

THEORY OF URANIUM DEPOSITION FROM ARTESIAN WATER IN THE EDMONTON DISTRICT, SOUTHERN BLACK HILLS¹

By
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INTRODUCTION

The words of Hutton "the present is the key to the past" may be applied to understanding processes of uranium deposition in the southern Black Hills. In the Edgemont uranium district present-day ground water offers clues to the source of uranium, to the flow and composition of mineralizing solutions, and to the environment of uranium deposition in the Inyan Kara Group, all of which have persisted since the establishment of the present pattern of ground-water recharge and artesian flow following Laramide uplift of the Black Hills.

Initial studies in the Edgemont uranium district by geologists of the U.S. Geological Survey during the 1950's concentrated upon detailed mapping of the complexities of fluvial deposition in the Inyan Kara Group of Early Cretaceous age and provided detailed geologic information on some of the contained uranium deposits. In addition, data pertinent to the study of the uranium deposition have been provided by related mapping of the Paleozoic and Mesozoic strata and younger deposits, an aeromagnetic survey covering part of the area (Meuschke, Johnson, and Kirby, 1963), a gravity survey (R. A. Black, unpublished data), and drilling information from the Atomic Energy Commission and private companies.

The following discussion of uranium deposition is based on ground-water analytical data from 32 water wells which were made available through the courtesy of William Chenoweth of the Atomic Energy Commission. The following interpretation of these data and of the relationship of ground water to uranium deposition results from a study of the southern Black Hills by Garland B. Gott, Don E. Wolcott, and the author.

GROUND-WATER MOVEMENT

Ground-water circulation through the Minnelusa Formation (Pennsylvanian and Permian) and Pahasapa Limestone (Mississippian), as well as the Inyan Kara Group, was established by late Eocene time when erosion had exposed these formations to recharge high on the domal structure of the Black Hills. An artesian flow of water occurred along fractures formed by recurrent structural deformation of northeast-trending Precambrian fault zones (fig. 1). Upward movement of water from the deeper

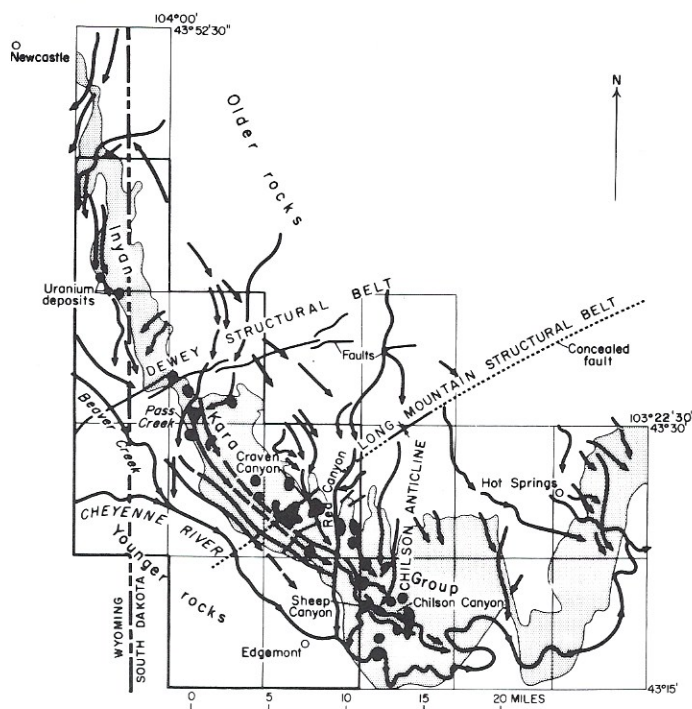


Fig. 1.—Map of the southern Black Hills showing distribution of Quaternary and Tertiary streams (arrows) and location of uranium deposits of the Edgemont district (shown in solid black). Area of ground-water study (fig. 4) indicated by heavy line.

