Radioactivity and Uranium Content, Sharon Springs Member of the Pierre Shale Kansas and Colorado

GEOLOGICAL SURVEY BULLETIN 1046-L

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By E. R. LANDIS

CONTRIBUTIONS TO THE GEOLOGY OF URANIUM

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CONTRIBUTIONS TO THE GEOLOGY OF URANIUM

RADIOACTIVITY AND URANIUM CONTENT, SHARON SPRINGS MEMBER OF THE PIERRE SHALE, KANSAS AND COLORADO

By E. R. Landis

ABSTRACT

As part of the program of the U. S. Geological Survey in the investigation of uranium-bearing carbonaceous rocks on behalf of the U. S. Atomic Energy Commission, a reconnaissance of the Sharon Springs member of the Pierre shale of Late Cretaceous age in western Kansas and eastern Colorado was made during 1954.

The Sharon Springs member of the Pierre shale and its lateral equivalents range from 155 to about 500 feet in thickness and generally contain about 0.001 percent uranium, but some beds contain larger amounts. A 6-foot shale bed in Cheyenne County, Colo., contains about 0.006 percent uranium; a 4½-foot sequence of beds in Crowley County, Colo., is estimated to contain between 0.004 and 0.005 percent uranium; and a 3½-foot sequence of beds in Kiowa County, Colo., contains about 0.004 percent uranium. At several outcrop localities, sequences of beds as much as 9½ feet thick contain about 0.003 percent uranium. Data from wells indicate that the 4½-foot thick sequence of beds in Crowley County, Colo., may have a lateral extent of at least 5½ miles. A gamma-ray log of a well in Yuma County, Colo., indicates a sequence of beds 66 feet thick which contains 0.005 to 0.010 percent equivalent uranium.

No definite pattern of areal distribution of radioactivity and uranium content in the Sharon Springs is indicated by available data. Lateral variation in uranium content of individual beds was not noted in outcrops, which seldom extend more than 150 feet. Subsurface data from gamma-ray logs of wells indicate however that both the maximum radioactivity and the thickness of radioactive beds are variable within distances of a few miles. Most of the gamma-ray logs show that only part of the sequence of rocks comprising the Pierre shale and Niobrara formation exhibits radioactivity in excess of the average radioactivity of the two formations. Comparison of gamma-ray logs of wells in northeastern Colorado suggests that the most radioactive parts of the Pierre shale and Niobrara formation are a laterally correlatable sequence of beds.

The stratigraphic position of the radioactive unit relative to the Pierre shale-Niobrara formation contact in oil industry scout reports, as identified from electric logs of wells, is variable within short distances. This may indicate that some of the Pierre-Niobrara contacts picked from electric logs may not correspond to the boundary that would be selected by examination of the rocks themselves, or it may indicate a facies relationship between the lowermost part of the Pierre shale and the uppermost part of the Niobrara formation.

INTRODUCTION

During the field season of 1954, reconnaissance and detailed studies of uranium-bearing black shales of Late Cretaceous age in western Kansas and eastern Colorado were made as part of the program of the U. S. Geological Survey in the investigation of uranium-bearing carbonaceous rocks on behalf of the Division of Raw Materials of the U. S. Atomic Energy Commission. Other investigations of the Sharon Springs member were made in South Dakota and northeastern Nebraska by R. C. Kepferle (written communication, 1958) and in the Chadron area of Nebraska and South Dakota by R. J. Dunham (1955, p. 164). The primary objective of these studies was to determine the content and distribution of uranium areally and stratigraphically in the Sharon Springs member of the Pierre shale of Late Cretaceous age. Other shales of Late Cretaceous age were also examined.

STRATIGRAPHY

The Sharon Springs member of the Pierre shale was named by Elias (1931, p. 56) from exposures in Wallace and Logan Counties, Kans. At the type locality, the Sharon Springs consists of 155 feet of flaky, black shale containing an abundance of small fish remains. Dane, Pierce, and Reeside (1937, p. 225) extended the name into eastern Colorado as an equivalent of the Barren zone of Gilbert (1897). Searight (1938, p. 137) used the name for the basal member of the Pierre in South Dakota, and Condra and Reed (1943, p. 17) applied the name to the lowermost part of the Pierre in Nebraska.

In western Kansas the Sharon Springs is overlain by Elias' Weskan member of the Pierre shale, which is the lowest of three units named by Elias (1931, p. 56) in 430 feet of Pierre overlying the Sharon Springs. In eastern Colorado the Sharon Springs is overlain by the Rusty zone defined by Gilbert (1897). Dane, Pierce, and Reeside (1937, p. 225) correlated the Rusty zone of Gilbert with the three units named by Elias (1931, p. 56) that overlie the Sharon Springs in western Kansas.

The Sharon Springs member is underlain in western Kansas by the Smoky Hill chalk member of the Niobrara formation; in eastern Colorado this is called the Smoky Hill marl member of the Niobrara formation. In the extreme western part of the area, the Sharon Springs is underlain by the Apishapa shale. The Apishapa is equivalent to the upper part of the Smoky Hill marl and chalk of eastern Colorado and western Kansas (Cobban and Reeside, 1952, pl. 1). The lithologic contact between the Pierre shale and Niobrara formation is apparently conformable and at some localities appears gradational. A few localities show an alternation of dark gray to black calcareous

and noncalcareous shales. The contact between the Pierre and the Niobrara is generally placed at the top of the youngest limestone or calcareous shale in the outcrop.

