

RELATION OF DIAGENETIC ALTERATION AND SOIL-FORMING PROCESSES TO THE URANIUM DEPOSITS OF THE SOUTHEAST TEXAS COASTAL PLAIN¹

by

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ABSTRACT

The Upper Eocene Jackson Group is the chief host rock of the uranium deposits in the Karnes area of the southeast Texas Coastal Plain. It is highly tuffaceous and the uranium deposits are within approximately 100 ft of the unconformity with the overlying Catahoula Tuff (Miocene ?). Glass shards, fragments of sanidine and plagioclase, grains of fine-grained volcanic rocks, and biotite and other minerals in these sediments were highly reactive chemically, causing complex diagenetic alteration and the development of alkaline carbonate pore water. Extensive caliche development and silica induration associated with a recent hotter, drier climate favored the concentration of uranium. The origin of these shallow uranium deposits is believed to have been controlled by the complex diagenesis of the highly reactive volcanic detritus, by development of a "built-in" solvent for uranium (the alkaline carbonate pore water), and by climatic, structural, and permeability conditions that allowed concentration and deposition of uranium rather than dilution and dispersal. The tuffaceous rocks are considered to have been the source of the uranium and associated molybdenum, phosphorus, and arsenic.

INTRODUCTION

The purpose of this paper is to outline the important relations between diagenetic and soil-forming processes in tuffaceous rocks and the origin of the uranium deposits in the southeast Texas Coastal Plain (Fig. 1). This discussion supplements the description of the uranium deposits given in the guidebook of the Coastal Plain field trip conducted as part of the program of the Tenth National Clay Conference (Eargle and Weeks, 1961a). The climate of the area, the character of the ground water, and the geologic structure are significant factors in the geochemical environment and origin of the deposits. It seems to us that the development of the uranium deposits in the Tertiary sedimentary rocks of the Texas Coastal Plain began with the diagenesis of the sediments and continued for millions of years. Modification of the deposits by soil-forming processes is still going on.

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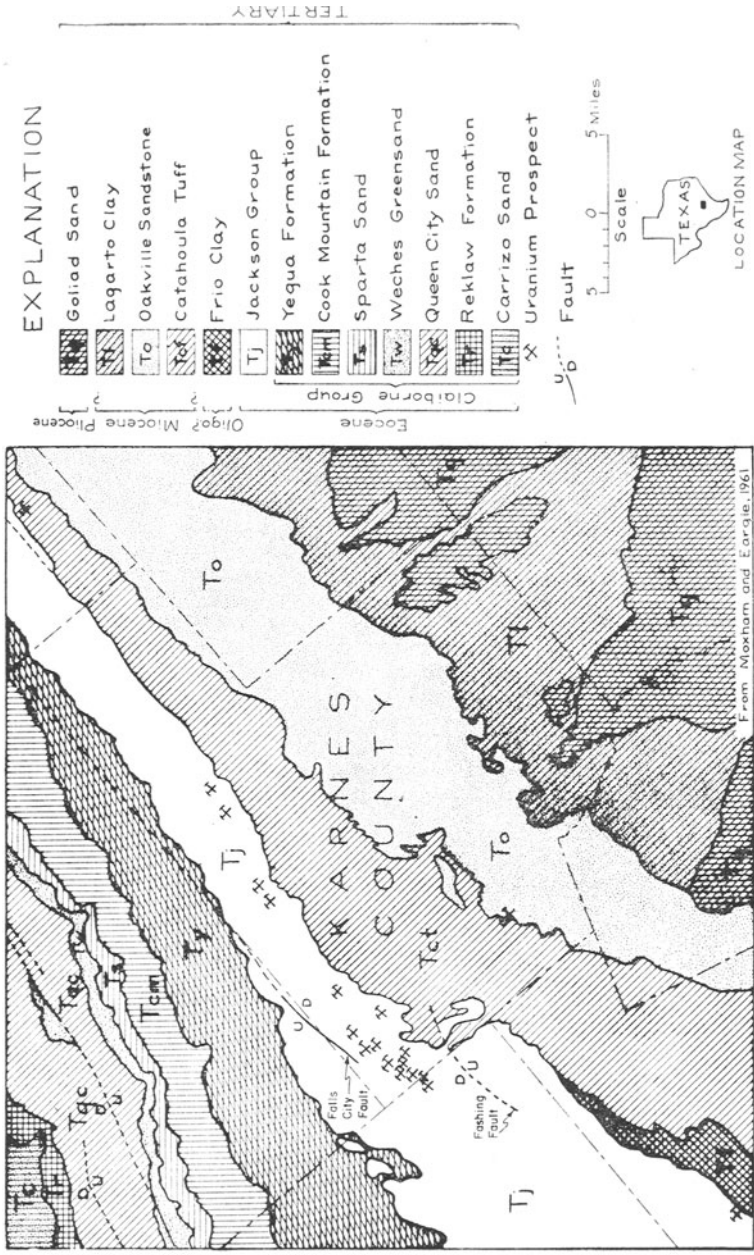


FIGURE 1.—Generalized geologic map of Karnes area, Texas.