aquifers permitted solution and removal of anhydrite in the Minnelusa Formation, which resulted in the development of solution collapses and breccia pipes (Bowles and Braddock, 1963; Braddock, 1963). Some pipes have stopped upwards as much as 1,300 feet into rocks of the Inyan Kara Group, forming conduits through which large volumes of artesian water rise to recharge the Lakota and Fall River Formations at the margin of the Black Hills. The subsequent flow of this ground water through channel sandstones within the Inyan Kara Group probably is most rapid in the vicinity of the Cheyenne River and larger tributaries which have eroded deeply into the overlying Skull Creek Shale. In these areas resistance to artesian discharge at the surface is at a minimum and some ground water probably is released either by springs or by subflows in stream beds and surficial materials.

GROUND-WATER COMPOSITION

Major Ions

Ground water in the Minnelusa, Lakota, and Fall River Formations is classified into three types: Calcium

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sulfate, sodium sulfate, and sodium bicarbonate—according to the most abundant pairs of cations and anions in solution (fig. 2). This system of classification was modified slightly so that ground-water composition could be mapped in the detail made possible by a plot of water composition on a multiple-trilinear diagram (fig. 3) of

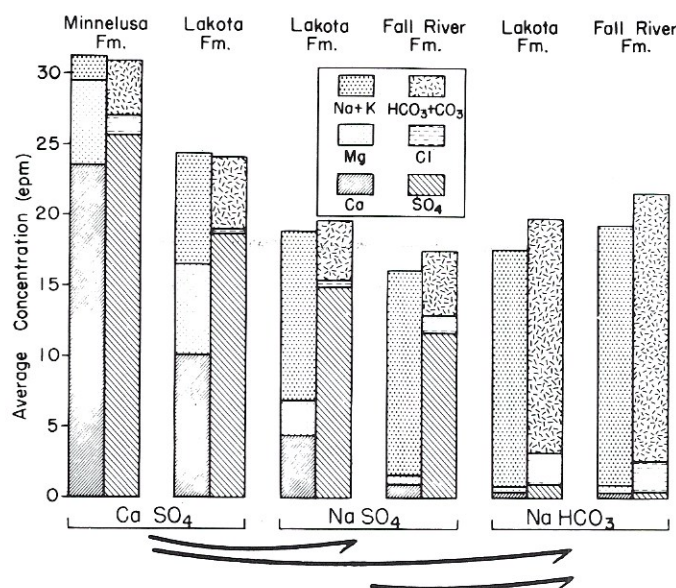


Fig. 2.—Average composition of calcium sulfate, sodium sulfate, and sodium bicarbonate ground water from the Minnelusa, Lakota, and Fall River Formations in the southern Black Hills of South Dakota and Wyoming. (Arrows indicate modification of water types.) Concentration expressed as equivalents per million (epm).

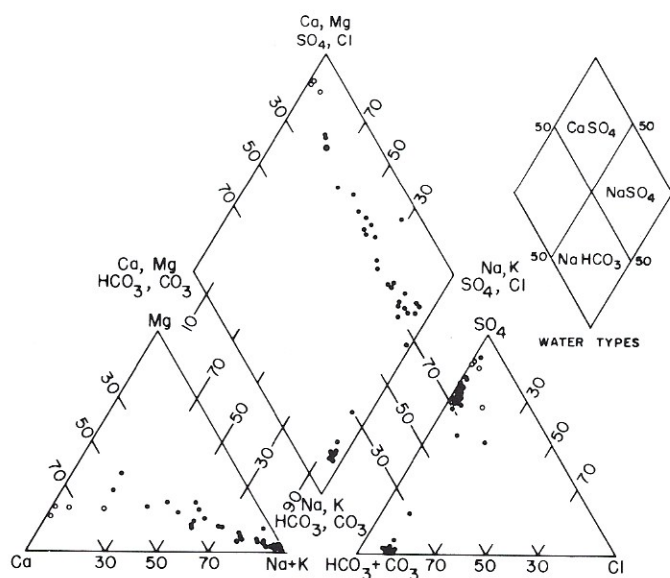


Fig. 3.—Multiple-trilinear diagram showing cation, anion, and combined cation-anion percentages for ground water from the Minnelusa, Lakota, and Fall River Formations in the southern Black Hills of South Dakota and Wyoming. (Minnelusa water shown by open circles.) (Diagram after Piper, 1944.)