The Sharon Springs is predominantly black to dark-brown, noncalcareous, organic-rich shale. The shale commonly breaks and weathers into tough, angular, fragments ranging from 1/20 to 1/5 of an inch in thickness and as much as 2 inches in diameter. Scales, spines, scutes, and other minute remains of fish are so common as to be a definitive feature of the Sharon Springs. Other fossils are so rare, however, that this part of the Pierre was named the Barren zone by Gilbert (1897). Fragments of mollusk shells were noted in several limestone concretions; and a few bone fragments, probably of a marine reptile, were found in Wallace County, Kans.

Bentonitic clay beds are common in the Sharon Springs and are not restricted to any particular stratigraphic horizon. The beds are usually less than 6 inches thick and the majority range from 1/4 to 2 inches in thickness. Tourtelot (1956, p. 63) reports bentonite beds almost 20 feet thick in the Sharon Springs in northwestern Nebraska and near the Black Hills, but no bentonite beds of that magnitude were observed in western Kansas or eastern Colorado. In most places the bentonitic clay beds, which are light gray where unweathered, are represented on weathered surfaces by an intimate mixture of soft, iron-stained, tan to yellow clay; red-brown limonite or hematite; and small, randomly oriented, prismatic crystals of selenite.

Selenite, in the form of rosettes as much as 6 inches in diameter and individual crystals, is usually abundant on weathered outcrops. Contact twinning of tabular crystals is common. On several weathered outcrops, small veinlets of selenite cut across the bedding planes of the shale. Selenite and gypsum commonly encrust the concretions in the Sharon Springs.

Ellipsoidal concretions of concentrically banded dense gray limestone or shaly limestone are present in the Sharon Springs. Oval calcareous shale concretions, some of which contain gypsum or selenite, are also common. The larger and more conspicuous concretions are septarian, in which the dense microcrystalline gray limestone is divided by radiating septaria of calcite and barite. A few of the nonseptarian limestone concretions have an outer crust of tan to light-gray cone-in-cone limestone. Several concretions noted consisted of opposed layers of cone-in-cone limestone without intermediate material. Small tabular concretions consisting of limestone and mudstone are common in parts of the Sharon Springs. A few oval iron carbonate concretions, which are abundant in the overlying Rusty zone of Gilbert, are also present in the Sharon Springs.

Elias (1931, p. 65) assigned a thickness of 155 feet to the Sharon Springs at the type locality in western Kansas. Fifteen miles southwest of the type locality the author measured about 194 feet of Sharon Springs. In eastern Colorado, Dane, Pierce, and Reeside (1937, p. 225) assigned a thickness of about 400 to 500 feet to the Sharon Springs. The author measured a columnar section in Las Animas County, Colo., in which the strata probably assignable to the Sharon Springs are less than 260 feet thick. Tourtelot (1956, p. 63) states that in South Dakota, the Sharon Springs and strata correlated with it range from 17 to 150 feet in thickness, and Condra and Reed (1943, p. 17) assigned a thickness of 20 to 80 feet to the Sharon Springs in Nebraska.

There are few distinctive laterally correlatable units in the Sharon Springs; hence, the stratigraphic relations between parts of the member in different outcrops is usually uncertain. Elias (1931, p. 59) subdivided the Sharon Springs into upper and lower parts according to the abundance of large concretions found in the upper part as contrasted to their scarcity and smallness in the lower part. Elias (1931, p. 60–61) also indicated that a zone of septarian concretions that occurs in the upper part of the Sharon Springs is laterally correlatable in Wallace and Logan Counties, Kans. Septarian concretions are also present in the Sharon Springs of eastern Colorado (Dane, Pierce, and Reeside, 1937, p. 225). As the concretions are the most resistant constituents of the Sharon Springs, they crop out more often than does the remainder of the member; and the tendency is to correlate the zones in which concretions occur. Several correlations of septarian concretion zones are indicated on plates 35 and 36, but some of them may be erroneous.

RADIOACTIVITY AND URANIUM CONTENT

SURFACE DATA

Figure 27 shows the locations of exposures of the lower part of the Pierre shale in Kansas and Colorado that were examined for radioactivity, measured, and sampled. Plates 35, 36, and 37 show columnar sections of the rocks at each of the localities and the equivalent uranium and uranium content of samples collected from the rock units.

Lateral correlation of parts of the Sharon Springs member of the Pierre shale and associated rock units exposed at the sample localities is somewhat uncertain, but the probable stratigraphic position of the beds examined at each locality relative to nearby localities is indicated on the columnar sections (pls. 35, 36 and 37). No definite laterally correlative stratigraphic sequence was consistently more uraniferous than other parts of the Sharon Springs. The radioactivity and