MEANING OF DIAGENESIS

Possibly because we define diagenesis broadly, we have trouble finding a break between the "end" of diagenesis and the "beginning" of uranium mineralization. Dapples (1959) has used the term diagenesis "in an informal sense to designate the modifications which a sediment experiences during its deposition and lithification". He distinguished three stages in the diagenesis of quartzose sandstones: (1) deposition characterized by rounding and pitting of quartz grains and instability of some minerals with minor but persistent solution of silica, (2) early burial characterized by precipitation of quartz as overgrowths, and (3) late burial characterized by addition of carbonate as cement and as a replacement of quartz. Some geologists would limit diagenesis to alterations which occur prior to cementation and others would include any transformation before metamorphism. Pettijohn (1957, p. 648) defined diagenesis as "the reactions which take place within a sediment between one mineral and another, or between one or more minerals and the interstitial or supernatant fluids", and considered the processes involved to include cementation, authigenesis, diagenetic differentiation and segregation, diagenetic metasomatism, intrastratal solution, and compaction. The latter definition is more inclusive and more applicable to the diagenesis of the tuffaceous rocks in the Karnes area of Texas.

CHARACTER OF URANIUM HOST ROCKS

In general, the host rocks of the so-called sandstone-type uranium deposits (outside of Texas as well as in Texas) are quite different geochemically from average marine quartzose sandstones, and their diagenesis is more complex. The uranium deposits are mainly in terrestrial sediments, representing alluvial plains, basin fill, coastal plains, and some lacustrine deposits. The host rocks are chiefly tuffaceous or arkosic sandstone with some conglomerate, shale, lignite, and limestone or sandstone closely associated with tuffaceous rocks. The rocks are characterized by silicic, calcitic, or dolomitic cements and by various types of clay and chloritic alteration products (Weeks, Truesdell and Haffty, 1957). Some show the development of one or more zeolitic minerals. The sediments have local areas of reducing environment associated with pyrite or other sulfide minerals, coalified wood, humic material, H₂S, or asphaltic(?) material.

In particular, the Upper Eocene Jackson Group of the Karnes area in the southeast Texas Coastal Plain has alternating marine and nonmarine sediments in thin lithologic units that include highly feldspathic and lithic (volcanic) sandstone, tuffaceous sand, shaly ash, lignitic clay, and marine fossiliferous sandy clays. The Catahoula Tuff, of Miocene(?) age and unconformable on the Jackson, consists of thick ash, tuffaceous sand, and thin conglomerates of volcanic rock fragments including andesite, trachyandesite, trachyte, rhyolite, and pumice. The tuffaceous, feldspathic and lithic sediments are unstable in the sedimentary environment and are much more

highly reactive chemically than normal marine sands and lagoonal clays, which consist chiefly of relatively insoluble quartz and clay minerals with traces of resistant heavy minerals. The volcanic shards are particularly unstable because of their glassy state and large surface area. The sand-size grains in the Jackson include many cleavage fragments of sanidine and zoned plagioclase phenocrysts, and grains of aphanitic to trachytic fine-grained volcanic rocks, with traces of "books" of biotite and other mafic minerals. In general, these are much more susceptible to alteration than is quartz.

DIAGENESIS IN THE KARNES AREA

Several types of diagenetic alteration and a variety of authigenic minerals have been noted in tuffaceous rocks of the Jackson Group. The alteration of tuffs to montmorillonitic clay is an irregular or nonuniform process, inasmuch as some layers have altered to fairly well-developed bentonite, and other layers are slightly altered with fair to good shaly texture still preserved. In the Karnes area all the parts of the Jackson Group, but not the Catahoula Tuff, show some zeolitic alteration with development of authigenic heulandite (probably the variety clinoptilolite) in microscopic interstitial crystals, or as a firm cementing material in the feldspathic and lithic sandstones; also the zeolite is present in fine-grained altered tuffs where it was detected only by an X-ray diffraction pattern. What seem to be authigenic feldspar overgrowths are found in several thin sections of feldspathic sandstones. The silica that was released in the alteration of volcanic glass formed much opal and chalcedony both as cements in the sandstones and as opalized wood and tuff. The pore water became saturated with silica from the volcanic glass before any appreciable etching of quartz had taken place. Etching of quartz grains is important only locally, and redeposition of silica as quartz overgrowths is minor compared to the amount of opaline coating and chalcedonic interstitial filling.

Diagenetic alteration also includes the migration of manganese and its redeposition as oxide in spots and seams. Locally in the Lyssy (San Antonio Mining Company) prospect trench in western Karnes County, seams were as much as $\frac{1}{2}$ in. thick. Fine-grained pyrite and marcasite are commonly, but not necessarily, associated with plant fragments or other organic material. Siliceous or calcareous concretions occur in several zones in the upper part of the Jackson Group; in particular, one layer in the Stones Switch Sandstone Member of the Whitsett Formation in the Luckett mine in western Karnes County has dense calcareous concretions several feet in diameter. Authigenic barite was noted in many heavy-mineral fractions, and siderite is present in a few samples.

A sharp distinction cannot be drawn between the authigenic minerals formed by diagenetic alteration and the uranium ore and gangue minerals. Neither can a specific paragenetic sequence of ore and gangue minerals be established for this type of shallow uranium deposit because several of the minerals probably formed at more than one time (see discussion of origin).

WEATHERING AND SOIL-FORMING PROCESSES
IN KARNES AREA

The Karnes area is generally soil-covered except for natural exposures of bare rock along the frontal slopes of the steeper cuestas and along banks undercut by streams. The weathering and soil-forming processes, conditioned by the climate, have played an important role in the migration and redeposition of uranium. The Karnes area is on the border between subhumid climate to the east and northeast and semiarid climate to the west and southwest. There is evidence of a change, since perhaps Middle Pleistocene time, from a hotter, drier climate with extensive caliche development and silica induration to a more humid climate with development of an organic-rich topsoil and with less caliche in the subsoil. In humid areas most of the soluble products are flushed out and removed from the area by ground and surface drainage. In drier climates soluble materials are removed to a lesser degree, depending on the amount of accumulation during hot, dry weather compared to the amount lost during occasional heavy rains; also soil and ground water tend to become alkaline and high in carbonate.