the type proposed by Piper (1944). Water types indicated on the combined cation-anion diagram are separated at the 50th percentiles and the waters are named for the most abundant pair of cations and anions present in water

of average composition for each type. This classification of waters is a matter of convenience and should not obscure the apparent genetic relationship between the three types of ground water.

As ground water migrates upward to the Inyan Kara Group and then basinward within the Lakota and Fall River Formations, the composition systematically changes from calcium sulfate water to sodium sulfate water, and locally, to sodium bicarbonate water (fig. 4). The first significant change in composition of the water occurs during ascension with precipitation of calcite and a resulting decrease in the proportion of calcium to other cations (fig. 5). Second, within the Inyan Kara Group a further decrease of calcium and magnesium ions in solution, accompanied by an increase in sodium ions, is interpreted as a natural base-exchange softening of the waters. A third change in the composition to sodium bicarbonate water occurs locally within the Lakota and Fall River Formations.

The change from sulfate water to bicarbonate water within the Inyan Kara is interpreted as a chemical reaction related to reduction of sulfate. Separate grouping of sodium bicarbonate waters plotted on both the combined cation-anion diagram and the anion diagram of Figure 3 suggest a rapid chemical change which completely transforms the water within the 1½-mile distance between the closest water wells. The presence of more than 50 ppm hydrogen sulfide in the bicarbonate water suggests that sulfate reduction is a part of this modification of the ground water. Calcite probably has precipitated from the water, because, even though little calcium is present in the sodium bicarbonate water, calculations based upon the equilibrium pH for calcium and bicarbonate activities in solutions in contact with calcite (Hem, 1961) indicate that the water is supersaturated with respect to calcite.

The processes of base-exchange softening and sulfate reduction result in two distinct patterns of distribution for the three different types of ground water in the Inyan Kara Group. Softening of the waters results in a progressive change from calcium sulfate water near the Inyan Kara outcrop to sodium sulfate water southwestward toward the Powder River basin (fig. 4). Superimposed on this pattern in the vicinity of the Long Mountain structural belt is a change to sodium bicarbonate water as a result of intense reduction of sulfate and accompanying chemical reactions.

Chemical composition of the ground water is influenced in some areas by structures that affect the rate and direction of ground-water movement. A higher proportion of calcium may be present in the water where structure favors a rapid circulation of artesian water from the Minnelusa. For example, composition of ground water changes across faults of the Dewey structural belt where water on the upthrown or north block has proportionally more calcium and magnesium and less sodium than water on the