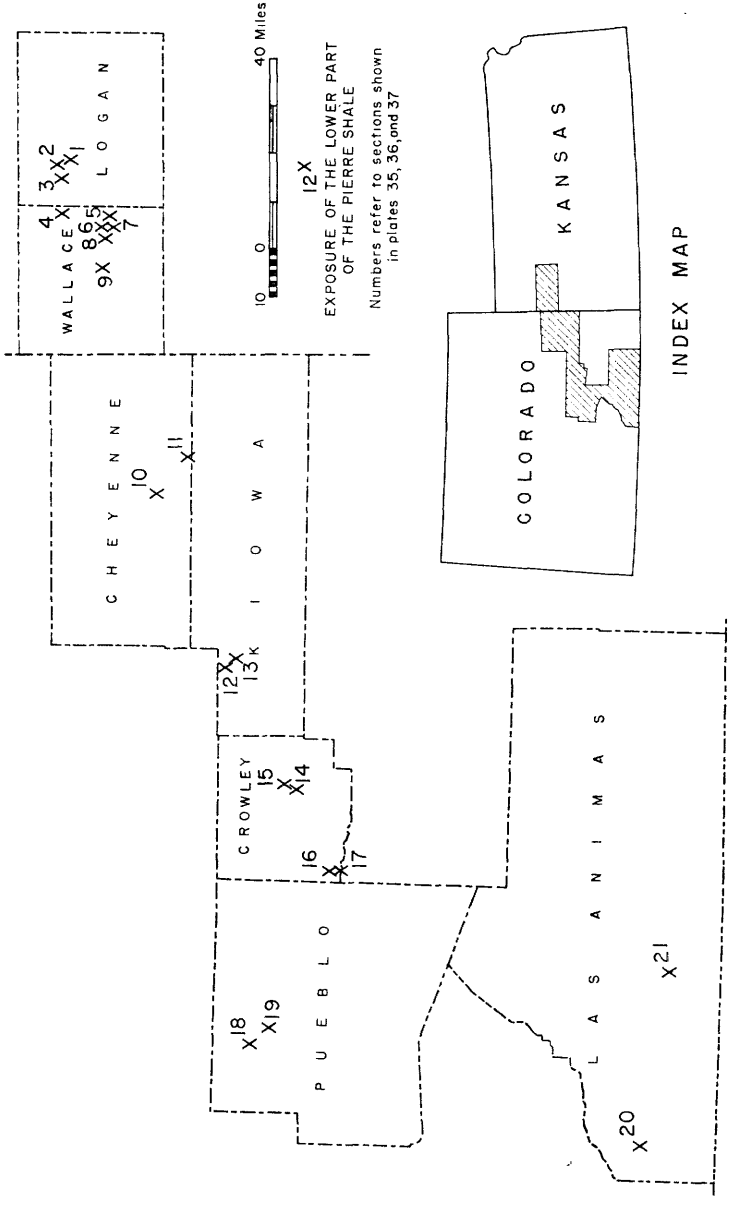

FIGURE 27.—Map showing locations of exposures of the lower part of the Pierre shale in Kansas and Colorado.

uranium content of individual beds were found to be laterally consistent within the outcrop area of the parts of the Sharon Springs and the adjacent parts of the Pierre which were examined. However, few of the beds were exposed for more than 150 feet at any of the localities.

The lower part of the Pierre shale in the area generally contains 0.003 percent equivalent uranium or less, and 0.001 percent uranium or less. Units containing more than 0.002 percent uranium and their thicknesses are given in table 1.

TABLE 1.—*Units containing more than 0.002 percent uranium and their thicknesses*

Locality (pls. 35, 36, and 37)	Thickness		U content
	Ft.	*In.*	*Percent*
2	1	10	0.003
3	2	0	.004
	[1] 3	0	.003
	1	0	.004
9	1	0	.004
10	6	0	.006
12		6	[2] .003
	1	0	.006
	2	0	[2] .003
13	4	0	.003–.002
15	1	4	.004–.003
	2	2	.005
	1	0	[2] .007–.005
17	3	1	.003
18	1	2	.003
20	9	6	.003
	[1] 4	9	.003

[1] Between this unit and the one above is a unit containing 0.002 percent uranium or less.
[2] These figures are interpolated from scintillation counter readings of the tabulated unit and scintillation counter readings and chemical analyses of contiguous beds.

The disequilibrium between the equivalent uranium content and the uranium content in most of the samples may be due to leaching of uranium from the shale. Tourtelot (1956, p. 68) suggested that the equivalent uranium content of weathered shale of the Sharon Springs member in South Dakota and Nebraska may be representative of the uranium content of some of the unweathered shale. Many samples collected in this investigation contained exactly as much uranium as equivalent uranium and lend support to Tourtelot's suggestion. However, the equivalent uranium and uranium determinations of the weathered shale samples reported here generally differ by 0.001 to 0.002 percent uranium; for example, samples with 0.003 percent equivalent uranium generally contain from 0.001 to 0.002 percent uranium. Some of the excess radioactivity indicated by these relationships probably results from potassium in the shale.

SUBSURFACE DATA

Figure 28 shows the location of wells in northeastern Colorado for which radioactivity logs were studied. Radioactivity logs normally consist of two curves: the gamma-ray log, which records the natural gamma radiation emitted by the rocks through which the well passes; and the neutron log, which records the gamma radiation emitted by the rocks as a result of neutron bombardment from a source introduced into the hole, the gamma radiation given off by the introduced source and reflected back to the gamma-ray detector, as well as the natural gamma-radiation of the rocks. Only the gamma-ray curve indicating the natural radiation of the rocks was considered in this report. Significant parts of the gamma-ray logs of those wells, indicated on figure 28 by a solid circle and a number, are shown on plate 38. The equivalent uranium content of the shale in some of the wells indicated by "X" on figure 28 is taken from gamma-ray logs reported by Tourtelot (1956, fig. 6); the others are based on the author's examination of logs.

The maximum deflection produced by rocks in the Pierre and Niobrara formation on the gamma-ray logs of the wells on figure 28 is expressed as percentage of equivalent uranium. Gott and Hill (1953, p. 70) found that in the Rangely field of northwestern Colorado, an equivalent uranium content of about 0.0007 percent in core samples of the Weber formation caused a deflection of 1 inch in the gamma-ray curve at a 10-inch sensitivity scale. The accuracy of this figure is dependent on many complicating factors, such as the thickness versus the radioactivity of the bed, fluid content of the well, shielding effect of the well casings, differences in individual instruments, and the rate of movement of the ionization chamber. However, analyses of core samples from a well penetrating the Bakken formation of local usage in North Dakota were compared with the gamma-ray log of the well, and the findings of Gott and Hill were found to be applicable to within an accuracy of 0.001 percent equivalent uranium (R. C. Kepferle, personal communication). The maximum radioactivity shown by the gamma-day logs is at locality 1, where a sequence of beds about 66 feet in thickness has an estimated equivalent uranium content ranging from 0.005 to 0.01 percent.

