

Release of Uranium from Volcanic Glass in Sedimentary Sequences: An Analysis of Two Systems*

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Abstract

Uranium can be released from volcanic glass shards by solution of the shards. Studies of the Tertiary Tascotal Formation of Trans-Pecos Texas suggest that total solution of shards during diagenesis in an open meteoric flow system does not release uranium for migration. Instead, uranium is only redistributed locally. In the Tertiary Catahoula Formation of the Texas Coastal Plain, uranium also was not mobilized for long-distance migration and ore formation during diagenesis of glass in the zone of saturation within an open meteoric flow system but was released during solution and argillation of glass by subaerial soil-forming processes and diagenesis in the vadose zone. Tuffaceous facies are depleted in proportion to the intensity of vadose and pedogenic processes. It is unclear why uranium mobility is limited within meteoric flow systems.

Release for long-distance migration can be documented by chemical evidence for depletion of uranium in potential source beds. Soil processes impart typical vadose microscopic textures and cause formation of distinctive outcrop features. Diagenesis in open meteoric flow systems occurs below the water table producing characteristic isopachous rims of secondary minerals. Together such field, textural, and geochemical criteria allow recognition of functional sources of uranium, which in turn provides a rapid, inexpensive evaluation of regional resource and exploration potential.

Introduction

IN the United States, the overwhelming majority of uranium reserves are in epigenetic deposits that formed by deposition from meteoric ground water. Young (1977) indicates that 97 percent of domestic reserves are in sandstone deposits, one of the best known of the epigenetic types. About 22 percent of reserves in foreign, noncommunist countries are in sandstone, and over 4 percent are in calcretes, which also constitute an epigenetic deposit. Even some veins and the deposits beneath Proterozoic unconformities have been interpreted to be products of secondary, low-temperature meteoric processes (Langford, 1977; Ojakangas, 1977; Yellich et al., 1978).

Epigenetic deposits can all be analyzed in terms of the same conceptual formative system, though the details of each part of the system can differ from occurrence to occurrence. Uranium is released from a source, migrates in solution in ground water, and is concentrated to form a deposit. To date, most research has concentrated on the trapping component of the general system; numerous excellent descriptions of concentrating mechanisms and ore paragenesis in sandstones and calcretes are available. Research

into the migration of uranium in ground water has called attention to ionic complexing and the importance of two oxidation states of the metal. Hostetler and Garrels (1962) showed that the uranyl (+6) ion is easily complexed by common constituents of meteoric ground water, such as carbonate ions, and that reduction causes precipitation as insoluble uraninite or as other U^{+4} minerals. Recently, Langmuir (1978) calculated free energy values and phase diagrams for various uranium species. He also called attention to the importance of several additional complexing agents. Regional and local flux patterns within the uranium-enriched ground-water flow system determine the uranium transport paths and influence the location of the ultimate concentration sites (Galloway et al., 1979).

Perhaps the weakest link in the model of formation of epigenetic uranium deposits is our inability to define and recognize potential uranium source rocks that have released sufficient quantities of uranium at the appropriate time in the hydrologic history of the basin to produce economically significant deposits (Galloway et al., 1979). Although a few papers have specifically addressed the question of mobilization mechanisms from potential source rocks (Denson et al., 1956; Rosholt and Noble, 1969; Stuckless, 1977; Rosholt et al., 1971; Zielinski, 1977, 1978; Szalay and

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Samsoni, 1973; Doi et al., 1975), there is no clear consensus for specific geological, mineralogical, and geochemical criteria that identify such a functional uranium source rock.

The implications of this fact can be appreciated by analogy with petroleum exploration. The most efficient approach for evaluation of the petroleum potential of a sedimentary basin is the early determination of the presence and spatial distribution of potential petroleum source rocks, coupled with an analysis of their thermal history to determine the likelihood that they have yielded significant quantities of hydrocarbons (Tissot and Welte, 1978). Strata that have sufficient organic material of the correct types and that have experienced sufficient thermal diagenesis to have generated fluid hydrocarbons satisfy the criteria for functional hydrocarbon source rocks. Further exploration in a basin will likely be guided by the location and abundance of such functional source strata.

This approach recognizes a fundamental principle applicable both to petroleum and epigenetic uranium exploration or resource assessment: the volume of functional source rocks, which contain only very small amounts of the resource material, must be very large relative to the volume of producible deposits (the volume of potential uranium source sediments must be on the order of 10^3 times the volume of objective ore deposits even if 100 percent efficient trapping at economic grade and in economically extractable deposits of mobilized uranium occurred). Thus, it is easier to locate, sample, and test possible source units than to test and evaluate the plethora of potential reservoirs and traps that are likely to be present.

Well-documented potential uranium sources include (1) alkalic granites, (2) bedded volcanic flows, (3) volcanoclastic sediments, and (4) siliceous volcanic air-fall ash. All are characterized by a high or potentially high trace uranium content and have been shown to release the uranium during some types of weathering or diagenesis (Rosholt et al., 1971; Szalay and Samsoni, 1973; Stuckless, 1977; Zielinski, 1977, 1979). Granite and glassy volcanic ash or ash-rich sediments are generally accepted functional sources for major uranium deposits in some districts. Intensely weathered granite provides the uranium concentrated in western Australian calcrete deposits (Mann and Deutscher, 1978). Interbedded volcanic ash is the only available source for epigenetic uranium deposits in the Catahoula Formation of the South Texas uranium province (Galloway, 1977). In many other major uranium provinces both granitic and volcanic sources are available and have been invoked, with different amounts of supporting data. Certainly the limited distribution of large-scale, ore-grade uranium enrichment in both time and space indicates that functional source rocks represent only a small portion of all potential source units (Malan, 1968).

The objective of this paper is to describe and compare the mechanisms and relative uranium mobilization efficiency of common diagenetic processes that alter newly deposited volcanic glass. We describe two natural systems in which sediment containing abundant detrital volcanic glass experienced diagenetic processes that potentially could release uranium into solution. As such, this study extends the work of Rosholt et al. (1971) and Zielinski (1978), who examined uranium mobilization from glassy and crystalline rhyolitic lava flows and ash-flow tuffs. We hope to make three points: (1) uranium is demonstrably released from glass in sedimentary rocks by two common diagenetic processes that result in dissolution of the glass; (2) conditions under which dissolution occurs will control whether released uranium will actually migrate long distances to become available for concentration in deposits; and (3) functional source rocks, that is, those that have released a significant proportion of their contained uranium for migration and concentration, can be distinguished by field, petrographic, and geochemical criteria.

Possible uranium release mechanisms

Uranium occurs dispersed within volcanic glass (Zielinski, 1978; Henry and Duex, in press). Typical analyses of rhyolitic glass shards indicate a uranium content of several ppm to several tens of ppm. In addition, uranium may occur adsorbed onto the surface of shards when they are first released into the atmosphere. Thus, four possible modes exist for the release of uranium from volcanic glass in sedimentary sequences: (1) washing and removal of the external adsorbed coating of uranium along with other metals or ions, (2) gradual preferential leaching of uranium during incongruent dissolution or hydrolysis, (3) congruent solution of the glass with proportional release of uranium, and (4) release from alteration products of glass.

Washing of adsorbed material: Taylor and Stoiber (1973) analyzed soluble surface material from fresh volcanic glass that had never been exposed to rain. They found Cl, F, SO_4 , Na, K, Ca, Mg, Zn, Cu, and Mn on all samples, in amounts ranging from an average of 12 ppm of Zn in the ash to 7,760 ppm of Cl. Taylor (pers. commun., 1978) indicates uranium is also present. Although Taylor and Stoiber's data pertain only to calc-alkaline Central American volcanoes, they established that radicals and metals are adsorbed on the surface of glass shards and can be readily leached by the most gentle washing. Subsequent investigation by Smith and Zielinski (1979) shows that virtually no uranium is actually present on the surfaces of ash particles erupted from calc-alkaline intermediate Central American volcanoes.

Uranium might be more abundant on silicic ash particles, especially alkaline ones, because such highly differentiated magmas contain more uranium than

other types (Rogers and Adams, 1969). If present, such uranium could be washed from ash immediately after deposition. The water that washed the soluble uranium off the glass might then recharge the local ground-water system. In addition, such waters would be charged with SO_4^{2-} to make them initially acid, and with fluoride ions to complex the uranium (Langmuir, 1978). Reactions with underlying glass would quickly neutralize the acidity, destabilize fluoride complexes, and add dissolved carbonate to recomplex any uranium.

Even if abundant uranium is present on ash from some volcanoes, this mode of U release could be important only in newly deposited air-fall ash beds—soluble material would have been removed from water-laid ash sediment long before final deposition. Fresh ash must be deposited directly on a regional ground-water recharge zone for efficient transfer of sorbed uranium to the subsurface flow system. The lack of abundant uranium on any ash surfaces examined to date and the special conditions under which an ash would have to be deposited to release uranium for concentration lead us to suspect that washing of adsorbed uranium is not a likely source of uranium for economic deposits.

Selective leaching from glass: The second conceivable mode of uranium release is at most of minor importance and may not occur at all. Rosholt et al. (1971) and Zielinski (1978) both analyzed pairs of fresh and hydrated volcanic glasses of various ages from the western United States and found no difference in uranium content, indicating that glass does not lose uranium during hydration. Ash-flow tuff samples from Trans-Pecos Texas show similar results (Henry and Tyner, 1978). This conclusion is supported by the observation that concentrated acid leach techniques used in conventional fluorimetric uranium analysis do not release uranium completely from glass shards; samples must be totally dissolved.

Dissolution of glass: Glass shards are extremely reactive components in sedimentary rocks and in tuffs, altering to form clay minerals, opal, clinoptilolite, calcite, and other minerals. Petrographic evidence shows that the process of alteration is one of dissolution of the glass and migration of its constituents at least short distances (Walton, 1975, 1978c). Experiments demonstrate that glass solution releases uranium: Zielinski (1977, 1979) dissolved glass under mild hydrothermal conditions and found that silica—which made up most of the structure of the glass—and uranium were present in solution in the same proportion that they were present in the glass. Glass dissolution should be the most effective mode of release of uranium.