Of interest in relation to the uranium deposits are the caliche development and the silicification. In the Karnes area, the thick caliche layer of a former drier climate is largely removed; much has been redistributed as veinlets in the subsoil, but some fairly continuous patches remain on the outcrop of the Catahoula Tuff. This area is about the northeastern limit of a large area of caliche which extends southwest and south through Duval County, Texas, into Mexico. It is also the northeastern limit (as far as known in 1961) of commercial uranium deposits in the Texas Coastal Plain. The carbonate ground water from which the caliche developed also could have held the uranium in solution as uranyl carbonate complex ions. The warm, dry conditions that caused the caliche accumulation through evaporation and loss of CO_2 also favored concentration rather than dispersal of uranium. Caliche commonly forms by deposition of calcium carbonate derived from limestone or carbonate minerals; calcium carbonate can also develop in altered dacitic or andesitic tuffs by the release of calcium from volcanic glass or from calcium-bearing minerals and pick-up of carbon dioxide from the air.

As the tuffaceous sediments are altered, considerable silica is released. It may be transported only a few feet or perhaps much farther before forming opalized wood or opalized ash, or coating detrital grains in sandstone. Many silicified sandstone beds are found along the outcrop of the Jackson Group and of the Catahoula Tuff in Karnes County and a short distance southwest into Atascosa County. Fine-grained sandstone commonly has thin rims of opal on the sand grains and medium-grained sandstone generally has alternating opal and chalcedony bands. A few samples show an interstitial fill chiefly of chalcedony with very little opal. This silicification is a surface phenomenon that rarely extends more than 10 ft below the surface, as seen in many of the uranium prospect trenches as well as in drill cores. It is not continuous at the surface, but gives the impression of being related to a slightly older erosion

surface that is now being gently dissected and from which the caliche cap has been removed. At most of the uranium prospect trenches and open-pit mines the silicified rock has little or no uranium content. The ore is usually in friable sand under the silicified cap. In a few places friable sand of ore grade has been found close to the surface without the silicified cover, and at one prospect (Jacobs Ranch in southwestern Gonzales County) uranyl vanadate minerals were in a silicified coarse sandstone directly at the surface of the ground.

CHARACTER OF THE GROUND WATER

Recent publications on the ground-water geology of Karnes County (Anders, 1960), Wilson County (Anders, 1957), and Live Oak County (Anders and Baker, 1961) indicate certain characteristics of the ground water in formations of the Karnes area that are pertinent to our discussion of altered tuffs and the origin of the uranium deposits. With some precautions, ground-water data may be interpreted to reflect the nature of the formation pore water—particularly in this subhumid to semiarid area where many of the rocks are poor aquifers, recharge is very slow, and the wells are mostly of moderate depth. Only in the one good aquifer, the Carrizo Sand of Middle Eocene age, is there much recharge, and fresh water extends to a depth of several thousand feet.

In Wilson County just north of the uranium area, a small number of wells in the Jackson Group generally have rather highly mineralized water of poor quality. In Karnes County, a larger number of wells in the Jackson range from a small yield of 10 to 50 gal per min to moderate yield of 50 to 500 gal per min. Quality ranges from "fresh" (containing less than 1000 ppm total dissolved solids) to moderately saline (with total dissolved solids between 3000 and 10,000 ppm).

Of interest are the silica, sodium, bicarbonate, fluoride, boron, and pH. Only the more recent chemical analyses include the determination of silica, or about 100 of the several hundred analyses in these reports (Anders, 1957, 1960; Anders and Baker, 1961). Figure 2 shows the silica content in ppm in water samples from the Lagarto Clay (Miocene?) and Oakville Sandstone (Miocene?) grouped together, the Catahoula Tuff (Miocene?), the Jackson Group (Upper Eocene), the Yegua Formation (Middle Eocene), and the Carrizo Sand (Middle Eocene). It is not possible to be certain that each water sample came exclusively from the formation indicated. To avoid confusion, samples known to be mixed Jackson and Catahoula water or Catahoula and Oakville water have been omitted from the graph. Although the number of silica determinations for some of the formation waters is small, the Catahoula water samples tend to have much more silica than the others because of the large percentage of volcanic detritus in the Catahoula. Silica averages 80 ppm in the Catahoula samples and the largest number of samples are in the 90 to 100 ppm bracket, a content much higher than in most natural waters (Hem, 1959, pp. 56-57). The Jackson samples with an

average of 49 ppm and the Oakville and Lagarto samples with 46 ppm are notably less than the Catahoula but are still above the common 0 to 30 ppm range. The Jackson originally contained considerable volcanic material interbedded and partly mixed with nonvolcanic material. Its volcanic detritus is finer grained and more altered than that in the Catahoula, and more time

