserved within alteration zones with the known geochemical attributes and the flux patterns of fluids derived from available reservoirs in the ground-water regimes. The modern, and therefore observable, hydrogeology provides the logical beginning for the reconstruction.

Modern Flow Dynamics and Hydrochemistry

The shallow Oakville aquifer system is characterized, in Live Oak County, by development of two intermediate flow cells that collect meteoric recharge and move it basinward and along strike toward a focus of discharge along the topographically low Nueces River valley in the east-central part of the county (fig. 20). Dip-oriented, regional flow cells characterize the aquifer across southernmost Live Oak County and northward in adjacent Bee County. The result of an intermediate flow system within the regional coastward pattern is a major updip salient of saline water coincident with the highly transmissive George West fluvial axis (fig. 20).



HYDROLOGIC BOUNDARIES

-  Cretaceous fault zone
-  Tertiary fault zones
-  Oakville outcrop
-  Sand isolith trends

0 10 20 30 km
0 10 20 mi

HYDROLOGIC ZONES

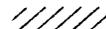
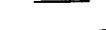
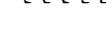
-  Surface recharge zone
-  Generalized discharge zones for subjacent aquifers
-  Recharge from underlying aquifer
-  Discharge of intermediate flow cells
-  Regional discharge zone
-  Relict or intruded connate brine (TDS ≥ 7,500 mg/L)

Figure 20. Modern ground-water flow directions and boundaries of the Oakville aquifer in Live Oak and adjacent counties. Principal recharge occurs along the outcrop and shallow subcrop by infiltration of meteoric water, and by some discharge from deeper aquifers. Waters move basinward in regional flow cells, or toward the topographically low Nueces River Valley in intermediate flow cells. At depth waters are discharged upward into overlying aquifers.

Interpreted flow directions within the George West district (fig. 4A) conform closely with the intermediate-scale flow pattern. In the Ray Point district (fig. 4B) faults and topographic irregularities produce complex local flow cells that may be further compounded by discharge of more saline waters into the Oakville from deeper meteoric aquifers (Smith and others, 1980).

Regional patterns of epigenetic oxidation (fig. 3) are consistent with the commonly accepted interpretation that flux of oxidizing ground water is at least partly responsible for the development of limonitic alteration in the aquifer. Hydrochemical profiles across alteration zones in the George West district (fig. 21) further confirm this assumption. Measured Eh values greater than +200 mV and dissolved oxygen values greater than 5 ppm (Henry and others, 1980) prove that the actively circulating ground waters are aggressive, oxidizing fluids at depth in confined parts of the aquifer. Dissolved oxygen disappears, Eh drops markedly, and traces of hydrogen sulfide appear where such waters flow into reduced, sulfidic alteration zones (fig. 21). Although modern flow is dominantly subparallel to the inferred alteration zone boundaries, a vector component of cross-flow exists, particularly along the updip mineralization fronts (fig. 4A). Hydrochemical zonation accordingly is better defined along the updip part of the profile (fig. 21, wells 65 through 80).

Calculated saturation indices are also consistent with expected mineralogical changes associated with development of epigenetic oxidation fronts. Waters remain essentially saturated with respect to silica gel, chalcedony, and calcite, showing no apparent zonation (fig. 21). Indices for clay mineral phases show no consistent lateral changes (however, significance of such calculations is limited by the generalized thermodynamic properties that must be used). As expected, iron oxyhydroxide, expressed as amorphous $\text{Fe}(\text{OH})_3$, is supersaturated with respect to waters exhibiting a positive Eh, and thus is potentially forming