Release from secondary phases: Diagenesis is a progressive chemical and mineralogical process that does not cease with solution of glass. Initial diagenetic minerals commonly alter to form new minerals either

because the minerals that form first are metastable or because the course of diagenesis gives rise to new conditions. In volcanic sediment from Trans-Pecos Texas, late diagenetic changes in tuffaceous sediments include conversion of opal to quartz (or chalcedony), conversion of clinoptilolite to analcime, and possible solution of clay (Walton, 1975). Uranium can also be reversibly adsorbed after release from volcanic glass, then released later by either phase changes or leaching of adsorbed uranium.

Two examples of adsorption-desorption and adsorption-mineral alteration illustrate possible release mechanisms:

1. Adsorption of uranium by diagenetic minerals is well documented, e.g., silica gel (Zielinski et al., 1977; Henry, 1978), montmorillonite (Galloway and Kaiser, 1980), clinoptilolite (Katayama et al., 1974), and Fe-Ti-Mn oxyhydroxides (Langmuir, 1978; Henry and Duex, in press). Efficiency of adsorption is a function of temperature, the particular mineral, and the chemical composition of the solution, especially the pH and the availability of complexing agents (Langmuir, 1978). Thus, if uranium is not somehow fixed following adsorption and any of the variables listed above changes, uranium could be released.

2. Uranium is retained by some minerals with open crystal structures that grow rapidly during diagenesis, particularly opal, probably because it is physically occluded. However, both continued diagenesis and postdiagenetic alteration convert opal to quartz (or chalcedony) (Ernst and Culvert, 1969; Kastner et al., 1977). Henry (1978) suggests that this conversion releases uranium by excluding it from the quartz lattice. A similar process is conceivable during replacement of clinoptilolite by analcime or potassium feldspar in higher grades of diagenesis or by aging of iron oxyhydroxides. Such processes are typically geologically slow, progressive phenomena.

Documentation of uranium release from phases formed during diagenesis is not available. A major uncertainty concerns the site within the rock system to which uranium moves after release from glass during dissolution. Analyses presented below indicate no slow loss from zeolitized volcanic sediment in the Tascotal Formation in Trans-Pecos Texas relative to associated unaltered glass in overlying rocks. In contrast, both Rosholt et al. (1971) and Zielinski (1978) suggest that the primary release of uranium from devitrified volcanic glass and felsic extrusive rocks occurs slowly during long-term recrystallization or weathering. However, both studies were of formerly glassy volcanic rocks altered by high-temperature devitrification to quartz and feldspar and not by diagenesis. Zielinski's (1978) assertion of a time-dependent release of uranium that is greater for peralkaline rocks than for calc-alkaline ones is uncertain for the following reasons. The apparent loss for calc-alkaline

rocks is based solely on five data points from a single locality. However, a suite of samples of about the same age (27–28 m.y.) from another locality exhibits no such clear-cut depletion. Also, considerable variation in uranium content exists within sample suites from individual exposures in lithologically similar rocks, possibly indicating local depletion and adjacent enrichment.

If, as suggested by Zielinski (1978) and Rosholt et al. (1971), uranium is released slowly, by weathering of crystallized felsites, it might also be released by slow leaching from the products of glass alteration in volcanic sediments or tuffs. In fact, such a mobilization mechanism must be responsible for leaching of uranium from crystalline plutonic rocks. Until more is known about uranium mobility during the various alteration processes, it is safe only to state that uranium is released efficiently and rapidly from dissolving shards and that some may be released slowly from devitrified glass or from felsic-flow rocks.

Functional mobilization model

Of the four general categories of processes described above, only solution of glass can be expected to release uranium rapidly and efficiently from glassy constituents of sediments (cf. DeVoto, 1977, p. 35). Major uncertainties remain about the efficiency of the other processes to mobilize uranium. Certainly this conclusion should be regarded as preliminary. Considerable investigation remains to be done on surface materials on freshly erupted glass shards and processes of conversion of glass to crystalline substances. However, the model explains the present uranium distribution in two well-studied sequences of sediment that contained abundant glass shards when deposited. One of the sequences, the Catahoula Formation of South Texas, contains large, commercial uranium deposits that almost certainly are composed of metal released from interbedded tuffs (Galloway, 1977). The other, the Tascotal Formation of Trans-Pecos Texas, contains no known uranium deposits; in fact, uranium probably was released while the shards dissolved, but it did not migrate to be concentrated into deposits.

Tascotal Formation: A Nonfunctional Source

The Tascotal Formation (late Oligocene) is a 250-m-thick layer of volcanic sediment that is exposed on the eastern side of the Trans-Pecos volcanic field (Fig. 1). Most of the Tascotal Formation has been described as "tuff" by the several workers who studied it. In fact, it is mostly sediment consisting of fragments of volcanic origin deposited in several different environments. The part described in this article consists of two informal members, the active apron and eolian members of Walton (1978a). The active apron member records the latter part of the period of activity

of the Chinati Mountains volcanic center. Deposition of this rock was almost exclusively by stream processes with only a few thin interbeds of air-fall tuff. The eolian member contains excellent eolian cross beds and other eolian features (Walton, 1978a and b). These members together form a wedge that thickens over a distance of more than 20 km from its western pinch-out to about 200 m thick along its eastern eroded margin. The known north-south extent of the eolian member is about 25 km; the active apron member extends at least 60 km.

The rocks contained abundant glass shards when deposited, averaging about half of the original framework, but the proportion of glass shards was greatest in fine-grained rocks and least in medium sands or coarser rocks in which volcanic rock fragments and crystals predominate. In the lower part of the sequence, these glass shards have been dissolved and their constituents reprecipitated as clay, opal, calcite, and clinoptilolite. In part of the area, the upper part of the sequence contains unaltered glass shards in a zone up to about 70 m thick that pinches out to the north. Most of the fresh glass is in the eolian member, but the upper part of the underlying active apron member contains some unaltered shards as well.

Diagenesis of the Tascotal Formation

Examination of thin sections of Tascotal rocks under the microscope and of freshly broken surfaces with the scanning electron microscope allows an unequivocal interpretation of the order in which the several diagenetic phases formed and the relative time of major solution of glass and uranium release (Fig. 2). Several distinctly different, successive alteration assemblages can be recognized (Fig. 3). The most complex, consisting of clinoptilolite, clay, opal, and calcite, displays clear evidence that it went through the preceding several stages. The uppermost part of the section contains unaltered glass shards commonly coated by frothy montmorillonite clay (Fig. 4). Because the texture of this clay resembles that described by Wilson and Pittman (1977) for diagenetic montmorillonite and because the clay coats glass, grains of quartz, and feldspar and volcanic rock fragments alike, it must have precipitated from solution.

In rocks underlying those containing clay-coated glass, a layer of opal overlies the clay coating of every grain. The opal occurs in several textures—frothy opal, spherical opal, and opal rosettes. Evidence of minor solution of glass is present in all these rocks, mostly in the form of scattered hemispherical etch pits (Figs. 3 and 4). Before the glass dissolved, clay and opal formed an envelope that preserved the shape of the shards perfectly.

Calcite was the next phase to develop, beginning even as opal continued to form (Figs. 2 and 3). Calcite

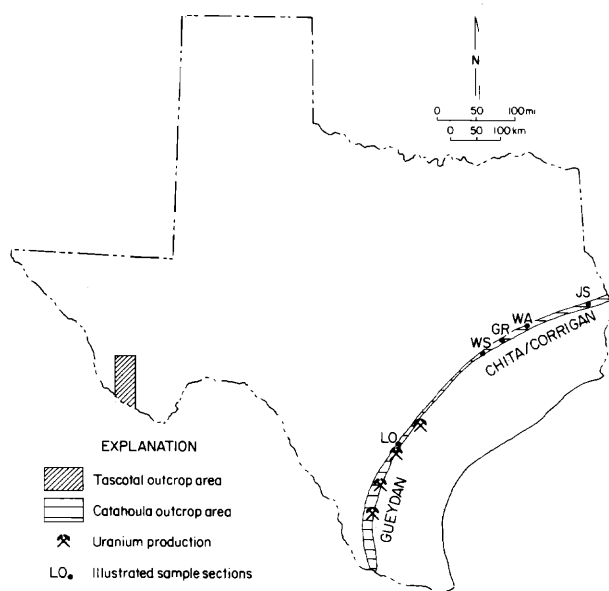


FIG. 1. Location of Tascotal and Catahoula Formation outcrop areas. Major Catahoula uranium-producing districts are indicated by mine symbols; all occur within the Gueydan fluvial system. Lettered points locate sample sections illustrated in Figure 7.

occurs as concretions rather than being disseminated throughout the rock as are opal and clay. Calcite formed before any great degree of solution of shards

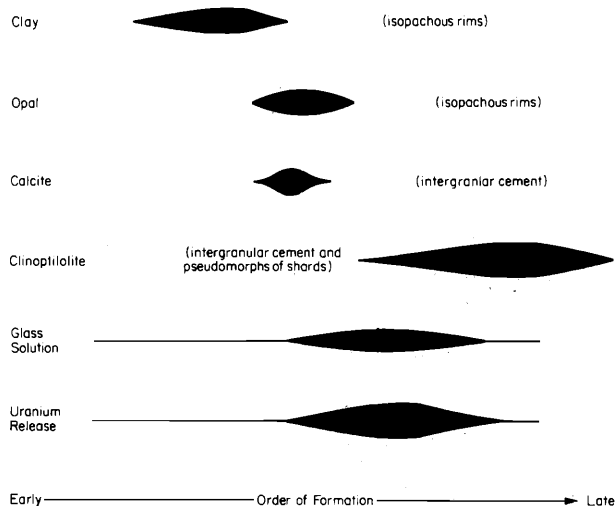


FIG. 2. Paragenetic sequence resulting from diagenesis of the Tascotal active apron and eolian members in an open hydrologic system.

because it forms poikilitic or drusy fillings of primary pores, but it does not commonly fill secondary pores formed as the glass dissolved. The coarse, poikilitic or drusy calcite textures indicate that the altering solution was of low ionic strength, i.e., nearly fresh water (Folk, 1974).