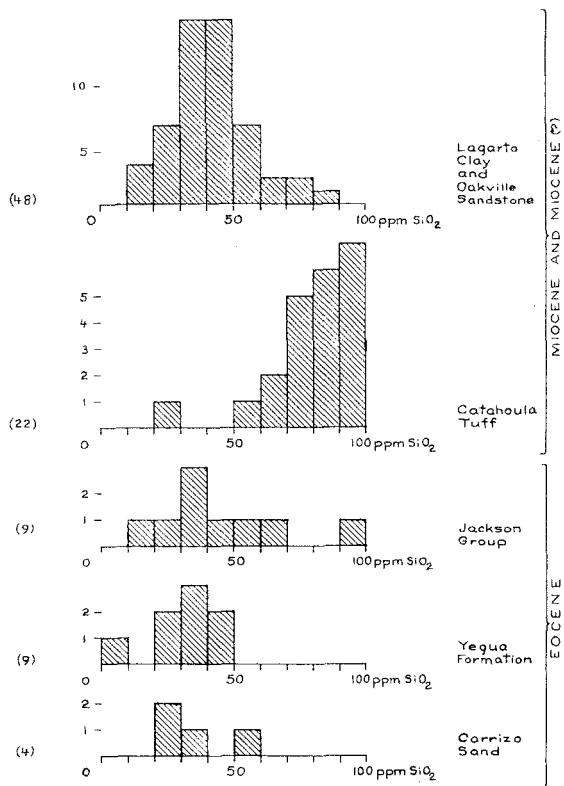


FIGURE 2.—Silica content in parts per million in ground-water samples from Karnes County and Live Oak County, Texas. (Analyses by the U.S. Geological Survey.)

has intervened since the Late Eocene for the formation of zeolite and authigenic feldspar and the precipitation of silica in opalized wood and as interstitial fill. The interbedded nonvolcanic material—sand, shells, and wood—has afforded local sites of deposition for much of the silica of the Jackson. The Oakville Sandstone and Lagarto Clay contain less volcanic material than the Catahoula and are not much altered. The high silica in the water of the Karnes area is accompanied by high sodium, a common association (Hem, 1959, p. 57).

The sodium content of the ground water is generally high and commonly Na^+ is the dominant cation. Anders' (1960) report on Karnes County includes in the tables of water analyses several calculated parameters useful in judging the quality: percent sodium, sodium-absorption ratio (SAR), and residual sodium carbonate. Nearly four-fifths of the samples have more than 50 percent sodium (with respect to total Na, Ca, Mg, and K), and the samples with more than 90 percent sodium are chiefly from the Catahoula or mixed Catahoula and Jackson waters. However, the average sodium content of the Jackson water samples is 675 ppm, somewhat above the average 533 ppm of the Catahoula samples. This is partly because the Jackson includes more marine beds and its water contains more chloride than the Catahoula.

In many analyses potassium has been included with the sodium as equivalent sodium, but in those analyses for which potassium is listed separately, it is commonly one-thirtieth to one-tenth as much as the sodium. Hem (1959, p. 91) states that the concentration of potassium seldom rises over 15 ppm in ordinary surface and ground water and is usually 10 ppm or less. In the Karnes County report only 57 potassium determinations are listed; the average potassium content is in the 25 to 30 ppm range for the Catahoula, Jackson, and Yegua samples, about 20 ppm for the Oakville, and less than 10 ppm for the Carrizo Sand and Lagarto Clay. The highest individual sample is 70 ppm from the Catahoula Tuff.

The high content of alkalis in the ground waters suggests that alkalis are being released by alteration of the volcanic glass and the water has not moved far enough for the usual selective removal of potassium. The Catahoula sediments probably have never been buried by more than a few hundred feet of overburden, which is too small a load to have squeezed out much pore water. In contrast, a few samples from a depth of several thousand feet in the Carrizo Sand have a potassium average of 7 ppm and sodium of 689 ppm. These waters have a high bicarbonate average of 1630 ppm, a small amount of carbonate (determined on only two samples) and pH ranging from 8.0 to 8.7. The range of pH for the Catahoula samples is 7.3 to 8.5 for 22 samples with an average of 7.73. The Jackson samples range in pH from 6.6 (only one sample below 7) to 8.3 with an average of 7.74. Other than the high bicarbonate samples of the Carrizo, only a few Jackson and Catahoula samples have a concentration of bicarbonate above 500 ppm (highest 831). Most of the Catahoula samples are in the 300 to 400 ppm range and average higher than the Jackson samples which show a wide spread and average 291 ppm. Silica tends to increase with increasing HCO_3 and alkalis up to a maximum controlled by the solubility and availability of silica. The Catahoula Tuff has the largest amount of available amorphous silica in the glass shards and the Carrizo Sand contains chiefly quartz with much lower solubility than glass, although the bicarbonate content of the Carrizo water is higher than that of the Catahoula water.

The presence of the fluoride ion and of boron (expressed as the element instead of one or more ions) is related to the tuffaceous nature of the sediments. Fluoride may be derived from the fluorine-bearing minerals apatite

and fluorite, but probably larger quantities are released more easily from volcanic glass. None of the water samples from the Karnes area have unusually high F, but many contain 1 to 3 ppm whereas normal surface waters commonly contain less than 1 ppm. Likewise none of the samples are exceedingly high in boron, but slightly more than half of the samples tested contained more than 1 ppm, and 30 percent contained more than 2 ppm, with the highest at 11 ppm. Most water from nonvolcanic terranes contains less than 1 ppm.

In summary, the composition of the ground waters in the Jackson and Catahoula sediments clearly reflects the influence of the alteration of the volcanic detritus by their high content of silica, alkalies, bicarbonate-carbonate, fluoride, and boron.