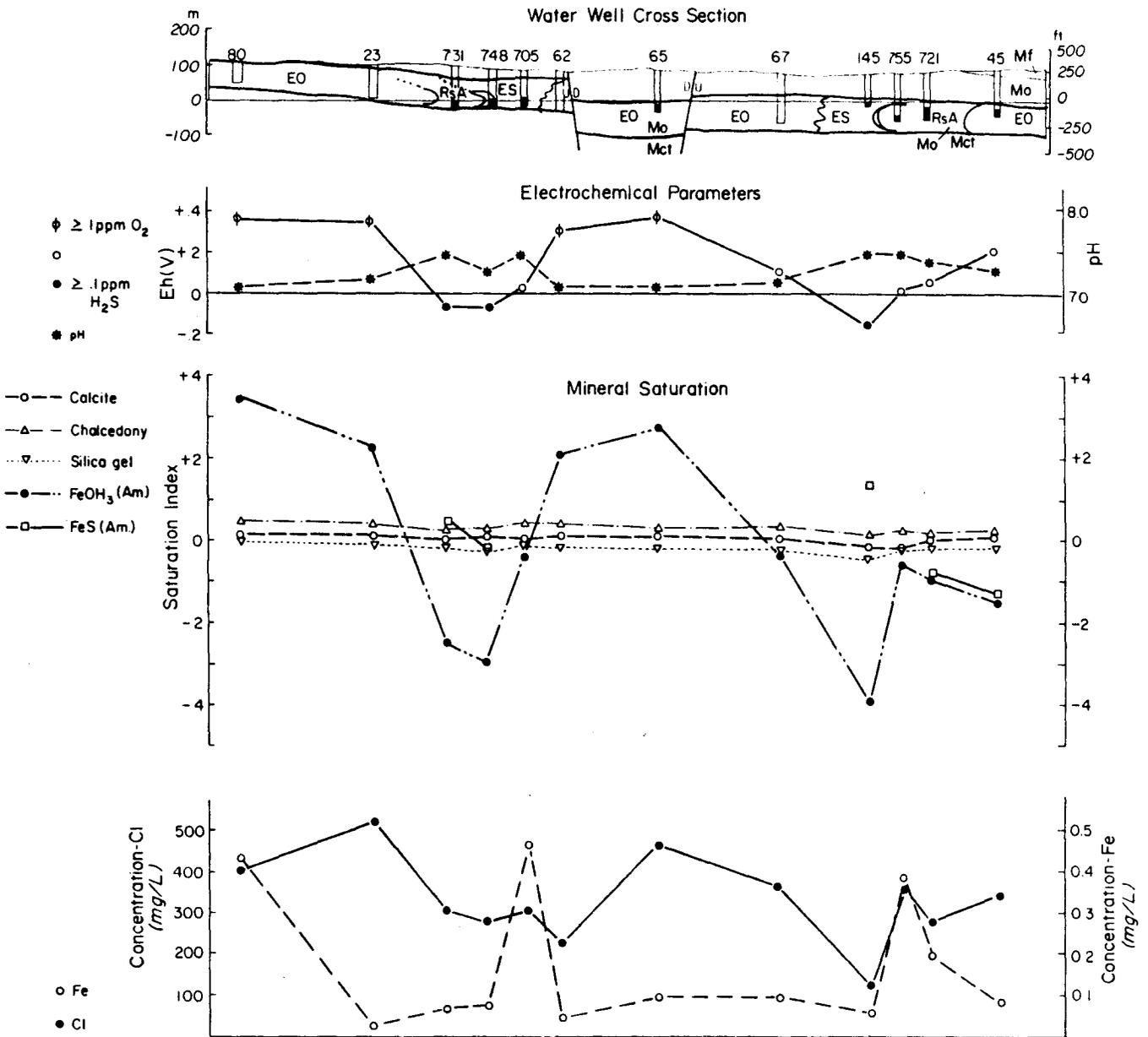


Figure 21. Water well cross section through the George West district showing lateral variation in hydrochemistry and saturation indices of potential reactive mineral phases characteristic of the modern meteoric ground waters. Data show that modern waters are aggressively oxidizing parts of remaining sulfidic zones and are capable of precipitating iron oxide and sulfide phases in the process of this oxidation. Data from Henry and others, in press. For section location, see figure 4.

in the epigenetic oxidization zone. Iron oxyhydroxide is undersaturated within sulfidic zones (fig. 21). Conversely, where measurable amounts of sulfide are present, amorphous iron monosulfide is slightly to moderately supersaturated, confirming the possibility of additional sulfide precipitation. The iron sulfide phase actually precipitated is unknown. Density of well samples does not show whether a local pH drop characterizes the active oxidation interface. Such a sharply reduced pH produced by rapid oxidation of iron disulfide is believed necessary for the precipitation of marcasite noted along mineralized oxidation fronts (Goldhaber and Reynolds, 1979; Galloway and Kaiser, 1980) and would account for the observed leaching of calcite from the epigenetic oxidation zone.