Available data do not indicate any definite areal distribution pattern of radioactivity in the Pierre and Niobrara sequence. More wells in the eastern and northeastern parts of the map area (fig. 28) exhibit radioactivity near the indicated maximum than do the wells in the central and western parts. However, no definite conclusions on this point can be reached until more subsurface information is

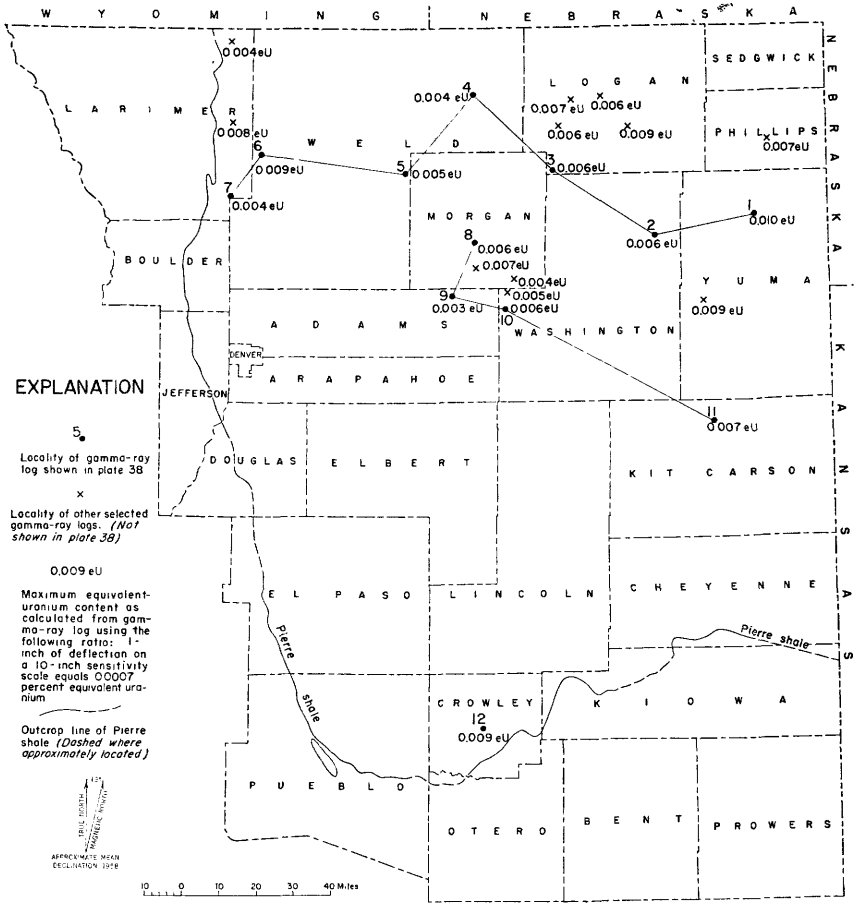

FIGURE 28.—Map of eastern Colorado showing the location of wells used in radioactivity log study of the Pierre shale and Niobrara formation.

available in the southern part of the area in which the Pierre and Niobrara are present.

The contact between the Pierre shale and the Niobrara formation as shown on plate 38 is as listed in oil industry scout reports. The contact listed in such reports is generally picked by resistivity and self-potential electric logs. At some places, however, the radioactivity log was probably used to pick the contact. For one well (loc. 7) no contact was listed, but the part of the gamma-ray log shown in plate 38 probably includes the Pierre-Niobrara contact. Examination of the electrical logs of several wells shown on figure 28 indicates a change in lithology at depths listed by oil industry reports as being the Pierre-Niobrara contact. At locality 10 (pl. 38) for example, the Pierre-Niobrara contact agrees closely with changes in

the electrical log curves that indicate a change in the lithology of the rock. The parts of the gamma-ray logs shown in plate 38 include the Pierre-Niobrara contact as picked in oil industry scout reports, and the part of the Upper Cretaceous series here considered is hereafter referred to as the Pierre and Niobrara sequence.

Gamma-ray logs show that usually only one part of the Pierre and Niobrara sequence exhibits radioactivity far in excess of the average amount generally shown by these formations. The gamma-ray logs indicate that the more radioactive part of these formations ranges in thickness from less than 10 feet to about 150 feet. Many peaks of radioactivity within the more radioactive part can be correlated in the gamma-ray logs of wells in northeastern Colorado. This suggests that the most radioactive part of the Pierre and Niobrara sequence in northeastern Colorado is a correlatable sequence of beds.

In northeastern Colorado the radioactive unit is located stratigraphically within about 200 feet of the Pierre-Niobrara contact as picked from electric logs. The radioactive unit varies in stratigraphic position relative to the Pierre-Niobrara contact, indicating that the contact picked from electric logs does not always correspond to the lithologic boundary that would be picked by examination of the rocks themselves. Another possibility is that the radioactive unit crosses formational boundaries, and there is a facies relationship between the lowermost part of the Pierre and the uppermost part of the Niobrara.

The gamma-ray log of the well at locality 12 (pl. 38) is interesting for several reasons. The approximate stratigraphic position of the Pierre-Niobrara contact is listed in scout reports as picked by use of rock samples from the well; it is about 130 feet below the base of the most radioactive part of the Pierre. The most radioactive and uraniferous part of the Pierre in nearby outcrops is a selenitic sandy shale unit, containing iron carbonate concretions, located at some distance above the top of the Niobrara formation (loc. 15, pl. 36). The radioactive unit shown in the gamma-ray log at locality 12 (pl. 38) may be the same as that observed at the surface. This is suggested by the presence of a sandy, gypsiferous, gray shale unit with a limy layer at the top that is 155 feet above the top of the Niobrara in a well 3½ miles west of locality 12 and absent in a well about 10 miles north of locality 12 (W. E. Hallgarth, personal communication).