STRUCTURAL SETTING OF THE KARNES URANIUM DEPOSITS

The uranium deposits are in the upper part of the Jackson Group in an elongate area that lies in a grabenlike structure in western Karnes County (Fig. 1). On the northwest is the Falls City fault, with the downthrown side toward the coast, and to the south and southeast are several less continuous faults, with the upthrown side toward the coast, such as the Fashing and Hobson faults (Eargle, 1959, pp. 35-38). The rocks dip generally southeastward toward the Gulf of Mexico, except for displacements along these faults. The faults seem to be part of the Mexia fault system, and they generally are *en echelon* along the trend, but individual faults may extend 5-25 miles along the strike. The faults apparently were initiated late in Early Cretaceous time and movement on some has been sporadic until at least Miocene time or later (A. W. Weeks, 1945, p. 1736). Local warping of beds along the faults produced several oil structures. Oil and gas are produced from beds of Eocene age at depths of a few thousand feet and gas and distillate from limestone of Cretaceous age at depths exceeding 10,000 ft. The possibility of a relation between the deposition of uranium and the reducing environment produced by H_2S from the petroleum has been considered (Eargle and Weeks, 1961b).

The uranium deposits in the upper part of the Jackson Group are close to the unconformity with the Miocene (?) Catahoula Tuff. The intervening Frio Clay (Oligocene ?) has been eroded and the Catahoula rests on progressively older members of the Jackson toward the north. The largest deposits are in the Stones Switch Sandstone Member of the Whitsett Formation and deposits generally below ore grade are in sand beds in the Dubose Member of the Whitsett (upper part of Jackson Group). The most favorable area in the Stones Switch is controlled by a permeability barrier in the form of a local silty clay zone down dip in the sandstone (MacKallor and Bunker, 1958) and by the less permeable Conquista Clay Member of the McElroy Formation underneath.

COMPOSITION OF THE TUFFACEOUS SEDIMENTS AND OF THE URANIUM ORES

Semiquantitative spectrographic analyses have been made on ore and low-grade samples from the uranium prospect pits and on samples taken for lithologic and stratigraphic studies away from ore. These analyses are summarized in graphs (Figs. 3, 4, 5 and 6) that show on a logarithmic scale the range of abundance of each element; also the number of samples in each spectrographic bracket, the approximate limit of sensitivity of the spectrographic method for each element, and the average abundance of each element in sandstone, as given by Green (1959). The samples are grouped as follows: (1) formations of the Claiborne Group (Middle Eocene), (2) formations of the Jackson Group, (3) ore and low-grade samples from the Jackson Group, and (4) Catahoula Tuff. The graphs afford easy comparison of the composition of the groups of samples with one another and with average sandstone.

The Claiborne samples (Fig. 3) contain only 25 elements detected by the spectrograph, a much more restricted suite than is found in the Jackson and Catahoula samples. The Al content ranges from that of sandstone toward that of clay because the Claiborne contains some sandy clays and glauconitic sands. The Ca, Na, and K are slightly low for both sandstones and shales. The amount of glauconite is small and has no appreciable effect on the Fe and K content. The only elements notably higher than in average sandstones are Sc and Y. Their contents are more typical of shales than of sandstones. The small number of elements in the Claiborne sediments suggests that they were more highly weathered and depleted resistates than the sediments in the Jackson Group.

Semiquantitative spectrographic analyses of 33 non-ore samples from various members of the Jackson Group (Fig. 4) show As, Ce, La, Nd, Co, Mo, and Sn in addition to all the elements of the Claiborne Group. This composition represents a transition to the ore suite, which contains an additional 6 elements: U, P, Ge, Zn, Tl, and Cd (Fig. 5). The Jackson samples contain a larger percentage of sodium, rare earths, arsenic, phosphorus and several metals than do the Claiborne samples. These elements in the Jackson are due to its large content of unweathered volcanic ash and other igneous fragments. Although the Jackson deposition was alternating lagoonal or shallow marine and nonmarine, the intervals of emergence apparently were not long enough for appreciable weathering or leaching of material before burial by more sediment.

Both ore and non-ore suites of samples have above average Al and Na, average K, and low Fe and Mg, which reflect the composition of many feldspar fragments, glass shards and sand-size grains of trachytic rock. The rare earths and trace metals could have been associated with these apparently somewhat alkalic volcanics. The ore samples (Fig. 5) show increased concentration of several elements that are present in the non-ore samples, such as Ba, V, and Mo, and the greatest concentration in U. Although not indicated by the graph, Mn probably has also been concentrated. In selecting samples for