Uranium content in the oxidizing waters is low, averaging about 5 $\mu\text{g/L}$ (Henry and others, in press). This value is nearly an order of magnitude below that commonly believed typical of an ore-forming ground water (Granger and Warren, 1978), an observation consistent with the lack of evidence for metallogenesis along modern oxidation front margins that lie upflow from existing deposits (fig. 12).

In summary, flushing by modern meteoric ground water is actively producing or expanding epigenetic oxidation tongues. Minor amounts of isotopically light sulfide that are produced as waters move into reduced parts of the aquifer (Goldhaber and others, 1979a) do not, however, account for the widespread development of isotopically heavy sulfidic alteration, nor does evidence favor modern waters as a primary ore-forming fluid.

Dynamics of Epigenetic Sulfidization

The importation of large volumes of isotopically heavy, dissolved sulfide is the definitive attribute of epigenetic reduction in shallow Gulf Coast fluvial aquifers. A simple calculation using geochemical data from the George West district (table 1); the inferred area of sulfidic alteration (fig. 3), and

reasonable solubilities of hydrogen sulfide in shallow and deep ground waters (Hunt, 1979, p. 170 and 391) shows that only a few pore volumes of thermobaric water from Mesozoic carbonate reservoirs could be responsible for the extensive sulfidic alteration (table 4). In contrast, several thousand pore volumes would be required for equivalent importation of sulfide by typical shallower abyssal or elisian waters from Tertiary clastic reservoirs. For comparison, hydrologic data (Galloway and others, in press) show that the meteoric flow system flushes the same area of lower Oakville aquifer with about one pore volume every 2,000 years. Thus, flushing by sulfide-enriched abyssal brines derived from the deep carbonate reservoir is most reasonable in both time and space, and is supported by isotopic typing of the sulfide.

Kharaka and others (1977) noted a slight increase in dissolved hydrogen sulfide in some thermobaric waters produced by condensation of steam and gases at the well head. Such condensed water vapors are quite acidic (pH 5.1 to 5.2), extremely fresh, and charged with ammonia and organic acids as well as up to 6 mg/L hydrogen sulfide. The very hot fluids, which are liquid under the high geopressures of the deep subsurface, vaporize during rapid pressure decline associated with natural gas production. Such a process could conceivably act naturally if fluid pressure were abruptly released along an active fault. However, the low hydrogen sulfide content of gases from clastic reservoirs, along with the few well test data reported, suggests that hydrogen sulfide content in the resultant shallow, condensed waters increases by less than an order of magnitude. Isotopic analysis of sulfur from shallower, terrigenous clastic reservoirs would further test the suitability of this potential source. In either interpretation, the mechanics of upward migration of such deep-seated fluids along faults poses a challenging problem; however, no viable alternative reservoir of sulfide seems to exist.

Table 4: Volumes of sulfide and associated water required for sulfidization of the lower Oakville aquifer in the George West district and environs.

Assumptions

Area	=	192 km ²
Thickness	=	100 m
FeS ₂ content	=	0.5 wt %
Bulk specific gravity of sand	=	2.0 g/cm ³
Porosity	=	30 %

Calculations

Volume of sulfidized zone	=	1.9 x 10 ¹⁰ m ³
Pore volume of sulfidized zone	=	5.8 x 10 ⁹ m ³
FeS ₂ content of sulfidized zone	=	10 kg/m ³
	=	1.9 x 10 ¹¹ kg
Total sulfur content	=	1.0 x 10 ¹¹ kg

Conclusions

For Tertiary abyssal waters (H₂S=1 mg/L), 10¹⁷ L or 1.7 x 10⁴ pore volumes of water must be discharged into the shallow aquifer.