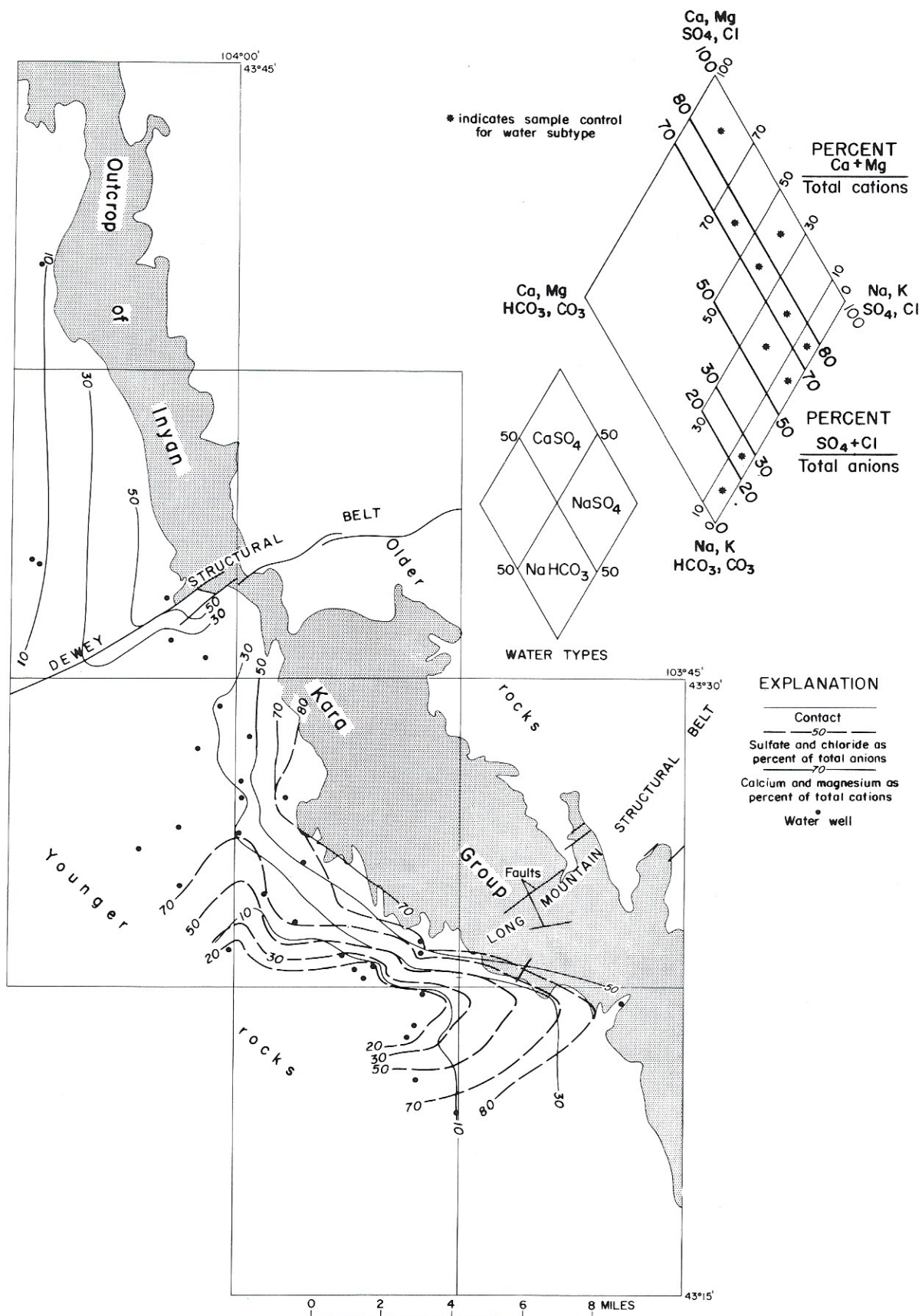


Fig. 4.—Map showing carbonate and bicarbonate as percent of total anions, and sodium and potassium as percent of total cations in ground water of the Inyan Kara Group, southern Black Hills, South Dakota and Wyoming. (Only sampled water wells shown.)