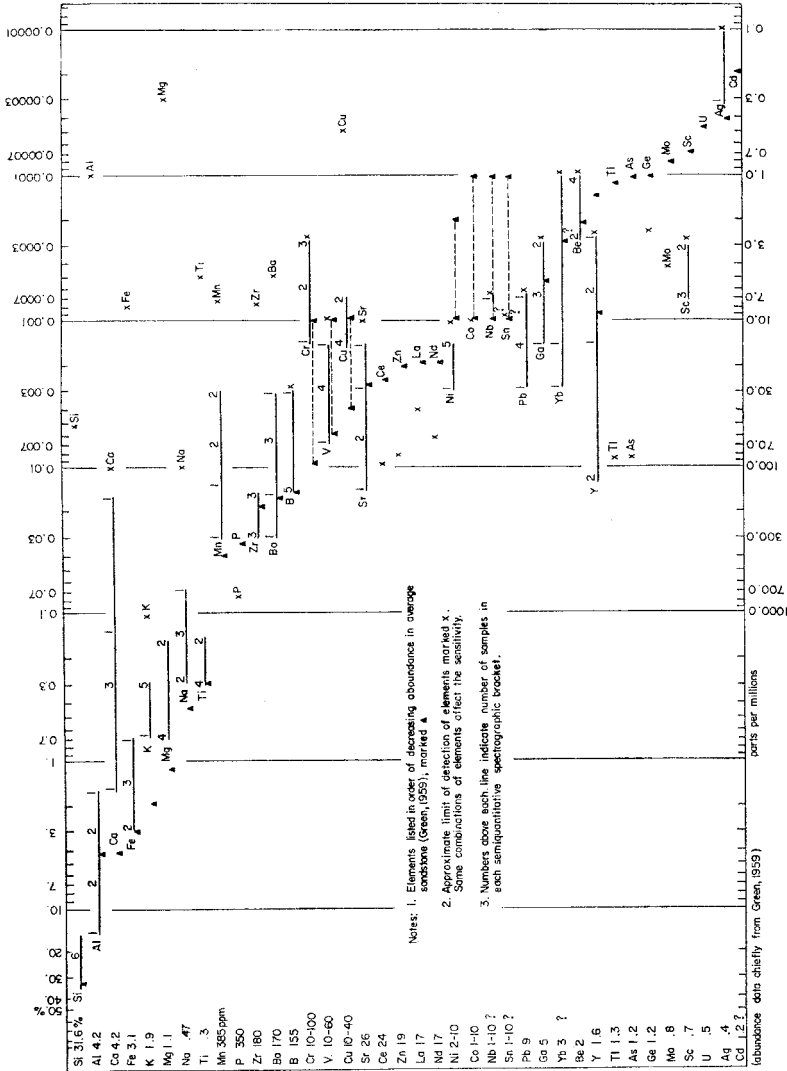


FIGURE 3.—Range of composition of samples from the Claiborne Group (Middle Eocene), Karnes area, Texas, as shown by semiquantitative spectrographic analyses, compared with the composition of average sandstone. Analysts: K. V. Hazel and H. W. Worthing.

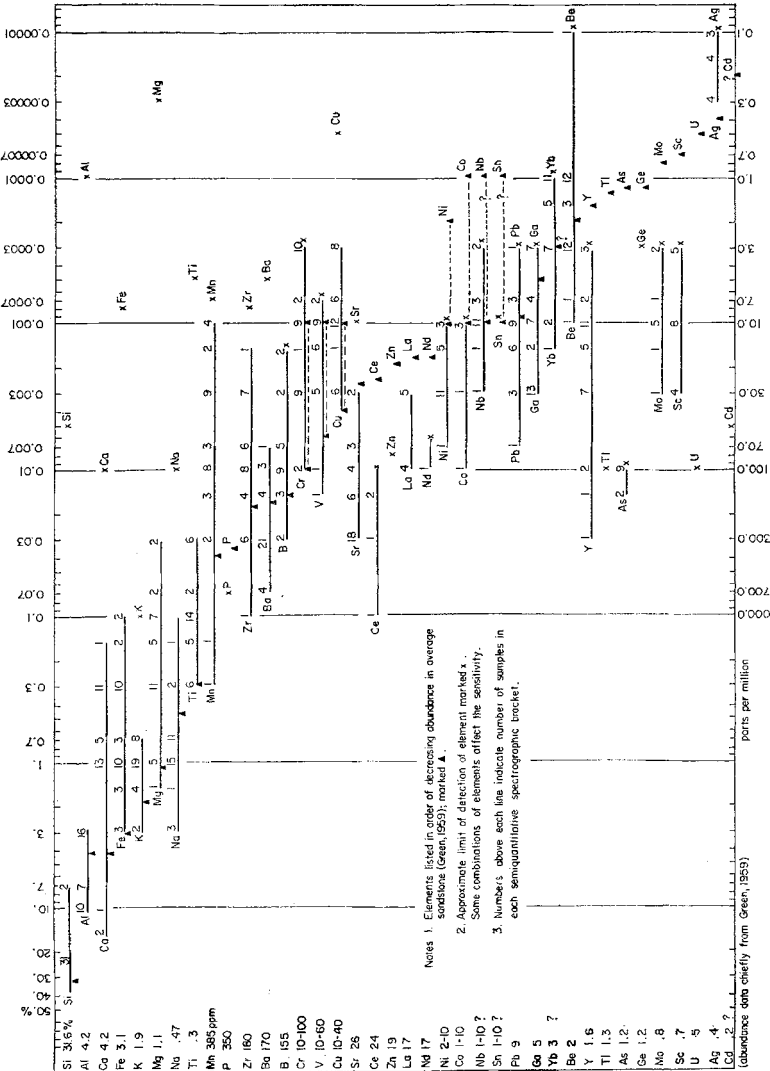


FIGURE 4.—Range of composition of “non-ore” samples from the Jackson Group (Upper Eocene), Karnes area, Texas, as shown by semiquantitative spectrographic analyses, compared with the composition of average sandstone. Analysts: Joseph Hafty, H. W. Worthing, K. V. Hazel and C. L. Waring.

spectrographic analysis, one tends to avoid a sample with conspicuous manganese oxide coatings, and this bias results in an "apparent" lower average Mn content in the ore. Uranyl phosphates or arsenophosphates are common ore minerals, but the spectrographic limit of detection of As and P is too high for the determination of these elements except in rich samples. The volcanic glass of the Jackson could easily have supplied the phosphorus and arsenic that have combined with the uranium in the oxidized deposits. Wilcox (1959, p. 458) gives the bulk composition of three ash samples from the 1912 eruption of Mt. Katmai, Alaska, and reports P_2O_5 as 0.22, 0.14 and 0.05 percent. He points out that an ash mantle several inches thick contains large absolute amounts per acre of such mineral nutrients (for plants) as potash, lime, and phosphorus. In the ore, uranium is concentrated from 0.5 ppm in average sandstone or perhaps 10 to 20 ppm in alkalic volcanic ash to about 0.25 percent or 2500 ppm ("average" ore depending in part on mining and milling economics), a concentration factor between a few hundred and a few thousand. The airborne radioactivity survey (Moxham and Eargle, 1961) indicates that the Jackson and Catahoula tuffaceous rocks probably had an average content of at least 10 to 20 ppm uranium. Molybdenum has been concentrated about 100 times and vanadium about 10 times more than in average sandstone, but neither the molybdenum nor vanadium has any commercial value in the Karnes area.