For Mesozoic abyssal waters (H₂S=10³ to 10⁴ mg/L), 10¹⁴ to 10¹³ L or 17 to 1.7 pore volumes of water must be discharged into the shallow aquifer.

A part of the upward-migrating fluid might include gases. However, Reynolds and Goldhaber (1978) show that diffusion rates of gases, once in the shallow aquifers, are inadequate to explain the wide-scale sulfidization far removed from faults actually observed. Further, solubility of hydrogen sulfide and other gases in shallow ground waters, though high, is limited. Direct leak-

age of large volumes of gas would be expected to form a gas cap, which is not evidenced by the generally homogeneous distribution of iron disulfide within the aquifer. Evidence favors large-scale expulsion of abyssal waters highly charged with dissolved sulfide along fault zones and subsequent updip, lateral, and some downdip migration along highly transmissive parts of the shallow fluvial aquifers.

Flow Dynamics of Aquifer Metallogenesis

Uranium mineralization and associated epigenetic zonation of fluvial aquifers of the South Texas uranium province record a sequential interplay of meteoric and thermobaric waters. Three different reservoirs are represented. Meteoric waters may contain either large or small amounts of metals; both varieties were capable of producing limonitic alteration. Sulfide-rich abyssal waters produced both replacement and authigenic pyrite within invaded parts of the aquifer system, leaving reduced sands and bounding mudstones. The complex, polycyclic structure of some alteration fronts preserves the evidence for recurrent flushing by both meteoric and abyssal waters.

Figure 22 provides a graphic summary of the principal epigenetic events and flow phenomena that are recorded by alteration and metallogenesis in the Oakville Sandstone of Live Oak County.

1. During and immediately after deposition of lower Oakville fluvial sands of the George West axis, shallow, unconfined to slightly confined, oxidizing meteoric ground water flushed much of the aquifer (fig. 22A). Such waters might have contained uranium and associated metals, but syngenetic geochemical barriers were poorly developed in the dominantly oxidized and leached suite of lithofacies.

2. The first of a series of pulses of thermobaric waters invaded the aquifer (fig. 22B). The reducing waters, moving in response to the extreme pres-

sure head developed within the faulted, geopressured Mesozoic carbonate section, spread laterally through the shallow aquifer. Sulfide reacted with iron, producing epigenetic pyrite in decreasing abundance away from the feeder fault zone or zones. In addition to the abundant sulfide and possible additional iron contained in the thermobaric waters, excess silica, as well as other major anions and cations, may have reacted with the aquifer matrix. However, pervasive diagenetic phases directly related to this event are not apparent. Small but significant amounts of trace metals, including copper, zinc, lead, and nickel, may have been introduced. Data do not convincingly prove general trace metal enrichment in sulfidized ground, but local anomalies do occur. This flushing and associated reduction was a critical precursor for subsequent large-scale uranium concentration.

3. Following the intrusion of the aquifer by thermobaric waters, normal coastward meteoric circulation was reestablished (fig. 22C). Upflow parts of the sulfidized aquifer were epigenetically oxidized as meteoric ground waters containing dissolved oxygen moved coastward down regional hydrodynamic gradient. Early oxidizing waters were enriched in dissolved uranium, molybdenum, and selenium, which were concentrated where flow traversed the geochemical interface between limonitic and pyritic sediment. (The dynamics of oxidation tongue development and mineralization are treated by Granger and Warren, 1978, and Galloway, 1979.) Reduced, thermobaric waters were flushed from the aquifer, but reducing conditions remained because of the epigenetic pyrite within the aquifer matrix. Oxidative attack of this pyrite produced a sharp pH drop, which favored the authigenesis of marcasite as the ore stage iron sulfide and the leaching and redistribution of calcium carbonate along the advancing front.