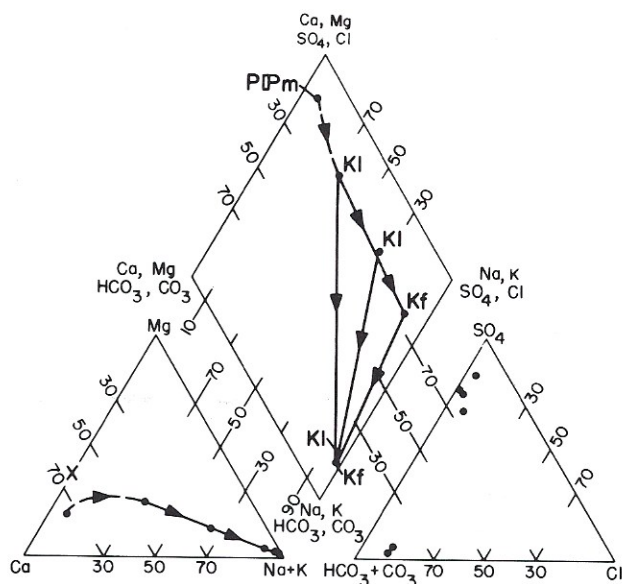


Fig. 5.—Multiple-trilinear diagram showing average cation, anion, and combined cation-anion percentages for ground water of calcium sulfate, sodium sulfate, and sodium bicarbonate types from the Minnelusa (PIPm), Lakota (KI), and Fall River (Kf) Formations in the southern Black Hills of South Dakota and Wyoming. Arrows indicate direction of evolution of water composition. X indicates percentage calcium and magnesium cations in precipitates from ground water in the Inyan Kara Group.

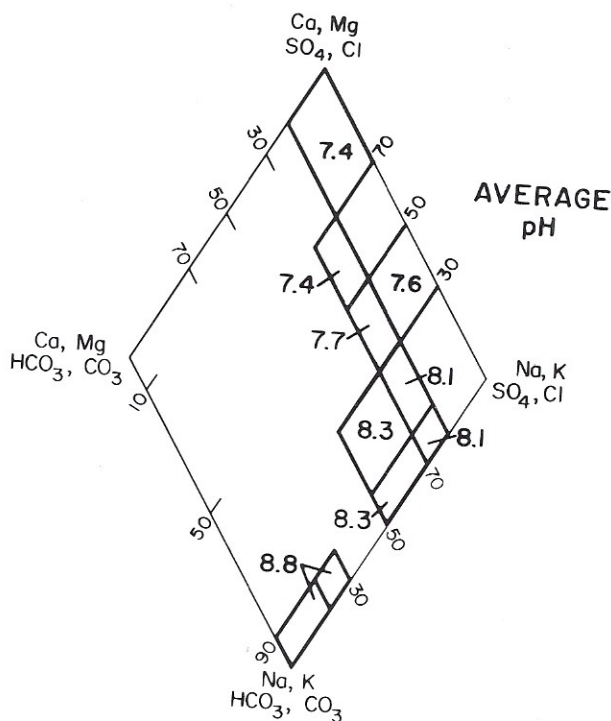


Fig. 6.—Trilinear diagram showing average pH for ground-water subtypes in the Minnelusa, Lakota, and Fall River Formation in the southern Black Hills of South Dakota and Wyoming.

downdropped or south block. Similar variations in water composition also occur across the southwestward projection of the Long Mountain structural belt.

pH

The pH of ground water in the Inyan Kara Group increases in a basinward direction as composition of the water changes. The average pH (fig. 6) ranges from pH 7.4 for calcium sulfate waters near the outcrop of the Inyan Kara to pH 8.1 for sodium sulfate waters farther basinward. Waters of the sodium bicarbonate type have an average pH of 8.8 (fig. 6), and large differences in pH occur in a limited area circumjacent to the sodium bicarbonate water. Differences in pH on either side of the Dewey structural belt reflect the variation in ground-water composition related to structural control of ground-water movement.

Hydrogen Sulfide

Hydrogen sulfide in the ground water ranges from less than 0.05 ppm in calcium sulfate water of the Minnelusa Formation to at least 50 ppm in sodium bicarbonate water in the Inyan Kara Group. Generally, the calcium and sodium sulfate water of the Inyan Kara Group contains a trace of hydrogen sulfide (about 0.05 to 0.1 ppm H₂S), although none was detected in some water samples.