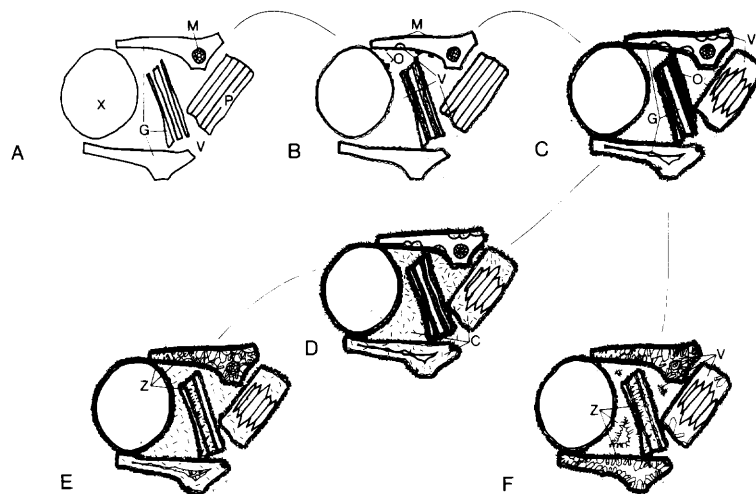


FIG. 3. Paths of diagenesis and the textures that result. A. Initial condition: glass shards (G), a crystal of quartz or feldspar (X), and a pyroxene or hornblende grain (P). This composition is characteristic of fine sandstones of the active apron. Voids (V) between grains. Montmorillonite (M) fills a bubble in a shard. B. A clay coating (M) covers all surfaces. Opal spheres and rosettes (O) are present. A hemispherical etch pit ash formed on the glass shard and the inosilicate grain is beginning to dissolve. Note clay filling pumice tubes. C. Dissolution of the glass and inosilicate grains has continued—one shard is reduced to a small fiber near the center of the shard-moldic pore. The opal rim is now complete, but the pores are still large. From this point, either of two paths can be followed: directly to F or through D to E. This is followed by dissolution of remaining glass and precipitation of zeolite (Z). F. The other route occurs outside calcite concretions where the glass dissolves and zeolite forms druses in pores, shard pseudomorphs, and inosilicate pseudomorphs. Crystal size of the clinoptilolite is smaller in the pores than in pseudomorphs, and voids remain.

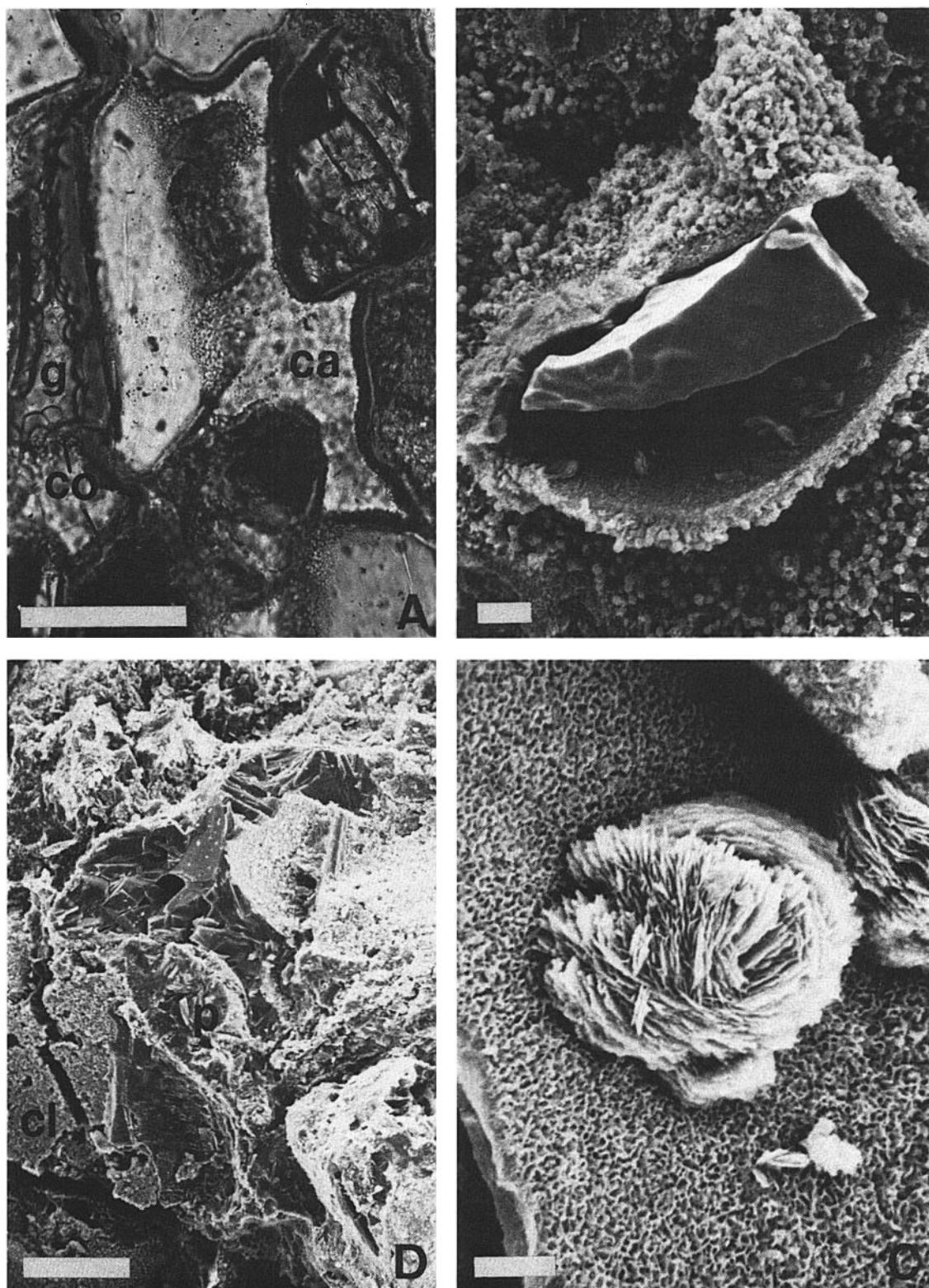


FIG. 4. A. Sample containing etched, unaltered glass (G), coated by clay and opal (CO) with calcite pore-filling cement (Ca). Notice the isopachous nature of the clay and opal cement. B. Scanning electron micrograph of a shard in a rock similar to that in Figure 3A but without calcite cement. Frothy clay and opal spheres define the original margin of the shard of which only an etched fragment remains. Some small opal rosettes occur within the void left by the dissolved glass. C. Scanning electron micrograph of an opal rosette on frothy, diagenetic clay. D. Crystals of zeolite fill in the primary pore (P) and the space left by a dissolved shard (S) in this rock which now contains no glass. Frothy clay (Cl) lines other surfaces. Scales: A, 0.1 mm; B, 0.01 mm; C, 0.005 mm; D, 0.01 mm.

Clinoptilolite is the last silicate phase to form (Figs. 2, 3, 4, and 5). It fills primary pores not filled by calcite and occupies the voids left by dissolved shards. Clinoptilolite cement in primary pores typically has a finer texture than in shard molds, and it fills primary pores more completely than the shard molds. This implies an overlap of glass dissolution and zeolite formation.

The cement in the Tascotal Formation—clay, opal, calcite, and zeolite—occurs as successive, isopachous rims (Figs. 3, 4, and 5). Carbonate petrologists routinely interpret such rims as indicating alteration in water-saturated sediment below the water table (Bathurst, 1975). Similar interpretation of isopachous silicate textures as being formed in the phreatic zone is a reasonable extension of this idea. The logic of the carbonate workers is based not on the nature of the minerals involved, but on the distribution of water in pores in the phreatic zone as opposed to that in the vadose zone.

The Eh of the diagenetic system is difficult to determine. Recharging ground water initially contains dissolved oxygen, especially in dry climates and highly permeable sediments (Galloway et al., 1979). The sediment itself preserves no evidence of a reducing nature; pyrite and organic matter are absent. On the other hand, mafic silicates like augite and hornblende have dissolved, but the iron in them was not directly converted to abundant ferric hydroxides as described by Walker (1967). Instead, the iron must have entered clay or been leached out of the system. Electron probe analyses of clay indicate a higher iron content than in glass, but the analyses of clay are unreliable because of its frothy texture. Low in the section, below the level at which clinoptilolite pore fillings appear, minute red dots stain the clay, and magnetite is commonly associated with red pigmentation—presumably iron oxide or hydroxides. At the high pH inferred for this alteration system, iron oxides and hydroxides would be stable even at slightly reducing conditions (Garrels and Christ, 1965). Probably the Eh of this system was close to zero, either slightly oxidizing or slightly reducing.

In thin section, the altered rock of the Tascotal closely resembles paisley-print fabrics, with glass shard ghosts coated with opal and clay and pores partially filled with druses or radial aggregates of clinoptilolite (Figs. 3, 4, and 5). This paisley texture is present in most volcanic sediment sequences where matrix-free, glass-rich sandstones have undergone diagenesis in an open hydrologic system (Fig. 6; Hay, 1963; Walton, 1975; Hay and Sheppard, 1977).

Open hydrologic systems are common in alluvial fan settings, such as the active apron member of the Tascotal Formation. The reactions occur as the pH increases with hydrolysis of glass in the phreatic zone. Because of the general gradient of the fan, water will flow roughly in the same direction as the stream flow.

Diagenesis begins during deposition, after a critical thickness of sediment has accumulated, and continues as more sediment is deposited, as each successive increment of sediment passes through the water table.