4. Discharge of thermobaric fluids from the fault again invaded the aquifer (fig. 22D). Sulfide precipitated additively in parts of the aquifer not affected by epigenetic oxidation, and a new generation of iron disulfide formed

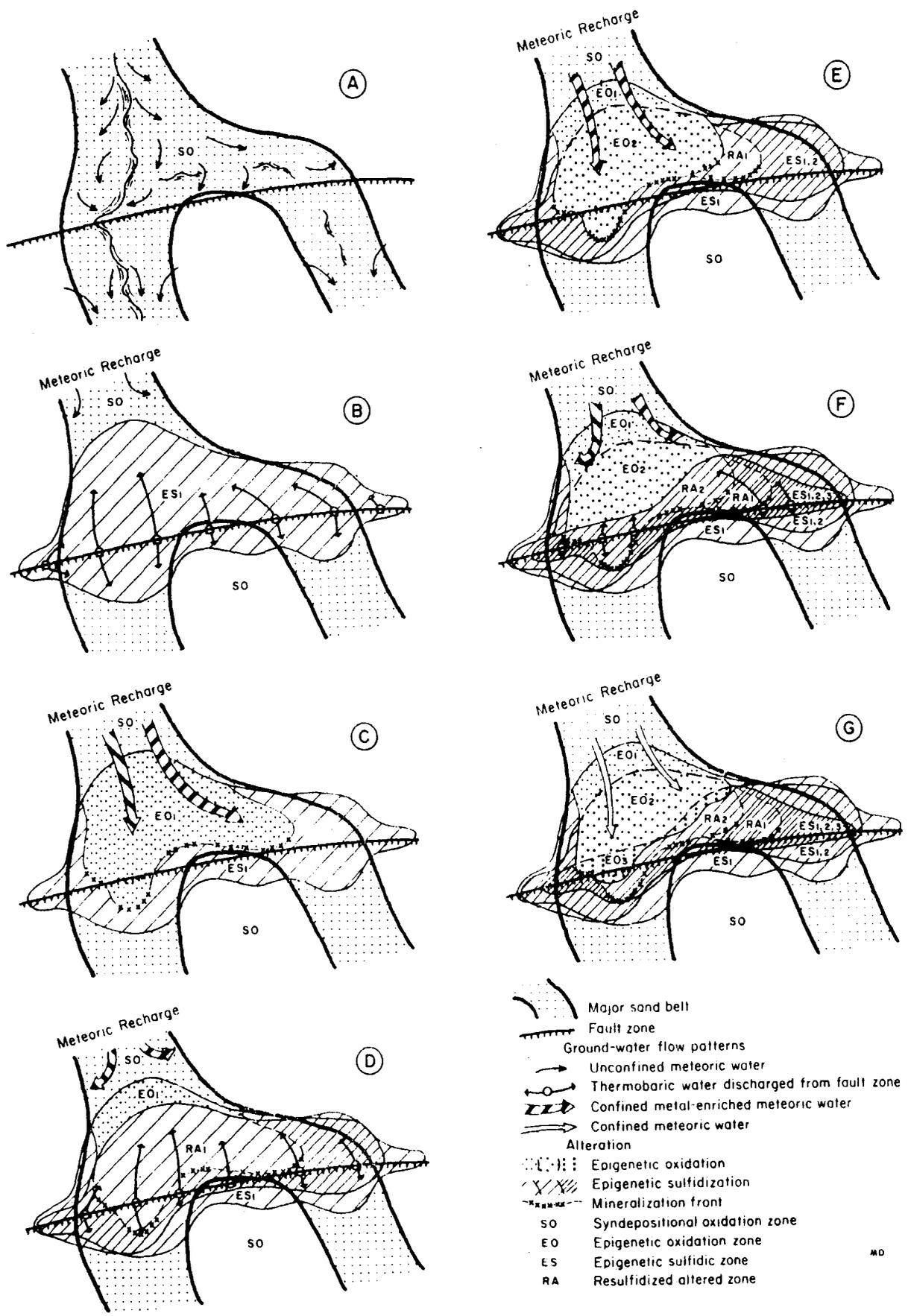


Figure 22

within intruded parts of the epigenetic oxidation tongue, producing the first resulfidized altered zone.