The spectrographic analyses of the Catahoula samples (Fig. 6) show a close resemblance to those of the Jackson samples, and more to the Jackson non-ore because all but two of the Catahoula group of samples are non-ore samples. No calicheified Catahoula samples were included in the graph, although one sample of the uppermost part of the Catahoula close under the Oakville Sandstone contact at the Hoffman prospect is quite calcareous. The Catahoula samples show 33 elements including rare earths and niobium, and the ore samples contain uranium with higher than average V, Mo, and As; the same suite as in the Jackson samples. The only elements found in Jackson samples but not found in the Catahoula samples are P, Zn, Cd, Sn, and Ge. The first four of these have a high limit of detection in the spectrograph and were detected in only a few Jackson samples. The fifth, Ge, is commonly associated with lignitic beds which are lacking in the Catahoula. Thus, the spectrographic analyses show no significant compositional difference between the Jackson and Catahoula sediments.

ORIGIN OF THE KARNES URANIUM DEPOSITS

From the time the writers first made a reconnaissance study of the Karnes area uranium prospects in 1955, they were impressed by the environment of these shallow deposits in partly altered tuffaceous rocks, with alkaline carbonate ground water, lenticular character of moderately permeable and poorly permeable beds, and subhumid to semiarid climate with evidence of intense caliche development in the recent past.

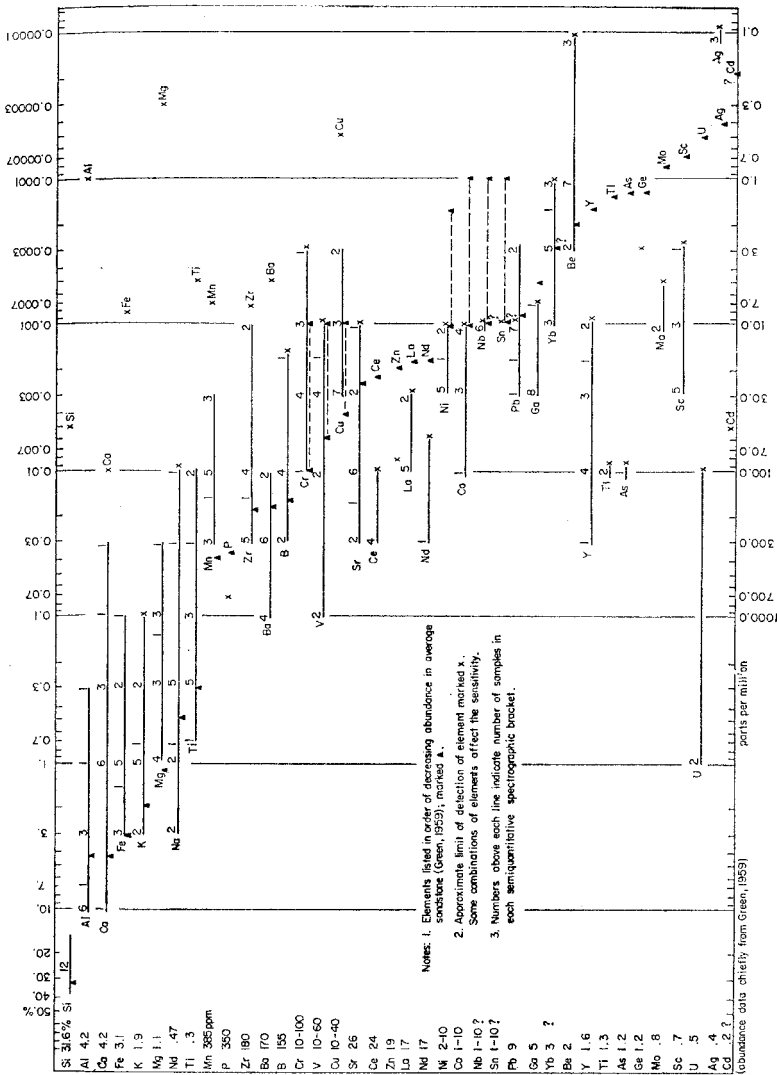


FIGURE 6.—Range of composition of samples from the Catahoula Tuff (Miocene?), Karnes area, Texas, as shown by semi-quantitative spectrographic analyses, compared with the composition of average sandstone. Analysts: Joseph Haffty, H. W. Worthing, C. L. Waring and K. V. Hazel.