ORIGIN OF THE URANIUM

Most of the problems relating to the origin of uranium in such black shales as the alum shales of Sweden and the Chattanooga shale of the Eastern United States are unsolved. As a group, the uraniferous

black shales of the world are sapropelic, highly carbonaceous, high in sulfide content, noncalcareous, and somewhat phosphatic. These shales are believed to have accumulated slowly, probably under anaerobic conditions (McKelvey, 1955, p. 15). The Sharon Springs member of the Pierre shale possesses most of these distinguishing characteristics, though quantitative data are lacking for some of them.

The uranium in most of the black shales thus far studied has a definite relationship to the organic fractions. Bates and Wright (written communication, 1953) studied thin-section autoradiographs of the Chattanooga shale and found that the observable alpha tracks emanated from the interstitial organic matter and larger organic fragments associated with pyrite. Small amounts of uranium are present in the Upper Cambrian black shales of Sweden, and greater amounts of uranium are concentrated in layers of kolm—a black kerogen of obscure origin (V. E. McKelvey, written communication, 1955). However, Breger and Deul (1955) have found that their study of a pyrite-rich sample of the Sharon Springs member from South Dakota indicates that the uranium in the shale may be associated with the mineral fraction.

Conditions producing a low redox potential seem to have been conducive to the formation of most uraniferous black shales, but other physical and chemical factors, such as the rate of accumulation of sediments, variation in the available supply of uranium, variation in the relative concentration of other elements in solution, and the pH, which affect the precipitation of uranium from aqueous solution, may be equally important.

The uranium in the shales may have been deposited syngenetically; that is, adsorbed by organic matter or precipitated from aqueous solution and deposited simultaneously with the associated material of the shale. All or part of the uranium may have a penecontemporaneous origin, that is, adsorbed by organic matter subsequent to deposition and prior to compaction and burial.

At several of the localities where outcrops of the Sharon Springs were examined, the most uraniferous beds in the exposure were associated with bentonitic clay beds, though the clay generally contains very little uranium. In South Dakota, the part of the Sharon Springs that contains the most uranium is commonly associated with bentonites (R. C. Kepferle, personal communication, 1955). However, many parts of the Sharon Springs in Kansas and Colorado, which are associated with bentonitic clay beds, are no more uraniferous than the remainder of the exposed rocks; and at several localities, where parts of the Sharon Springs were found to be most uraniferous, no bentonitic clay beds were apparent. At several ex-

posures, concentrations of uranium believed to be secondary accumulations on the present land surface are intimately related to the presence of bentonitic clays.

No obvious relationship exists between the syngenetically or penecontemporaneously deposited uranium in the shales and the bentonitic clay beds in the sequence. Tourtelot (1956, p. 78) suggested, however, that the uranium content of a sea in which volcanic ash was deposited would be increased during the alteration of the ash to bentonite. In this manner the bentonitic clays could have contributed uranium and other metals to other parts of the Sharon Springs without any direct relationship being apparent between the bentonitic clays and the uranium content of adjacent sediments.

Concentrations of uranium believed to be epigenetic in origin are associated with bentonitic clays at localities 12 and 15 (pl. 36). Many bentonitic clay beds and the adjacent shales were sampled and found to contain no more uranium than the exposed rocks as a whole. At locality 12 (pl. 36), however, the shale unit exhibiting the greatest radioactivity in the field and containing 0.004 percent equivalent uranium and 0.006 percent uranium is associated with a ½-inch bed of altered bentonitic clay which contains 0.005 percent equivalent uranium and 0.006 percent uranium. It is probable that only part of the uranium present in the shale is epigenetic, and the remainder syngenetic or penecontemporaneous, but no quantitative estimate is possible. At locality 15 (pl. 36) the part of the measured section containing the most uranium immediately overlies a sandy shale and clay unit that is evidently the lateral equivalent of a 4-inch bentonitic clay bed a short distance away. The 4-inch bentonitic clay bed contains 0.002 percent equivalent uranium and 0.001 percent uranium, but the weathered mixture of clay, limonite or hematite, and selenite that underlies the bentonitic clay contains 0.007 percent equivalent uranium and 0.006 percent uranium; and the weathered mixture above the clay contains 0.018 percent equivalent uranium and 0.020 percent uranium.

A zone of weathered shale and clay ranging in thickness from less than ½ inch to about 3 feet, is generally present where the bentonitic clay beds crop out. The bentonitic clay is usually almost entirely altered and replaced by a mixture of soft clay, limonite or hematite, and selenite; the adjacent strata are coated and permeated with iron oxide and selenite. A possible explanation of the relationship of the bentonitic clay to the epigenetic concentrations of uranium is that the clay by its impermeability creates a local perched water table that controls the direction of flow of water in the rocks superjacent to the bentontic clay beds. At locality 15 (pl. 36) there is a

marked differential in uranium content between the weathered mixtures above and below the clay bed. The sampling procedure at locality 12 (pl. 36) does not indicate whether this differential also exists at that locality.

The persistence of iron oxide in the more radioactive units suggests that the concentration of uranium in these units is partly due to iron. Lovering (1955, p. 186) concluded that when acid sulfate waters carrying uranyl sulfate and ferric sulfate are neutralized, the ferric sulfate hydrolizes to form colloidal ferric oxide hydrate, which adsorbs the uranyl ion and later expels it to form secondary uranium minerals when the ferric oxide hydrate crystallizes to form geothite.