5. Multiple alternating episodes of oxidation by meteoric waters and sulfidization by thermobaric fluids ensued (fig. 22E and F). The preserved record is expectably incomplete because each episode of oxidation destroyed all or part of preexisting sulfidic zones. Ore grade mineralization developed where successive oxidation fronts stacked, forming a single, highly enriched mineralization front. Additional increments of iron disulfide were added to the sulfidic ground during the periodic flushing by thermobaric brines, and by sulfide redistribution during advance of epigenetic oxidation fronts. Consequently, the reduced area became an increasingly sulfide-rich island within the regionally oxidized aquifer.

6. At some point, active epigenetic sulfidization by intrusion of thermobaric waters seems to have slowed or ceased, at least within the study area. Age dates for the deposits at Ray Point suggest that active metallogenesis ended with a final resulfidization event at about 5.1 m.y. B.P. (Reynolds and others, 1980b). Subsequent supergene redistribution of sulfide (and uranium) is charac-

Figure 22. (left) Schematic ground-water flux and alteration history characteristic of mineralized parts of the Oakville aquifer. A. Syndepositional oxidation by local, unconfined circulation of meteoric waters and by weathering above the water table in an arid climate. B. Early intrusion along fault segments of sulfidic thermobaric waters and consequent epigenetic sulfidization. C. Renewed meteoric circulation and partial epigenetic oxidation of sulfidized ground. Initial mineralization occurs along the advancing oxidation front. D. Further pulses of thermobaric waters resulfidize all or part of the epigenetic oxidation zone. E. Another cycle of aggressive oxidation by meteoric waters advances through the aquifer. Where oxidation advances to or beyond its previous limits, continued importation of uranium and associated metals in the meteoric waters increases the grade of mineralization. Where later oxidation does not attain its former extent, weakly mineralized relict fronts remain entombed in sulfidic zones. F. Much of the aquifer near leaky fault zones was subjected to a final intrusion of sulfidic thermobaric water, which resulfidized downdip parts of oxidized and mineralized ground. G. Finally, rejuvenated circulation of oxidizing meteoric ground water due to valley incision during Pleistocene time has initiated a renewed cycle of epigenetic oxidation. However, little additional uranium is being introduced by modern waters. Significant concentrations of dissolved uranium occur only where waters are aggressively oxidizing existing deposits and redistributing the metals.

terized by isotopically light iron disulfide and dissolved hydrogen sulfide (Goldhaber and others, 1979a; Galloway and others, 1979; Austin, 1970). With the evolution of coastal plain topography and drainage patterns during Pleistocene time, the modern ground-water flow system evolved, and epigenetic oxidation again aggressively attacked parts of both mineralized and barren sulfidic zones (fig. 22G). However, modern meteoric waters do not contain sufficient dissolved uranium and associated metals to constitute an ore-forming fluid.

PERSPECTIVES

The well-known roll-front model of sandstone uranium mineralization presumes a relatively uniform distribution of intrinsic reductants, primarily organic material and early diagenetic iron disulfide, throughout the mineralized aquifer. Reducing capacity is thus an inherent characteristic of the rock. This assumption is violated in many continental sedimentary sequences that were deposited in subarid to arid climates and thus subjected to intensive syndepositional oxidation. Uranium concentration in such oxidized aquifers requires earlier alteration by extrinsic reductants.

The obvious mobility of hydrocarbon and hydrogen sulfide gases has made them principal suspects where epigenetic reduction has been inferred. However, although upward migration of a reducing fluid is commonly indicated by geologic relationships of the resultant alteration, evidence for buoyant segregation of a free gas phase has rarely been documented. Characteristics of sulfidic alteration in South Texas aquifers contradict a model dominated by free gas migration. However, appropriate reducing and sulfidic geochemistries exist in deep-basin ground-water regimes, and the existing pressure head drives these waters upward where they may interact with the supergene environment. A thick, subsiding

basin fill can be viewed as a dynamic cauldron, capable of transporting and mixing large volumes of soluble oxidants, reductants, and, in some rather specific fluids, metals. Such large-scale fluid migration systems have produced major uranium deposits in the South Texas Coastal Plain. Better understanding of other epigenetic mineral deposits undoubtedly awaits more sophisticated study and application of fundamental concepts of basinal hydrology.

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