Uranium in the Tascotal Formation

Volcanic glass separated from unaltered volcanic sediments contains an average of 9 ppm uranium (Table 1). Crude estimates based on only the known, preserved volume of the Tascotal active apron and eolian members indicate that it contained 0.5×10^6 to 1×10^6 tons of U_3O_8 , an amount of the same order of magnitude as the known domestic reserves of the metal (Young, 1977). Had this been released to migrate and concentrate, ore deposits of immense proportion could have been formed.

Whole-rock analyses of uranium (Table 2), however, indicate that migration did not occur on other than a local scale (Fig. 6). Analyses of 12 samples from the unaltered upper section of the Tascotal averaged 4.2 ppm uranium, whereas 4.5 ppm was the average for 10 samples from parts of the same outcrop sections where the zeolite assemblage was developed (all except the Manny Howard section of Table 2). Eight samples collected from a transition interval, about 10 to 20 m thick, between the altered and unaltered parts of the section contained 3.8 ppm uranium (Table 2). These values are nearly identical. Only the variability is different; the range of values in the altered interval is greater than that in the other parts, perhaps indicating original inhomogeneities or local redistribution. Other samples, collected from sections where rock containing unaltered glass does not overlie the interval containing altered rock, have similar values, except for one sample that contains 26 ppm (Table 2).

These samples were all chosen because they had an estimated average grain size of medium sand. Volcanic sediments, such as the Tascotal, show strong variation of grain composition with grain size, with glass shards normally being fine, volcanic rock fragments coarse, and crystals of intermediate size. Medium sands have a measure of all of these components (Walton, 1977). Using only medium sand, however, reduced the chance of variation that might result from comparing conglomerates with siltstones.

Additional evidence for immobility of uranium during diagenesis of the Tascotal Formation is given by Henry and Duex (in press). They found similar uranium concentrations and thorium/uranium ratios in glassy and diagenetically altered sediment. Fission-track maps of these samples showed that iron hydroxides in altered sediments are enriched in uranium, probably as a result of adsorption. Additional uranium occurs disseminated through the groundmass of the rocks without a distinct mineral association. Other diagenetic minerals, including opal, cal-

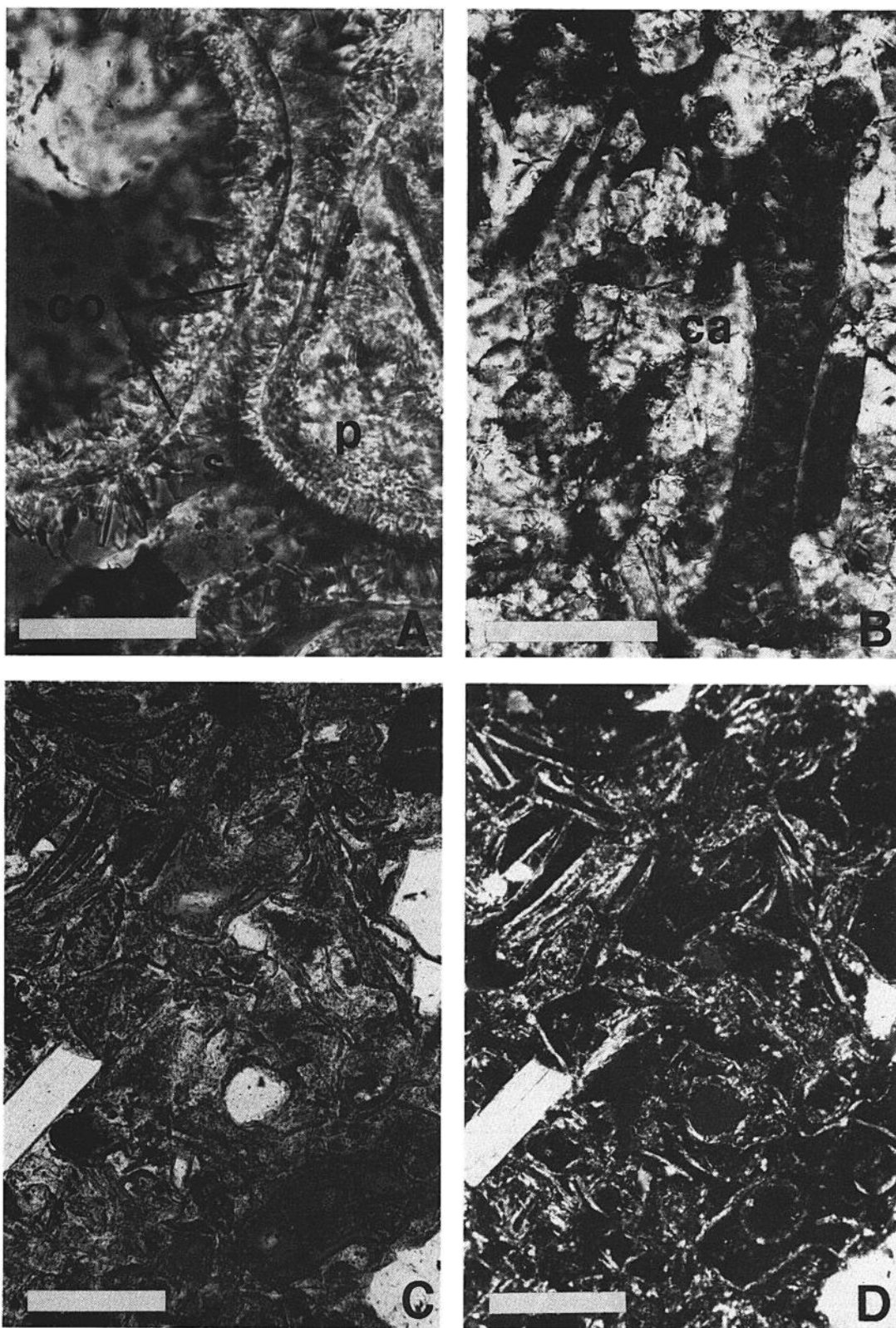


FIG. 5. A. Photomicrograph of drusy clinoptilolite partially filling a void left by solution of a glass shard (S) and adjacent pores (P). A thin clay/opal layer (CO) has preserved the outline of the shard (plane polarized light). B. Photomicrograph (crossed polarizers) of clinoptilolite-filled shard pseudomorphs (S) cemented by calcite (Ca). If the calcite formed after the shards dissolved, it should fill them as well as the primary pores. C and D. Photomicrographs in plane polarized light (C) and with crossed polarizers

cite, clinoptilolite, and analcime, contain little uranium.

The actual mass balances for uranium and other constituents have not been worked out, but there is little evidence of an overall volume decrease of these rocks. Instead, some volume increase may have taken place as hydrated clays, opal, and clinoptilolite replaced less hydrous glass and filled primary porosity, although potassium may be depleted from montmorillonite, opal, and clinoptilolite assemblages compared to glass (Walton, 1975).

Discussion

The chemical data suggest that uranium was not significantly mobilized during an open hydrologic system solution of glass; although perhaps locally redistributed, it was not transported long distances. Furthermore, the data suggest that once uranium was effectively trapped in secondary phases, it did not move for about 30 million years, since diagenesis.

Zielinski et al. (1980) reported that diagenesis of tuffs, including volcanic sediments, of the Keg Mountain area of Utah also did not release uranium for long-distance migration, but he interpreted certain activity ratios between ^{238}U and its daughters as suggesting that uranium had been mobile in the past 8×10^5 years. Zielinski et al. (1980) point out that their study could not detect any loss of a small amount of original uranium and even a small amount could form large deposits. The same criticism could be made of our results, but in the following sections we will point out a far more effective process of mobilizing uranium which leads us to suggest that uranium for economic deposits does not come from phreatic, open system diagenesis of glass-rich sediments.

The question arises of why uranium is not mobile in these systems even though the structure of the glass is broken down by solution and the uranium must be released. Zielinski et al. (1980) say that stagnant ground-water conditions favor the formation of zeolites and inhibit the mobility of uranium. Walton (1978c) suggested that common complexing agents (dissolved CO_2 or P) are precipitated by Ca during the diagenesis of glass in open systems before most solution of glass occurs. The system may actually have such a low Eh that the uranium was immobile. None of these ideas has been adequately tested.

Catahoula Formation: A Fertile System

The Catahoula Formation (Oligocene-Miocene) of the Texas Coastal Plain is composed of the deposits of two major coastal plain fluvial systems (Galloway,

1977, 1978). The Gueydan fluvial system, centered in the South Texas Rio Grande embayment, was separated from the Chita-Corrigan fluvial system, which filled the Houston embayment of southeast Texas, by the intervening San Marcos arch (Fig. 1). The Gueydan system consists of bed-load channel fill and crevasse-splay facies surrounded by tuffaceous siltstone, mudstone, and claystone of flood-plain and coastal lake origin. Sediment was supplied primarily by a single large river system, which transported volcanic rock fragment and plagioclase-rich sand from sources in West Texas and Mexico. The Chita-Corrigan system is composed of a framework of mixed-load channel fill and associated crevasse-splay facies surrounded by flood-plain and interchannel lacustrine deposits. The system included at least three major rivers and several local streams. Sands of this system characteristically contain orthoclase and chert. Mud and clay in both systems consist dominantly of montmorillonite and kaolinite derived from the alteration of contemporaneous air-fall volcanic ash. Paleosoils, clay mineralogy, and other sedimentary features show that the Catahoula paleoclimate varied from relatively dry in South Texas to subhumid in East Texas.

Several significant uranium districts with cumulative known reserves in excess of 50 million pounds occur within the Gueydan system; small deposits have also been discovered in the Chita-Corrigan system. The uranium deposits occur along mineralization fronts within permeable host facies. The complex paragenetic history of studied deposits, which includes a variety of diagenetic events, indicates that a primary mineralization phase introduced uranium very early in the post-depositional history of the host units (Galloway, 1977; Galloway and Kaiser, 1980). During this early constructional phase, uranium was leached from the associated volcanic ash, moved with recharging ground water into shallow confined aquifers, and concentrated along Eh-pH-defined geochemical interfaces within the aquifer. Evolving ground-water flow patterns and composition have caused local modification or redistribution of primary uranium deposits.