The uranium may also be in the selenite. A sample of a selenite veinlet at locality 3 (pl. 35) contained 0.001 percent equivalent uranium and 0.002 percent uranium. Bain (1953, p. 207) has shown that calcium can precipitate uranium from uranyl sulfate solution by appropriating the sulfate ion. Substitution of uranium for calcium may occur, as their respective ionic radii are similar but it is unlikely because of the difference in ionic charge (McKelvey and others, 1955, p. 468).

Bentonitic clay beds and adjacent zones of weathered shale do not assure the presence of uranium, however, because many of these zones and clay beds that were examined and sampled contained no more uranium generally than did the adjacent rocks. Other factors, which appear especially essential in concentrating uranium on weathered outcrops, are the amount of uranium available in aqueous solutions for concentration; and the preservation of the uranium from subsequent leaching after it is concentrated. The availability of uranium is a function of the uranium content of the unweathered shale, and the preservation of the uranium is a function of the mechanisms of concentration, and possibly of the topographic setting.

Some other uranium occurrences probably are partly or totally epigenetic in nature. At locality 2 (pl. 35) uranium is concentrated in one part of a limestone concretion, and at locality 3 (pl. 35) the outer crust of a concretion contains twice as much uranium as does its center. At locality 2 the uranium is evidently concentrated in the part of the concretion that contains the most organic material. Studies on the Colorado Plateau and other areas indicate that carbonaceous material may assist in the precipitation of uranium from solution by the creation of a localized reducing environment. This mechanism may be responsible for the concentration at locality 2. At locality 3 the calcareous shale that makes up the interior of a concretion contains 0.002 percent equivalent uranium and 0.002 percent uranium that may be of syngenetic origin. The outer, cone-

in-cone, limestone crust of the concretion contains 0.002 percent equivalent uranium and 0.004 percent uranium. The crust must have formed after the deposition of the enclosing sediments, but whether the uranium was emplaced in the crust at the time of formation or has been subsequently concentrated in it, is unknown.

OTHER TRACE ELEMENTS

Table 2 shows the results of semiquantitative spectrographic analyses of samples of the Sharon Springs member of the Pierre shale and other shales of Cretaceous age collected in western Kansas and eastern Colorado. Table 3 lists the standard sensitivities for the elements. Table 4 describes the samples shown in table 2.

The sample analyses shown in table 2 include a black shale from the Cheyenne sandstone member of the Purgatoire formation, a black shale from the Blue Hill shale member of the Carlile shale, a calcareous shale from the uppermost part of the Smoky Hill chalk member of the Niobrara formation, and twelve samples from various horizons in the Sharon Springs member of the Pierre shale.

The sample of shale from the Purgatoire formation (139759) contains less barium than any other sample. The trace element constitution of the sample is generally similar to the samples of the Sharon Springs member except that it contains less scandium, vanadium, and barium, and more zirconium, than do most of the Sharon Springs samples.

Although the trace element composition of the Blue Hill sample (139758) is in general similar to the analyses of the Sharon Springs, several striking differences are apparent in the comparative contents of the rare earth elements. Three of these elments, cerium, lanthanum, and neodymium, are in the semiquantitative range from 100 to 500 ppm and were not detected in any of the other samples. The relative concentration of lanthanum and neodymium in the Blue Hill sample (139758) is particularly noteworthy because the minimum concentrations detectable by the spectrographic method are 30 ppm lanthanum and 60 ppm neodymium. Thus the sample contains more than three times as much lanthanum and more than twice as much neodymium as do any other samples. Cerium, lanthanum, and neodymium are closely related in chemical properties (Goldschmidt, 1954, p. 310) and their association is not surprising. If the other elements of the cerium earth elements group, praseodymium and samarium, are present they occur in quantities less than the minimum detectable concentration by semiquantitative spectographic analysis.

The sample of the Smoky Hill chalk member of the Niobrara formation (139726) is distinct from all of the other samples by the larger

TABLE 2.—*Trace elements composition of some Cretaceous shales from Kansas and Colorado*

[Semiquantitative spectrographic analyses by C. Annell, U. S. Geological Survey. Leaders indicate that the element, if present, is in quantities less than the minimum detectable concentrations listed in table 3. Other elements listed in table 3 were also looked for but are not present in detectable amounts]

Code, parts per million

>100,000	11	100–500	5
50,000–100,000	10	50–100	4
10,000–50,000	9	10–50	3
5,000–10,000	8	5–10	2
1,000–5,000	7	1–5	1
500–1,000	6		

Sample	Be	B	Na	Mg	Al	Si	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Sr	Y
139759	------	5	7	7	11	11	8	7	2	7	3	4	5	9	3	4	3	------	4	5	3
139758	------	5	9	9	10	11	9	7	3	7	4	5	5	9	3	3	3	------	3	5	3
139726	------	5	7	8	9	9	8	11	3	6	5	5	5	9	3	5	3	5	3	5	3
139727	------	5	7	9	10	11	9	9	3	7	5	7	5	9	3	5	4	------	3	5	3
139732	------	5	7	7	11	11	9	9	3	7	4	3	5	9	3	5	3	------	4	5	3
139733	------	5	8	7	11	11	9	9	3	7	5	3	4	9	------	4	5	------	4	6	3
139734	------	5	8	7	10	11	9	9	2	7	5	3	4	9	------	4	4	------	4	5	3
139754	------	5	8	7	10	11	9	9	3	7	5	5	4	9	------	3	5	------	3	6	3
139755	------	5	7	7	10	11	9	7	3	7	5	5	5	9	------	3	4	------	3	5	3
139756	------	5	9	9	10	11	9	7	3	7	5	5	5	9	------	3	4	------	3	5	3
139757	------	5	9	9	10	11	9	9	3	7	5	5	5	9	3	5	5	------	3	6	3
139760	1	5	9	9	10	11	9	9	3	7	4	4	6	9	3	4	3	------	3	5	3
139761	1	5	9	9	10	11	9	9	3	7	4	5	5	9	3	4	3	------	3	5	3
139762	1	5	9	8	10	11	9	8	3	7	5	5	5	9	------	3	4	------	3	5	3
139763	1	5	9	9	10	11	9	9	3	7	5	5	5	9	3	5	4	------	3	5	3