The possibility of tuffaceous rocks as source beds for uranium had been considered in the Dakotas by N. M. Denson, G. O. Bachman, and H. D. Zeller (written communication, 1950) and Denson and Gill (1955), in Wyoming by Love (1952), and in the Colorado Plateau by Waters and Granger (1953). By 1955, much previously classified work on solubility of uranium as uranyl carbonate complex ions had been released and received wide attention (Bullwinkel, 1954). This was related to the carbonate leaching process in the milling of uranium ores. However, the explanation given by Garrels (1957) first emphasized how alkaline carbonate pore water develops in tuffaceous rocks. A moderately reducing and moderately alkaline solution was shown to be the most probable type of medium to transport the uranium and associated vanadium, molybdenum, and copper (Garrels, Hostetler and others, 1957). Three diagrams given by Garrels (1960, pp. 186–189) illustrate the stability relations among the uranyl carbonate and oxide hydrate compounds and vanadium compounds. He pointed out (1957) that the

original glassy material of the tuffs reacts with water as it . . . alters, releasing bases to solution and immobilizing hydrogen ions, with a concomitant rise in pH. As the pH rises, the partial pressure of CO_2 in the interstitial waters drops and the tuff becomes a CO_2 sink that can rob the atmosphere, or adjacent sediments, as the case may be, of CO_2 . If cations derived from external sources are not added to the system, the net result is that the waters in tuffs become moderately to strongly alkaline and high in carbonate. If the tuff is water saturated, oxygen disappears, and conditions become mildly reducing.

That carbonate-bearing solutions are excellent solvents for uranium is demonstrated in Fig. 6.32a and b in Garrels (1960) where the stability relations are shown for the uranyl dicarbonate $\text{UO}_2(\text{CO}_3)_2(\text{H}_2\text{O})_2^{-2}$ and tricarbonate $\text{UO}_2(\text{CO}_3)_3^{-4}$ ionic species.

The Karnes area has a large quantity of tuffaceous material, partly rhyolitic but largely trachytic to andesitic, in both Jackson and Catahoula sediments. The Jackson was deposited in a terrestrial coastal plain and shallow lagoonal environment, and the Catahoula is entirely terrestrial in the Karnes area. The present ground waters contain sodium bicarbonate-carbonate with considerable silica and many other elements derived from the volcanic material. In the past the climate was drier and caused deposition of extensive caliche in the soil, and the ground water was probably more alkaline than it now is. The pore water and its dissolved salts have had time to react with the rock instead of being flushed out of the area because the evaporation is high, the rocks are not very permeable, and the recharge is small (Anders, 1960). The precipitation of uranium from the solutions is brought about either (1) by reduction to very fine-grained, low-temperature uraninite in the reducing environment of plant fragments and by H_2S , or (2) by loss of CO_2 and reaction with vanadate, phosphate, arsenate, and molybdate ions in the oxidized zone to form relatively insoluble carnotite or somewhat less stable minerals of the autunite group. The soil moisture varies greatly because the rainfall is very irregular, the area being subject to occasional downpours alternating at times with prolonged and severe drought

and with high temperature and high evaporation rate. At intervals, an increase in CO_2 would take some of the minerals back into solution.

Studies of radioactive disequilibrium (Rosholt, 1959, and written communication, 1960) indicate that intermittent migration of uranium has continued over a long period of time. Since the Karnes deposits were first known, geologists and prospectors have been aware of the fact that ore samples are commonly out of radioactive equilibrium; that is, the percentage of "equivalent uranium" measured radiometrically differs from the percentage of uranium determined by chemical analysis. The disequilibrium is caused by leaching and migration of uranium or one or more of the daughter products. Results of radiochemical analyses of several key daughter products in two vertical suites of samples from the Korzekwa prospect trench and one from the Gemblor open pit mine (J. N. Rosholt, written communication, 1960) showed that some uranium deposited more than 240,000 years ago has been leached and transported along joints and bedding plane fractures into adjacent beds where it gives "apparent ages" ranging down to a few thousand years. One sample in pyritic dark gray silty clay just beneath the oxidized ore sand in the Gemblor pit contained minute aggregates of very fine-grained uraninite associated with plant fragments. The hand sample as a whole indicated that uranium had been deposited within the last 14,000 years and the uranium in carbonaceous material separated from the sample gave an apparent age of 3000 years. In other words, the only uraninite found in the Karnes deposits (by August 1961) gives the youngest age determined, and indicates downward migration from the oxidized "ore-sand" bed to the unoxidized pyritic silty clay underneath, about 40 ft below the surface of the ground.

A survey of the "equivalent uranium" and chemical uranium determinations on more than 530 samples ranging from high-grade ore down to 0.001 percent uranium indicates that the equivalent uranium is about 5 percent higher than the chemical uranium. This deficiency of uranium in comparison to daughter products suggests some loss of uranium from the area that was sampled, an area that is wide in lateral extent but not more than 40 ft deep. The "lost" uranium has either gone down dip in more permeable beds or been carried off in surface water to streams. The first alternative seems the more likely.

Deposits in Duval County about 80 miles to the southwest are closely related to the Karnes deposits. A much more continuous caliche cover remains in Duval County and several uranium prospects have been found in partly altered tuffaceous rock just under the caliche. Locally traces of uranyl vanadates were found directly at the surface in exposed silicified coarse sandstone. Of interest is the largest deposit known in Duval County where uranium occurs at a depth of about 325 ft in a reducing environment above the caprock of Palangana salt dome (Weeks and Eargle, 1960). It is believed that alkaline carbonate water carrying uranyl carbonate complex ions in solution migrated down dip and deposited the uranium by reduction to uraninite in the reducing environment of the H_2S that rises from the sulfurous caprock.

Thus, the origin of the uranium deposits in the Texas Coastal Plain seems to have been controlled by the complex diagenesis of these highly reactive tuffaceous source rocks, by the development of a "built-in" solvent in the alkaline carbonate pore water, by favorable climate, and by geologic structural conditions and permeability barriers that allowed concentration and deposition of the uranium, rather than dilution and dispersal of it.

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