Diagenesis of volcanic glass in the Catahoula Formation

Catahoula sand and ash sequentially experienced diagenesis by (1) pedogenesis and leaching above the syndepositional water table, (2) early alteration within unconfined to semiconfined shallow aquifers, (3) later alteration during burial, and (4) local exhumation and

(D) of glass-rich volcanic sediment with fully developed paisley texture. Drusy clinoptilolite partially fills shard pseudomorphs and more completely fills pores. In D, interference colors show the presence of oriented clay surfaces of shards and crystal fragments. At this magnification opal is difficult to recognize. Scales: A, 0.05 mm; B, 0.1 mm; C and D, 0.2 mm.

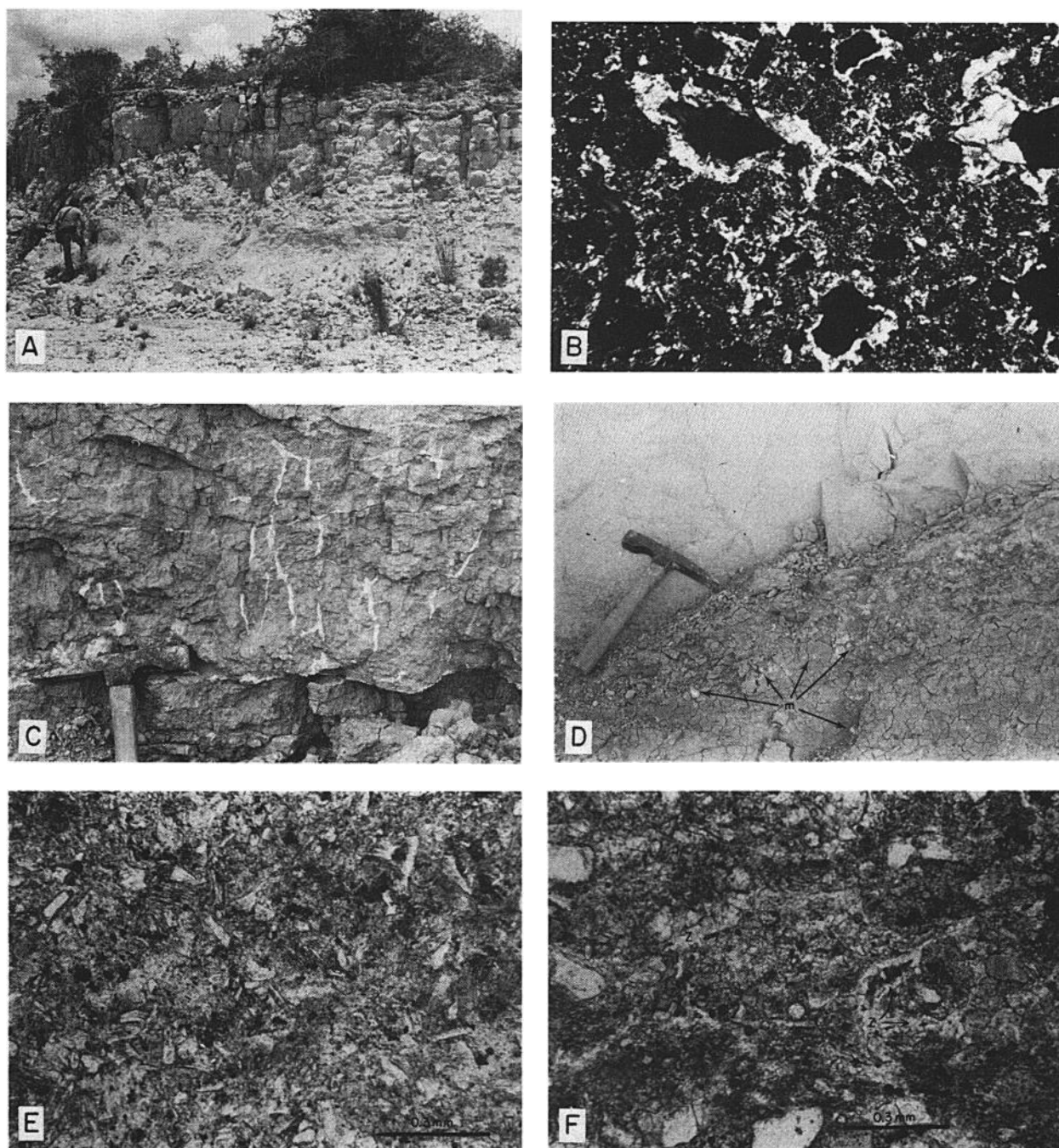


FIG. 6. A. Massive, blocky paleosol horizon developed on a bedded, tuffaceous lake margin mudstone. B. Well-developed clay cutans (C) lining framework grains. Note massive, homogenized matrix typical of thoroughly altered Catahoula paleosols. C. Clay-filled root tubules (T) in massive, pedal tuffaceous mudstone. Paleosol zone developed on crevasse-splay, sandy ash marginal to a fluvial channel. D. Scattered diffuse micrite nodules (M) in massive flood-plain mudstone. Homogeneous unit above hammer head is the base of a crevasse or flood runoff channel, which was initially filled with ash-rich silt and fine sand that has completely altered to clay-sized material. E. Large ash shards dispersed in a matrix of authigenic montmorillonite and fine sand to silt-sized sand. Clay rims (R) surround framework grains. F. Euhedral clinoptilolite (Z) filling pores within root tubules and leached glass shards.

outcrop weathering. The chemistry of circulating pore waters changed with the evolution from phase to phase (Galloway and Kaiser, 1980).

The paragenesis and distribution of a variety of authigenic minerals present in tuffaceous silt, mud, and claystones of the Catahoula Formation document

TABLE 1. Uranium Content of Glass or Zeolite-Opal Fraction of Tascotal Rocks (in ppm)

Fraction	Windmill section		Tascotal Mesa North section		Manny Howard section	
	Sample no.	U content	Sample no.	U content	Sample no.	U content
Glass	135.5	9.4	118	8.0	(No unaltered glass present in this section)	
	127.5	9.1	727	11.0		
	126NZ ¹	8.2	63	9.8		
	124.5 ¹	5.4	42.1 ¹	9.4		
			41.8 ¹	10.3		
Zeolite + opal	113.5	1.8	37.1	4.4	364	4.4
	111	6.6	8	4.5	274	35.4
	101	5.4			227	2.9
	12.3	6.8			180	4.9
	8	6.2				
	7	5.3				

¹ These samples may contain appreciable amounts of opal in addition to glass

two major diagenetic episodes: (1) early soil formation and phreatic leaching of fresh ash produced a variety of features, including pedogenic montmorillonite (locally, kaolinite) clay coats or cutans and colloidal masses, diffuse and discrete micrite nodules, and diffuse silica nodules, as well as complete argillation of the glass particles; and (2) postdepositional diagenesis in an unconfined to semiconfined meteoric flow system produced characteristic assemblages of authigenic montmorillonite, leached glass shards, clinoptilolite, and calcite.

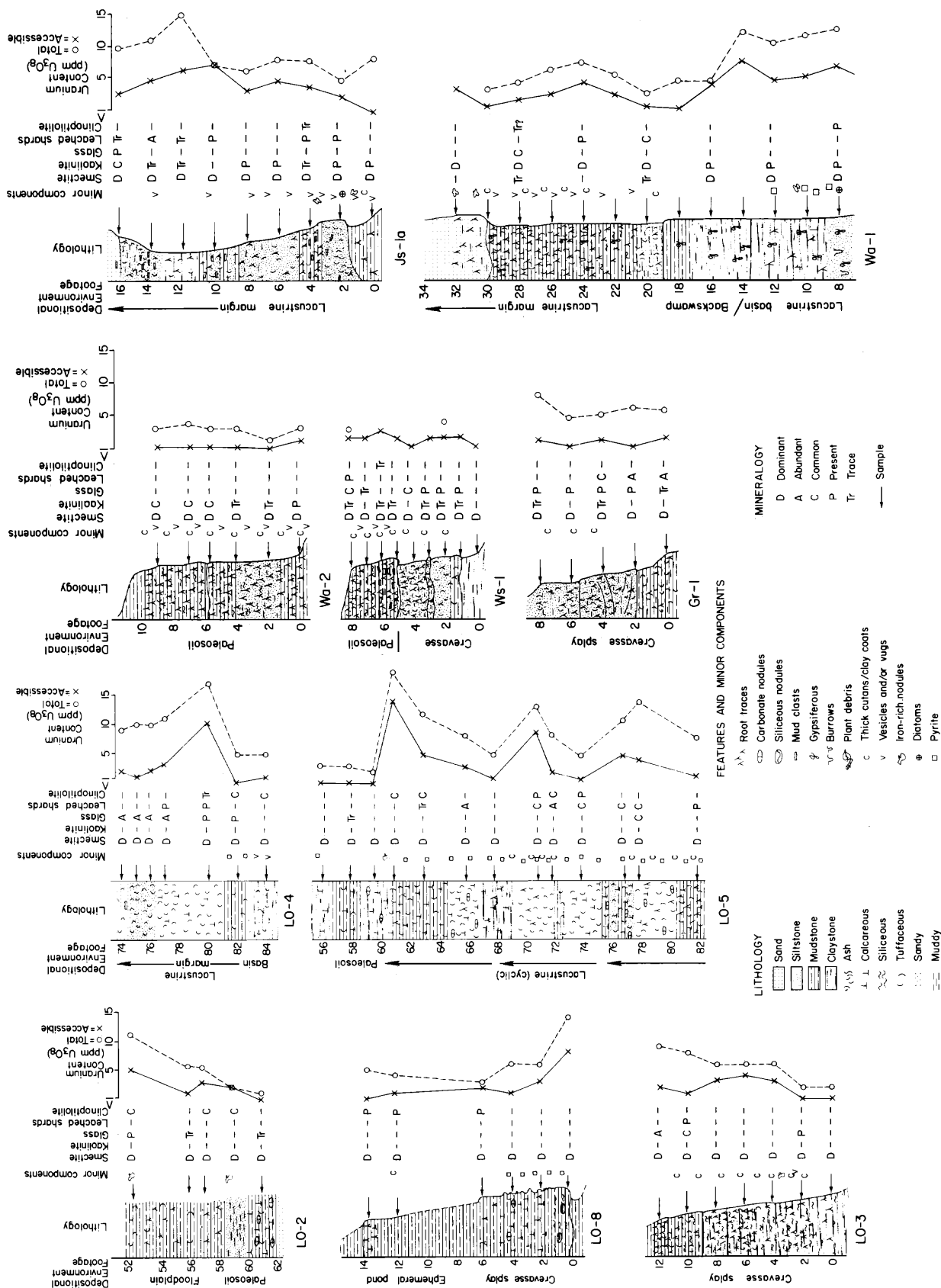
Syn depositional diagenesis: Syn depositional diagenetic features and minerals are dominantly the product of pedogenesis (soil formation processes) and repeated flushing of newly deposited sediment by meteoric water within the vadose zone. Such processes

are quite rapid and may modify or completely alter the texture and mineralogy of vitric volcanogenic sediments within a few tens to a few thousands of years (Davies, 1977; Hay, 1977).