Sample	Zr	Mo	Ag	Sn	Ba	La	Yb	Pb	Ce	Nd	Se [2]	As [2]	U [2]
139759	5	------	------	------	3	------	1	3	------	------	2(<0.001)	3(0.002)	3(0.002)
139758	5	------	------	------	6	5	1	3	5	5	2(<.001)	3(.002)	2(<.001)
139726	3	4	------	------	5	------	1	3	------	------	3(.005)	4(.007)	3(.002)
139727	3	3	------	------	5	------	1	3	------	------	3(.002)	3(.002)	2(.001)
139732	3	4	------	------	5	------	------	3	------	------	2(.001)	3(.004)	3(.002)
139733	3	4	------	------	5	------	------	3	------	------	3(.005)	4(.006)	3(.004)
139734	3	5	(1)	------	5	------	------	3	------	------	3(.002)	4(.006)	3(.004)
139754	3	5	------	------	5	------	1	3	------	------	2(.001)	3(.004)	4(.006)
139755	4	3	------	------	5	------	1	3	------	------	2(.001)	3(.005)	3(.002)
139756	4	5	------	4	6	------	1	5	------	------	3(.002)	3(.004)	3(.002)
139757	4	3	------	------	6	------	1	3	------	------	3(.003)	3(.002)	3(.003)
139760	4	------	------	------	6	------	1	3	------	------	2(<.001)	2(.001)	2(.001)
139761	4	------	------	------	7	------	1	3	------	------	2(<.001)	3(.002)	2(<.001)
139762	5	4	------	------	6	------	1	3	------	------	2(.001)	3(.002)	3(.003)
139763	5	3	------	------	6	------	1	3	------	------	2(.001)	3(.003)	2(.001)

[1] 0.1 to 0.5 ppm Ag present.
[2] Selenium, arsenic, and uranium contents were determined chemically by M. Delevaux and J. Goode, U. S. Geological Survey. The figures shown in the table in parentheses are percent.

TABLE 3.—*Minimum concentrations of the elements detectable by the semiquantitative spectrographic method, in parts per million*

[Revised January 13, 1954. Washington laboratory, U. S. Geological Survey]

Element	Minimum concentration	Element	Minimum concentration	Element	Minimum concentration
Ag	0.1	Hf	300	Re	400
Al	1	Hg	800	Rh	40
As	100	Ho	10	Ru	80
Au	10	In	4	Sb	100
B	50	Ir	300	Sc	10
Ba	10	K	3,000	Si	50
Be	.5	La	30	Sm	80
Bi	50	Li	400	Sn	40
Ca	100	Lu	50	Sr	10
Cd	50	Mg	.3	Ta	1,000
Ce	300	Mo	5	Tb	100
Co	80	Mn	7	Te	800
Cr	6	Nb	10	Th	800
Cs	8,000	Na	100	Ti	5
Cu	.5	Nd	60	Tl	400
Dy	60	Ni	50	Tm	10
Eu	30	Os	1,000	U	800
Er	30	P	700	V	10
F	800	Pb	10	W	700
Fe	8	Pd	30	Y	30
Ga	40	Pr	100	Yb	3
Gd	60	Pt	30	Zn	80
Ge	10	Rb	70,000	Zr	8

TABLE 4.—*Description of samples in table 2*

Sample	*Description*
139759	Black shale 6 in. thick separating sandstone units of the Cheyenne sandstone member of the Purgatoire formation. Sec. 34, T. 28 S., R. 51 W., Las Animas County, Colo.
139758	Black shale representative of upper 50 ft of Blue Hill shale member of the Carlile shale. Sec. 34, T. 23 S., R. 55 W., Otero County, Colo.
139726	Gray calcareous shale from upper 10 ft of Smoky Hill chalk member of Niobrara formation. Collected on same exposure as 139727. Sec. 33, T. 12 S., R. 36 W., Logan County, Kans.
139727	Black shale from lower 10 ft of Sharon Springs member of Pierre shale. Collected on same exposure as 139726. Sec. 33, T. 12 S., R. 36 W., Logan County, Kans.
139732	Black shale representative of 4 ft of shale underlying lowest septarian concretion zone in Sharon Springs member at McAllaster Buttes. Sec. 13, T. 12 S., R. 37 W., Logan County, Kans.
139733	Medium gray shale from Sharon Springs member, representative of 1-ft unit 6 ft above upper concretion horizon at McAllaster Buttes. Sec. 13, T. 12 S., R. 37 W., Logan County, Kans.
139734	Black shale from Sharon Springs member, representative of 2-ft unit at upper concretion horizon, McAllaster Buttes. Sec. 13, T. 12 S., R. 37 W., Logan County, Kans.