The presence of hydrogen sulfide in the artesian waters is attributed to bacterial reduction of sulfate within the Inyan Kara. Jensen (1958), Lisitsyn and Kuznetsova (1967), and others have stressed the role of microorganisms in the reduction of sulfate and the formation of ore deposits. Sulfate may be reduced by the bacteria *Desulfavibrio desulfuricans* to hydrogen sulfide where carbonaceous material is present to support the bacteria. Large volumes of calcium-magnesium sulfate water rapidly transmitted through aquifers or collapse structures to highly carbonaceous host rocks enable the intensive reduction of sulfate and the formation of a large quantity of hydrogen sulfide. A restricted flow of ground water through slightly permeable beds to carbonaceous matter permits only limited sulfate reduction, and a sparse distribution of the carbonaceous matter limits the intensity of the reduction process.

Eh and pH conditions also limit the reduction of sulfate as shown by a study of sulfate reduction in soils by Connell and Patrick (1968). In soils, reduction of sulfate generally occurs between pH 6.5 and 8.5, with the greatest accumulation of sulfide near pH 7. Reduction occurs at a high rate from pH 7 to 7.8 and then decreases to almost zero at pH 8.5. The same experiments indicate that reduction of sulfate to sulfide is intense below a threshold redox potential of about -150 millivolts Eh, but very slight at higher Eh values.

Application of the findings by Connell and Patrick to the problems of ground-water reactions in the southern Black Hills suggests that a basinward decrease in sulfate

reduction probably occurs as waters increase in pH from near neutral in the calcium sulfate waters to about 8.1 in the sodium sulfate waters. Similarly, the rate of sulfate reduction probably occurs as waters increase in pH from waters of pH 8.8. Within high bicarbonate waters the near depletion of sulfate and the high pH suggest that little reduction of sulfate is occurring, and that the high concentration of hydrogen sulfide in the water is possibly the result of basinward migration from the primary site of reduction.

The reduction of sulfate within the Inyan Kara Group probably occurs within the above limitations of Eh and pH. It is postulated that anhydrite and gypsum in the Minnelusa Formation are the chief sources of sulfate in the ground water. Reduction of sulfate is slight until the artesian water first encounters abundant carbonaceous material in the Lakota and Fall River Formations. Where carbonaceous rocks are present, the most intense sulfate reduction probably occurs in calcium sulfate water having an alkalinity ranging from near neutral to about pH 7.8. Intense sulfate reduction is probably limited to the more carbonaceous rocks, which are carbonaceous shale and sandstone in fluvial unit No. 1 in the Chilson Member of the Lakota Formation, interbedded carbonaceous sandstone and siltstone of the lower unit of the Fall River Formation, and locally, other strata of the Lakota and Fall River Formations shown on recent maps of the U.S. Geological Survey.

Uranium

The uranium content of the calcium sulfate water from the Minnelusa Formation, sampled from seven springs and reported by Gott and Schnabel (1963), averages about 9 ppb (parts per billion) uranium. Similar calcium sulfate water sampled in a well in the Lakota Formation contained about 11 ppb uranium (fig. 7), or approximately the same concentration as the Minnelusa water.

Uranium in the calcium sulfate water is probably derived from a multiple source, but the major contribution at the present time is from calcium sulfate minerals of the Minnelusa Formation. Analyses of anhydrite in drill cores taken from the Minnelusa Formation at Pass Creek ranged from 1 to 9 parts per million uranium, with an average uranium content of nearly 4 ppm for a 200-foot aggregate thickness within the Permian strata. Higher concentrations of uranium occur toward the base of the evaporite interval. Additional probable sources for minor amounts of uranium are other sedimentary rocks and the exposed granites of Precambrian age in the central part of the Black Hills. During Tertiary time, uranium may have been derived from volcanic ash of the White River Group of Oligocene age as well as from other sources.