Samples of Gueydan and most Chita-Corrigan paleosoils as well as intensely altered crevasse-splay and flood-plain sediments consist of massive, homogenized, poorly bedded to blocky, disturbed silt or sand in a clay matrix (Fig. 6A). Matrix clay is submicroscopic, and pedogenic features such as cutans (Fig. 6B), papules, and clay-filled root traces (Fig. 6C) indicate its pedogenic origin. Extremely oxidized paleosoils (Fig. 7, lower LO-2) contain submicroscopic zeolite (clinoptilolite), common micrite, and silica nodules and may be red or brown, even where entombed within a generally reduced pyritic section.

TABLE 2. Whole-Rock Uranium Content of Tascotal Samples (in ppm)

	Wire Gap section		Windmill section		Tascotal Mesa North section		La Viuda section		Manny Howard section	
	Sample no.	U content	Sample no.	U content	Sample no.	U content	Sample no.	U content	Sample no.	U content
Diagenetic assemblage			187	3.2						
			163.8	3.3						
	687	6.5	137	3.0	118	5.2				
	640	2.2	135.5	3.0	727	5.7				
	476	6.2	130	3.0	63	2.9	264	6.2		
Transition			127.5	0.9	42.1	5.8				
			126NZ	4.1	42	7.7				
			126Z	2.3						
			124.5	1.2	41.8	5.6				
			122.5	2.7						
Zeolite assemblage			111	1.4			220	11.3	364	4.2
			109	2.6	31.2	4.6			274	25.8
	418	5.6	60.9	3.1					227	5.0
			42	3.5	8	5.8			180	5.0
			33.5	3.4					65	6.8
			33	3.9					10	7.8



Calcite occurs as replacement micritic nodules or layers (Fig. 6D) and more rarely as dispersed intergranular cement. Early calcite is characteristically finely crystalline; staining of thin sections shows it to be iron-poor but possibly magnesium-bearing.

Montmorillonitic paleosols in the Gueydan and most of the Chita-Corrigan fluvial systems have many features characteristic of vertisols (Fitz Patrick, 1971). Pedogenic processes active within such soils, which are characteristically developed on volcanic debris in arid to semiarid areas, include (1) weathering of the parent material to produce abundant colloidal montmorillonite, which can then be washed about and coat grains or pores to form cutans; (2) precipitation of calcium carbonate as dispersed cement, crusts, or nodules; and (3) low content of organic material.

Significant kaolinite enrichment in paleosols occurs only in the easternmost portions of the Chita-Corrigan fluvial system, particularly in sequences formed along the densely vegetated margins of interchannel lakes (Fig. 7, Wa-1). Abrupt vertical changes in clay mineralogy from nearly pure kaolinite to pure montmorillonite within continuous depositional sequences indicate the diagenetic origin of the kaolinite. Examination of sections containing abundant kaolinite shows that vegetation (as indicated by the abundance of root tubules) was dense; detrital organic matter is preserved locally in kaolinite-rich muds. Weathering of volcanic ash in a wide range of humid climates produces andosols, which are characterized by allophane, an amorphous aluminosilicate gel (Fitz Patrick, 1971). Further intensification of leaching by organic acid-rich waters, particularly in highly saturated environments such as the margins of interchannel lakes, could strip virtually all cations and transform the early formed montmorillonite to kaolinite (Ahschuler et al., 1963; Huang and Keller, 1972). Kaolinite-rich sequences are notably free of carbonate and clinoptilolite, further suggesting efficient cation leaching and probably slightly acidic conditions.

In summary, pedogenic and vadose processes included the widespread argillation of volcanic glass, the precipitation of microcrystalline calcium carbonate, and, rarely, the precipitation of clinoptilolite.

Postdepositional diagenesis: With continued burial (perhaps to a few hundred feet), ash-rich units that had escaped argillation and retained some permeability were flushed by chemically evolving circulat-

ing meteoric waters. Further water-rock diagenetic reactions resulted in solution of the finest ash particles and authigenesis of montmorillonite rims on the remaining framework grains (Fig. 6E), the complete solution of large glass shards leaving pores or shard molds, and the precipitation of euhedral clinoptilolite in parts or all of the available pore space (Fig. 6F). Diagenetic montmorillonite is the dominant mineral component of many samples; zeolite rarely constitutes more than a few percent of the rock volume. Sparry calcite cement and opal also characterize this sequence.

The three diagenetic facies (fresh glass with montmorillonite rims, dissolved glass, and clinoptilolite) occur in a consistent spatial relationship. Fresh glass is characteristically separated from clinoptilolite-bearing samples by a transition zone of leached glass (Fig. 7, LO-4). This diagenetic sequence typifies the alteration of volcanic glass in open meteoric groundwater flow systems, such as the Tascotal Formation, and has been described in studies of several thick volcanic ash deposits (Hay, 1977; Walton, 1975).

The formation of both montmorillonite and clinoptilolite indicates complete dissolution of glass and at least some transport of the soluble products within moving ground water. The release of uranium would certainly be expected. Clinoptilolite is rare in the Chita-Corrigan sequences which formed under more humid paleoclimatic conditions.

Highly permeable, ash-rich units are prime candidates for thorough leaching and subsequent formation of zeolite. Paleosols and other units argillized by syngenetic destruction of ash have low permeability and rarely contain good examples of leached or zeolitized shards. In contrast, well-sorted lacustrine-margin tuffs, which were subjected to minimal pedogenic destruction of glass, provide the best examples of diagenetic zeolite formation (see Fig. 7, LO-5, for example). Similarly, tuffaceous sequences that overlie highly permeable sand facies commonly show abundant glass dissolution and zeolitization.

Because the flux of ground water in a coastal plain fluvial aquifer such as the Catahoula is spatially variable and time dependent, distribution of the various open system meteoric diagenetic facies is much more complex than that of a simple system such as the Tascotal. Extensive sampling would be necessary to outline the three-dimensional distribution of diagenetic facies within even a single local aquifer unit.

FIG. 7. Vertical distribution of lithology, mineralogy, and trace uranium content of selected depositional sequences of the Gueydan and Chita-Corrigan fluvial systems. LO-2, LO-4, and LO-5 are cores; the remainder are measured sections. The general locations of the sample areas are shown in Figure 1. Both the total and accessible uranium contents are generally higher in vitric sediments (such as LO-4 and LO-5) and lowest in thoroughly leached tuffaceous muds (such as LO-8 and Ws-2). Most glass survives early alteration in water-saturated lacustrine environments; consequently, open hydrologic system diagenesis is best developed in this facies (LO-4 and LO-5).

TABLE 3. Uranium Content (ppm U_3O_8) of Various Depositional Facies: Catahoula Fluvial Systems

	Common_____	Vadose flushing _____	Rare		
	High _____	Pedogenic _____	Weathering intensity_____	Low	
		Crevasse-splay/ lacustrine delta plain	Flood plain/ backswamp	Lacustrine	
	Paleosoils			Margin	Basin
Gueydan system					
Total U ₃ O ₈					
Average	2	6	7	9	5
Median	2	6	6	9	6
Accessible U ₃ O ₈					
Average	1	2	3	4	2.5
Median	<1	2	3	3	3
Bound U ₃ O ₈					
Average	1	4	4	5	2.5
Median	>1	4	3	6	3
No. of samples	5	21	3	22	6
Chita-Corrigan system					
Total U ₃ O ₈ (based on limited analysis)					
Average	3	5	7	7	11
Median	3	5	5.5	7.5	12
Accessible U ₃ O ₈					
Average	1	1	2.5	2.5	8
Median	1	1	2.5	2.5	6
Bound U ₃ O ₈					
Average	2	4	3	4	5
Median	2	4	3	5	5.5
No. of samples	10	9	18	18	17

The patterns are further complicated by local facies changes and structural discontinuities, and consequent cross-stratal flow and ground-water mixing. Waters saturated with respect to clinoptilolite may move laterally or vertically into beds containing no preserved shards. Zeolite could then precipitate in available intergranular pore space; or, if mixed with waters of differing composition, zeolite precipitation might be delayed or precluded. Despite local complexities, however, observed distribution and paragenesis are consistent with the open meteoric flow system hydrologic model developed in more lithologically homogeneous ash sequences.