TABLE 4.—*Description of samples in table 2*—Continued

Sample	*Description*
139754	Brown weathered shale from Sharon Springs member. Representative of 6-ft unit of shale below septarian concretion horizon. Sec. 29, T. 15 S., R. 46 W., Cheyenne County, Colo.
139755	Brown weathered shale from Sharon Springs member. Represents 1½ ft of section. Sec. 26, T. 18 S., R. 52 W., Kiowa County, Colo.
139756	Dark gray iron-stained shale from Sharon Springs member. Represents 1⅔ ft of section. Sec. 30, T. 20 S., R. 56 W., Crowley County, Colo.
139757	Black shale from Sharon Springs member in upper 100 feet represents 3 ft 1 in. of section. Sec. 4, T. 22 S., R. 59 W., Crowley County, Colo.
139760	Black shale adjacent to igneous dike, from Sharon Springs member. Sec. 30, T. 32 S., R. 68 W., Las Animas County, Colo.
139761	Black shale from Sharon Springs member. Sec. 29, T. 33 S., R. 62 W., Las Animas County, Colo.
139762	Black shale from Sharon Springs member. Sec. 8, T. 19 S., R. 65 W., Pueblo County, Colo.
139763	Black to dark brown shale from Sharon Springs member. Sec. 35, T. 19 S., R. 65 W., Pueblo County, Colo.

calcium content and smaller silicon and aluminum contents. The sample also contains more zinc, selenium, and arsenic than most of the other samples, although the contrast in selenium content is not great. Compared to samples from the Sharon Springs in general, the Smoky Hill sample (139726) apparently contains less sodium, magnesium, potassium, titanium, and copper. The arsenic and selenium contents of this sample are as high or higher than that of the Sharon Springs samples—some of which contain three times as much uranium.

Several areal distribution patterns of specific elements are indicated in the Sharon Springs samples. The samples from along the Front Range of Colorado (139760, 139761, 139762, 139763) contain more beryllium than other samples and tend to contain more sodium, magnesium, zirconium, and barium. The samples from the McAllaster Buttes locality (139732, 139733, 139734) contain more gallium and less chromium than other samples. These elemental variations may be largely due to differences in the detrital mineral content of the shale.

Sample 139756 contains more than twice as much lead as does any other sample. This increased concentration may indicate that at the time of deposition reducing conditions were much more favorable than at the time of deposition of the other rocks from which samples were collected; or it may indicate an increased available supply of lead at the time of deposition.

No definite correlation between uranium and any other element, or elements, is apparent from the spectrographic analyses. However, the molybdenum and arsenic contents are generally greater in the samples containing the larger amounts of uranium. An even less definite relationship of the same type may exist between the elements selenium and uranium.

SUMMARY AND CONCLUSIONS

The Sharon Springs member of the Pierre shale in western Kansas and eastern Colorado is slightly uraniferous at all localities at which it was examined and sampled. Surface examination and sampling do not indicate the presence of any widespread zone that is more uraniferous regionally than the remainder of the member. At any given locality, the more uraniferous beds of the exposed shale vary little within the outcrop area, but individual beds were seldom exposed for distances exceeding 150 feet. Closely spaced samples indicate that the vertical differences in uranium content can be very sharp, especially adjacent to the more uraniferous parts; however the range of uranium content in the shale is not usually large.

Surface and subsurface data suggest that the most radioactive part of the Pierre in Crowley County, Colo., is persistent for at least 5½ miles (loc. 15, pl. 36 and loc. 12, pl. 38). The gamma-ray logs of wells penetrating the Pierre shale and Niobrara formation in northeastern Colorado indicate that the maximum radioactivity, thickness, and the stratigraphic position of the most radioactive parts of the Pierre and Niobrara sequence relative to the Pierre-Niobrara contact picked on electric logs are variable at distances of a few miles. In most of the gamma-ray logs studied, only part of the sequence exhibits radioactivity in excess of the average radioactivity of the remainder of the formations. Features of this more radioactive part can be correlated in the gamma-ray logs of wells in northeastern Colorado, suggesting a laterally correlatable sequence of beds. If the Pierre-Niobrara contacts picked by use of electric logs are accurate placements of the lithologic boundary between the Pierre and Niobrara, the radioactive unit crosses formational boundaries, and there may be a facies relationship between the Pierre and Niobrara. Another possibility is that some of the contacts picked from electric logs may not correspond to the lithologic boundary between the Pierre shale and the Niobrara formation that would ordinarily be picked by examination of the rocks themselves.

The Sharon Springs member of the Pierre shale and the other parts of the Pierre that were examined contain an estimated average of about 0.001 percent uranium. The most uraniferous sequence of

beds contains about 0.006 percent uranium and is 6 feet thick, as indicated by one sample (table 1). Another sequence of beds 4½ feet thick contains 0.004 to 0.005 percent uranium (table 1), and one 3½ feet thick is estimated to contain about 0.004 percent uranium (table 1). At several localities sequences of beds as much as 9½ feet thick contain about 0.003 percent uranium (table 1). The maximum radioactivity observed according to gamma-ray logs is in Yuma County, Colo., where a 66-foot sequence of beds shows radioactivity ranging from 0.005 to a maximum of 0.010 percent equivalent uranium (loc. 1, pl. 38).

The uranium contained in uraniferous black marine shales is generally believed to have a syngenetic or penecontemporaneous origin. Inasmuch as this report contributes no data to the contrary, it is presumed that the uranium in the Pierre shale and Niobrara formation has a similar origin. Several occurrences of uranium believed to be epigenetic in origin were located; but concentrations are small. In Crowley County, Colo., a 2-inch bed of mixed bentonitic clay, hematite or limonite, and selenite, contained 0.020 percent uranium. In Logan County, Kans., a carbonaceous part of a limestone concretion contained 0.016 percent uranium. Several other occurrences, in which part or all of the uranium is believed to be epigenetic, contain as much as 0.006 percent uranium. At two localities, uranium is of a possible epigenetic origin, and the occurrences are believed to be related to the effects of weathering and bentonitic clay beds.

No definite relationship is apparent between uranium and other elements in the semiquantitative spectrographic analyses, but generally, the samples containing the larger amounts of uranium also contain larger amounts of molybdenum, arsenic, and selenium.

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