The uranium content of ground water in the Inyan Kara gradually decreases in a basinward direction to about 3 ppb U_3O_8 (fig. 7) as the calcium sulfate water is modified to sodium sulfate and simultaneously is subjected to minor sulfate reduction. Within the more carbonaceous rocks where intensive reduction of sulfate occurs, the uranium content of ground water decreases very rapidly to an average of about 3 ppb U_3O_8 or less as sulfate is reduced and the water is modified to the sodium bicarbonate type. A sample of bicarbonate water analyzed by John N. Rosholt (written communication, 1967) contained only 0.03 ppb uranium oxide. The decrease in uranium content of these waters is interpreted as an indication of the reduction and precipitation of uranium from the ground water. The favorability of the ground-water environment for precipitation of uranium may be deduced from the rate of decrease in uranium content as the composition of the ground water changes during migration. The decrease in uranium content is more rapid in calcium sulfate waters than in sodium sulfate waters, and a maximum rate of precipitation may be expected where large concentrations of hydrogen sulfide and a rapid transition from calcium sulfate to sodium bicarbonate water mark intensive reduction of sulfate and the accompanying reduction in valence and rapid precipitation of uranium. Conversely, sodium sulfate water having a lower uranium content cannot precipitate as much uranium during sulfate reduction, and as indicated previously, sulfate reduction in waters having a higher pH probably is less intense; therefore the sodium sulfate water is considered less favorable for precipitation of a uranium deposit.

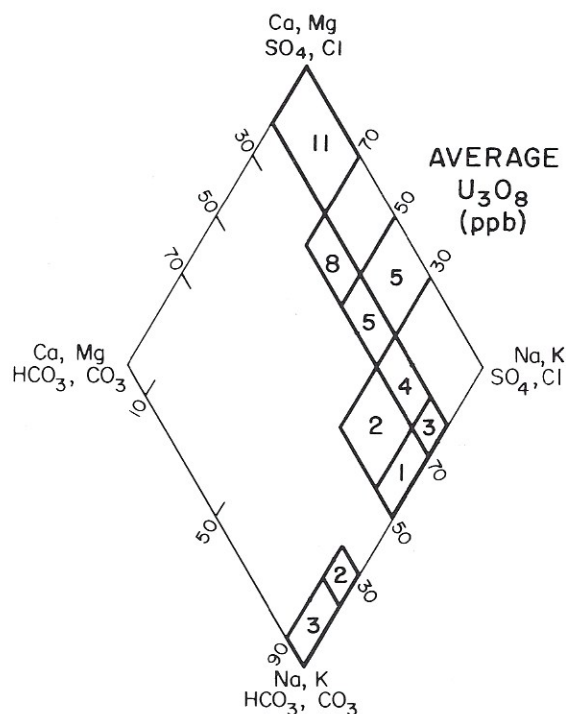


Fig. 7.—Trilinear diagram showing average uranium oxide content (parts per billion) in ground-water subtypes in the Minnelusa, Lakota, and Fall River Formations in the southern Black Hills of South Dakota and Wyoming.

CONCLUSIONS

Calcium-sulfate ground water carries uranium, derived from anhydrite and other sources, up fault, fracture, and breccia pipe structures to the Inyan Kara Group where, during basinward migration, the water is modified by base-exchange softening and sulfate reduction. Uranium is reduced and precipitated by a hydrogen sulfide environment, although, locally, organic acids may have affected deposition. Greatest precipitation occurs marginal to bicarbonate water having a large concentration of hydrogen sulfide. Ground-water conditions in the past, and at somewhat higher elevations on the flanks of the Black Hills, were similar to present conditions and similarly affected uranium deposition. Uranium from the older deposits in the Inyan Kara Group may be leached at higher elevations and reprecipitated downdip in this favorable environment.

Exploration for concealed uranium deposits in the southern Black Hills should be based on the coincidence of vertical conduits overlying the evaporites and the occurrence of favorable host rocks in which uranium deposits are present near the outcrop. Areas along the Long Mountain structural belt in the vicinity of terrace gravels of late Quaternary age, updip from the present hydrogen sulfide reducing environment, offer a favorable target for exploration above the water table.

Below the water table, water sampling during drilling exploration would supplement the usual stratigraphic,

mineralogic, lithologic, and radiometric studies conducted during exploration and would aid in the systematic search for uranium deposits.

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