Uranium mobilization

The extent of uranium mobilization must be assessed within the context of numerous interdependent variables, including an original abundance of glass or other uranium-bearing phases in the unit, depositional environment, and diagenetic history. One hundred twenty-nine samples were selected as representative of the variety of depositional and diagenetic facies present in the Catahoula Formation. The original glass content was, for the most part, impossible to determine because of the inherent pervasive alteration. However, all contained compositional or

textural features indicative of a high initial glass content. Splits of each sample were analyzed using hot nitric acid leach and total fusion extraction methods to give two values for the trace uranium content as summarized in Table 3. Total uranium (measured by sample fusion) is the sum of the accessible uranium (measured by acid leach), which includes loosely held uranium in surficial sites or other solid phases, and bound uranium, which includes uranium tightly bound within intragranular sites. Uranium that is accessible to hot nitric acid leach may not be accessible to cool, moderately to strongly basic ground water. Bound uranium is a measure of the minimum amounts held within glass or other insoluble mineral phases. Diagenetic alteration of the glass can lead to uranium mobilization with one of three consequences:

1. Uranium is flushed from the source unit. Both total and accessible uranium values will be low relative to samples containing abundant fresh glass.
2. Uranium is freed from the glass but is trapped in the precipitating insoluble mineral phases and returned to a bound state. Total uranium remains high and accessible uranium remains generally low.
3. Mobilized uranium is loosely trapped by other

diagenetic or detrital phases within the host unit. The average total uranium is thus not depleted, but all or most of the uranium occupies accessible sites. The extent of redistribution is indeterminable but must be sufficiently localized that little net whole-rock depletion of the depositional or diagenetic facies results. Sample to sample variation may be increased, however.

In a sample suite, comparison of bound, total, and accessible uranium is a useful guide to the extent of whole-rock depletion or enrichment. A high proportion of bound uranium indicates retention and limited mobilization. Enriched samples are readily indicated by their high proportion of accessible uranium.

Only uranium efficiently flushed from the source unit can contribute to the formation of ore deposits. Thus functional source rocks will be characterized by a low total uranium content. The efficiency of uranium mobilization can be estimated by a comparison of the average total uranium content of the sample suite with the known or inferred uranium content of the original source lithology. It is important to note that volcanic ash in the Catahoula was characteristically reworked and impure. Thus, the uranium content of a pure, fresh glass separate exceeds that of the impure, tuffaceous source units available for analysis.

A review of the uranium content in the sample suites (expressed as ppm U_3O_8) leads to several observations.

1. The intensity of syngenetic weathering and periodic leaching by oxidizing vadose meteoric water was a dominant control on bound, total, and accessible uranium within sample suites. Average and median uranium contents for each of five major environmental groupings within the Gueydan and Chita-Corrigan fluvial systems differ in proportion to the intensity of weathering and periodic flushing by oxidizing water in the vadose zone characteristic of each environment (Table 3). For example, the total U_3O_8 from five Gueydan paleosol samples that had undergone intense syngenetic alteration averaged 2 ppm compared with an average content of 9 ppm in 22 relatively unaltered lake-margin samples.

The details of uranium concentration within several representative sample sections further document the relationship (Fig. 7):

LO-2 is a highly oxidized paleosol zone capping a fluvial channel. It shows nearly complete uranium depletion relative to the overlying flood-plain muds.

LO-8 contains highly oxidized mud and claystone deposited in an ephemeral pond capping a crevasse channel; both are depleted in uranium. Less highly leached muds of the crevasse channel fill contain moderate amounts of uranium; slight enrichment may account for the high accessible amount of uranium and consequent high total uranium value in the base of the channel.

LO-3 shows a decreasing uranium content downward through a sequence of three crevasse-splay depositional units. The lowest splay unit also exhibits the greatest abundance of pedogenic weathering features such as iron oxide nodules, cutans, and vacuoles.

LO-4 and -5 are two lacustrine sequences, which include both lake basin and progradational lake margin deposits. They display a wide range of uranium content but are notable for the unusually high values found in a few samples and a high average uranium content. LO-5 is particularly interesting because three cycles of upward-increasing total and accessible uranium content correspond to three thin, progradational, lacustrine-margin cycles. The entire sequence is capped by a thoroughly leached and uranium-depleted paleosol.

A series of sections from the Chita-Corrigan fluvial system displays similar relationships among depositional setting, early weathering, and preserved uranium content (Fig. 7):

The Wa-2 section is a thick, highly weathered paleosol which exhibits a uniformly low uranium content. The intensity of syngenetic leaching is indicated by the abundance of kaolinite, particularly in the upper three samples.

Gr-1 is a section of vegetated crevasse-splay deposits, characterized by low available uranium and a low to moderate total uranium content.

The Js-1 section consists of interchannel lake-margin tuffaceous silt, mud, and claystone. It displays considerable vertical variation in available and total uranium content; however, total uranium ranges from moderate to high.

Wa-1 is made up of thick lake-basin clay and mud which contain moderate to high total and bound uranium. The capping progradational backswamp mudstone and interbedded muddy sand sequence, which exhibits abundant root traces and other pedogenic features, contains less than half as much uranium.

2. Destruction of glass by diagenetic alteration effectively releases uranium. In samples from the Gueydan system, 10 of them with approximately 10 to 50 percent fresh glass, average 10 ppm total uranium; an average of 7 ppm of this uranium is bound (Table 4). Significantly, none of the samples consist exclusively of fresh, unaltered ash. Typical Catahoula samples contain at least 50 percent clay, much of which is the diagenetic product of solution of the finest glassy debris. Thus 7 ppm is a minimum original average primary uranium content of fresh glass. Comparable values have been obtained for fresh glass separates from the underlying Whitsett Formation (Eocene). The actual primary uranium content could reasonably be assumed to have been several ppm greater; 10 ppm is a reasonable average.

Thorough diagenetic argillation of the glass reduced the total uranium content of glass-free samples

TABLE 4. Uranium Content (ppm U_3O_8)¹ of Various Diagenetic Facies: Gueydan Fluvial System Only

	Vadose pedogenic diagenesis		Open meteoric flow system diagenesis		
	Montmorillonite	Montmorillonite + zeolite	Fresh glass	Leached glass	Zeolite
Total U					
Average	5.5	4.0	10	6.5	9.5
Standard deviation	±3.0	±1.5	±3	±3.0	±5.0
Bound U					
Average	3.5	2.5	7.0	4	5.0
Standard deviation	±1.5	±2.0	±1.5	±2	±1.5
No. of samples	21	5	10	10	7

¹ Averaged to 0.5 ppm

to an average of 5.5 ppm (Table 4). The remaining bound uranium averages only 3.5 ppm. In thoroughly altered and oxidized paleosol zones typical of the bulk of updip Catahoula interchannel facies, the total uranium content is even lower (LO-2 and LO-5, top); the presence of minor amounts of syngenetic zeolite has no consistent measurable effect on uranium loss (LO-2 and LO-8).

Diagenetic alteration of glass in open meteoric ground-water flow systems further released uranium during shard dissolution. Samples showing common leached shards are highly variable but averaged 6.5 ppm U_3O_8 . Bound uranium averages 4 ppm (Table 4). Samples with well-developed pore-filling clinoptilolite average about 10 ppm total uranium but, significantly, individual values vary widely. Only half of the total, 5 ppm, is retained in sites where it is not leached by acid. The additional uranium is principally in an available form.

In summary, significant depletion of uranium from samples showing complete destruction of glass by pedogenic and vadose zone argillation is clearly documented. Further modest loss of uranium during open-system dissolution of glass is strongly suggested by the data. The effect of concomitant zeolitization downflow from the solution zone is more ambiguous. Open hydrologic system diagenesis seems to have produced primarily local redistribution with freed uranium trapped by zeolite, clay, or other alteration products. As in the Tascotal Formation, this slow intrastratal release of uranium seems to be ineffective in mobilizing uranium from potential source facies.

3. Uranium release processes, although somewhat different in mineralogical products, effectively mobilize uranium in the more humid climatic regime of the Chita-Corrigan fluvial system. The equivalent diagenetic facies of the Gueydan and Chita-Corrigan systems produced comparable average uranium contents, with the significant exception of the lacustrine

basin sections (Wa-1). A comparison of backswamp with lake basin and lake margin samples from both fluvial systems, grouped into kaolinite- and montmorillonite-dominated populations (based on semi-quantitative X-ray analysis), shows the average and median bound uranium content to be 3.5 ppm and 3 ppm, respectively. Likewise, available uranium averages 2 ppm in kaolinitic samples and 4 ppm in montmorillonite-rich samples. In general, uranium was thoroughly leached from tuffs by argillation during early diagenesis, assuming the original uranium content was comparable.

In summary (Fig. 8), analytical data indicate that: (1) the original uranium content of the glass-rich tuffs averaged at least 7 ppm U_3O_8 and was probably higher; (2) pedogenic and vadose zone argillation in both subarid and subhumid paleoclimatic regimes mobilized, on the average, over half of the original uranium present in the ash, releasing large quantities of uranium for migration into underlying aquifers; and (3) the additional dissolved uranium was released as buried ash was leached within open meteoric flow systems. However, because uranium mobilized by this mechanism appears to be rapidly sorbed by other alteration products present downflow from the glass-solution zone, no documented whole-rock depletion occurs.

The average tuffaceous Catahoula mudstone retains a median uranium content of about 6 ppm; of this total, about 4 ppm remains mineralogically bound. Assuming the sample suite is representative of the entire Catahoula¹, at least 1 ppm, and more likely 4 or more ppm of U_3O_8 , was released for ore formation. Though proportionally modest, the quan-

¹ The sample suite is in fact biased toward the diagenetically interesting but volumetrically less important uranium-rich lacustrine facies. However, quantification of the relative proportion of the different facies and appropriate weighting of the analytical results are extremely difficult because outcrop exposures are rare.

tity of mobilized uranium is staggering. One simple volumetric approximation gives 16 billion pounds per ppm mobilized in the updip Catahoula section of Texas. Equally important, the geology and paragenesis of epigenetic and possible syngenetic uranium and rapid sediment accumulation may have suppressed soil development.

deposits in the Catahoula are consistent with, and locally require, an early mobilization and primary mineralization event (Galloway and Kaiser, 1980).

Discussion

The analyses of glass diagenesis and uranium mobility in the Tascotal and Catahoula Formations suggest two conclusions and two subjects for further discussion. It is clear that shallow vadose and pedogenic alteration of volcanic glass leads to effective mobilization of uranium for long-distance migration and concentration in ore deposits. On the other hand, uranium dissolved from glass by diagenesis below the water table in an open ground-water flow system is typically redistributed only locally. Given these observations, how can we determine which type of diagenesis has affected potential source beds of uranium deposits. If further study bears out our conclusions about uranium mobility in different diagenetic systems, then the possibility arises of using functional source rock analysis as a tool in uranium exploration.

Criteria for alteration environments

The use of the conclusions of this paper for evaluating uranium potential requires that field, petrographic, or geochemical criteria for recognition of functioning source rocks be established. Field methods and microscopic analysis of textural features appear to be quite reliable, although recognition of key features may require considerable skill on the part of the observer. Chemical analyses should be used as a confirming technique, but they cannot yet be used alone because of the difficulty of establishing the initial uranium concentration against which to measure depletion.

Physical characteristics: Several interpretive and observational criteria may be used to aid in the recognition of rocks in which vitric material has experienced the pervasive syndeositional vadose alteration necessary for efficient uranium mobilization. General megascopic and microscopic features of soils and alluvium exposed to vadose diagenesis are reviewed by Brewer (1964) and Walker et al. (1978).

Depositional environments subject to long periods of subaerial exposure, such as dry flood-plain, natural levee, crevasse-splay, alluvial fan plain, and ephemeral lake environments, produce optimal source facies, provided vitric material was initially present.

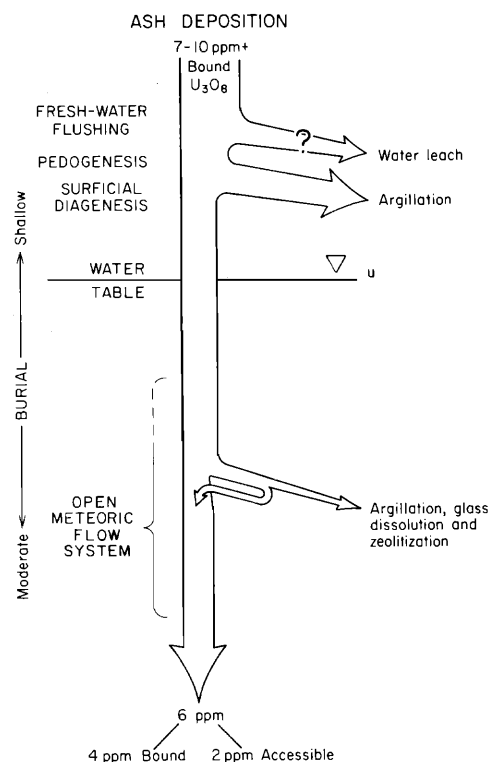


FIG. 8. Interpreted stages and relative efficiency of uranium mobilization from fresh ash-rich Catahoula tuff. Most effective leaching of uranium occurred soon after deposition in surficial and vadose diagenetic environments. On the average, several ppm of uranium have been effectively mobilized from vitric air-fall ash deposited around and above ore-host fluvial sand units.

Permanent lake, bay/lagoon, and marine deposits, which remain water saturated, are poor source facies. However, the exposed alluvial fanlike volcanic sedimentary aprons of the Tascotal Formation also do not contain abundant vadose features. An arid climate

Most soils, including those from which uranium is leached into circulating ground water for transportation and concentration, are characterized by a downward mobility of fluids and solids. Not only water but also clays and amorphous aluminosilicate materials move within the vadose zone. Solid particles commonly collect as coatings on grains or other elements of the soil, forming cutans. Soils also teem with organisms, including protists, plants, and animals, that during their growth or life have several effects on the soil. Animals burrowing through the soil churn and aerate it, leaving the burrows empty or filled with pellets or sand. Plant roots disturb the soil, make permeability channels, and create microenvironments in which certain mineralogical reactions occur. Both plants and animals die and decay in the oxidizing vadose zone, returning their nutrients to the soil.

The most abundant product of decay and of plant root respiration is CO_2 . Carbon dioxide levels in the soil atmosphere are commonly many times those in normal air. Together with rainwater and organic acids, CO_2 acts to break down unstable minerals into more stable ones. Feldspars and glass go to clay; mafic silicates alter to clay and iron oxides. The colloidal clays or soluble phases migrate in the soil, accumulating to form distinct horizons. Some constituents released by weathering form distinct concretions (papules) or precipitate as linings on voids (crystal-laria). Calcite is a common constituent of arid region soils, forming caliche (or calcrete).

Carbonate workers have developed a variety of criteria for recognition of microscopic textures developed during alteration in the vadose zone as opposed to the phreatic zone. The different textures result from the fact that the vadose zone is a three-phase system—water, gas, and solids—whereas the phreatic zone lacks the gas phase and all space not occupied by solids is filled with water. In the three-phase zone, surface tension causes water to draw up into nooks and crannies between grains or to form drops on the underside of grains. Evaporation or removal of water by plant roots causes precipitation of dissolved solids in masses that mimic the shape of the water droplets, generally rounding pores or outlining roots. Bathurst (1975) describes carbonate textures and Walker et al. (1978) illustrates vadose clay textures. Opal also forms excellent vadose textures, especially in rocks from the Texas Coastal Plain, including those from the Catahoula Formation.

Diagenesis in an open hydrologic system occurs beneath the water table and produces different textures, chiefly isopachous rims of cement. In many carbonate rocks, several such rims may be visible. In silicate cements adjacent layers may differ mineralogically, as well as texturally. In both the Tascotal and the Catahoula Formations, open-system diagenesis produced successive isopachous coatings of clay, opal, and clinoptilolite. Such textures are not known to form in soils or in vadose environments and, thus, are characteristic of diagenetic environments that are ineffective for uranium mobilization.

Specific evidence for pedogenesis and extensive vadose leaching in ash-bearing sediments, therefore, includes the following.

1. Mineralized crusts or nodular zones containing finely crystalline calcium carbonate or caliche, opal or chalcedony, or iron oxyhydroxides may be present.
2. A blocky, disturbed, massive, pedal fabric is indicative of shrink-swell attendant to alternating periods of wetting and drying.
3. Root-disturbed intervals exhibit clay-lined (cutans) to clay-filled or calcite-lined root tubules. Burrow churning by small mammals, insects, and worms is also common.

4. Unusual polymodal or poorly sorted textures suggest an abundance of authigenic clay.

5. Cutanic coatings around voids, root tubules, fracture planes, and framework grains are common. Clay segregations and cutans form by mechanical infiltration of dispersed aluminosilicate gels, which collect on available surfaces. Manganese coatings are also common.

6. The vertical zonation of several such features over intervals of one to several meters is particularly indicative of paleosoil formation.

7. Relict shard forms within the mud matrix.

8. There is evidence for abundant early diagenetic silicate minerals, particularly montmorillonite, kaolinite, and opal/chalcedony.

Geochemical criteria: Unfortunately, our analyses to date have not determined the concentrations of elements other than uranium. Consequently, the documented chemical criteria for functioning source rocks are limited to evidence of depletion of uranium. In order to establish this depletion, it is necessary to determine the amount of uranium originally present in the source rocks; in a completely altered suite of rocks, this may be difficult. Furthermore, variations in the whole-rock uranium content may arise because of differences in the initial uranium content of the glass, and the proportion of glass or other constituents in the sediment when it accumulated, as well as from redistribution of uranium during diagenesis or soil formation. Certain constituents, notably zircon, may contain very high concentrations of uranium but may be inert during the diagenetic process. If these are abnormally enriched in a set of samples, they mask the loss of a large proportion of uranium from the sources from which it is readily extracted. Several potentially useful methods of establishing uranium depletion do exist, however.

1. Comparison of altered and unaltered beds. This is probably the most useful technique and should be applied to both whole rocks and glass or mineral separates. Establishing the amount of uranium present in unaltered glass allows estimation of the primary uranium content of altered sediments for which it is possible to establish or estimate the initial glass content. Where whole rocks alone are used, one must establish the initial glass content of each sample and assume that the U concentration of the glass was the same.

2. Comparison of beds altered by different processes. Sygenetic alteration of glass-rich sediments or tuffs releases uranium for migration, but open meteoric flow system alteration does not. With care, the uranium content of rocks altered by open hydrologic systems can be used to estimate the average initial uranium content. This can then be compared to the content of beds that were compositionally similar but were altered by different processes. Some beds altered

by open hydrologic systems are locally enriched in uranium, but analytical procedures designed to contrast accessible and bound uranium will aid in their recognition.

3. Analyses through a paleosol zone into underlying altered or unaltered sediments. Unless enrichment of the lower levels has occurred, the uranium content should increase from the surface downward, with the maximum values best indicating the primary uranium content.

Conclusions

Although four possible modes exist for release of uranium from volcanic glass, only total solution of glass has been shown to operate at a significant scale. Selective leaching of uranium without complete solution probably does not occur and evidence for slow release from alteration products of glass is equivocal. Uranium is not present in significant quantities on the surface of freshly erupted shards, so washing of absorbed ions will release little uranium. Further, geologically continuous, slow release is not compatible with evidence for a temporally restricted mineralization epoch typical of major sandstone uranium districts (Galloway et al., 1979). Total solution of glass releases uranium to migrate only when it occurs in vadose environments very early in the history of the sediment. Complete solution of glass beneath the water table during diagenesis in open hydrologic systems causes only local redistribution of uranium.

These observations permit the development of rapid, inexpensive prospecting methods aimed at the recognition of functioning source rocks. Such source rocks are reliably recognized by genetic facies relationships and by textural features visible in hand specimens and thin section. The release of uranium can be confirmed by chemical analysis. Use of these techniques early in the evaluation of regions can lead to a ranking according to the likelihood of epigenetic uranium occurrence. Conventional geologic, geophysical, and geochemical prospecting techniques and models can then be concentrated in geographic areas and geologic horizons where deposits are most likely.

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