# TECHNICAL PAPERS

## Some Mechanisms for the Fixation of Uranium in Certain Sediments

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During a spectrographic analysis of a drill core of bauxite (*1*) several very weak lines were measured which indicated that uranium was present in the core. Because the most sensitive uranium line (4,241.67) was obscured by a heavy zirconium line (4,241.687), two preliminary samples were tested in a beta counter. When compared with a standard containing 0.0004 gm of $U_3O_8$, one of the preliminary samples, consisting essentially of the mineral gibbsite, showed an equivalent amount of 0.0002 gm of $U_3O_8$ or $13.1 \times 10^{-12}$ gm/gm of radium equivalent. The other sample contained 94% kaolinite and showed $9.6 \times 10^{-12}$ gm/gm of Ra equivalent. These results indicate that the samples contained an amount of uranium that approached the threshold sensitivity of the spectrograph for this element.

The following remarks on the chemistry of uranium taken from Latimer (*2*) have geochemical significance: The oxides of $UO_2$ and $UO_3$, as well as the intermediate oxide $U_3O_8$ and probably $UO_2 \cdot 2UO_3$ or $U(UO_4)_2$, are stable. Complex ions of the +3 and +4 states exist in solutions. Hydrates of the trioxide, $UO_2 \cdot H_2O$ and $UO_3 \cdot 2H_2O$, are quite soluble in acids, forming the uranyl ion, $UO_2^{++}$. This $UO_2^{++}$ ion is remarkably stable and has the properties of a large, simple, doubly charged metallic ion. It forms compounds that are slightly soluble, such as $Na_4UO_2(CO_3)_3$, $UO_2(IO_3)_2$, etc.

It is here suggested that the wide distribution of uranium throughout the sedimentary crust of the earth is due principally to its tendency to form large $UO_2^{++}$ ions. The resulting large ionic radius is comparable with the radii of potassium, rubidium, cesium, and other large ions of low ionic potential[1] that concentrate only in the evaporates[2] if they are not first adsorbed by base exchange on the clays and other layer-lattice minerals.

If the above statements are correct, much of the uranium in shales may be in the form of adsorbed ions and not of discrete minerals. Whether or not this deduction is true is not known. Some support for this suggestion, however, may be implied from the work of Rothe (*3*). Tests of source rocks demonstrated that kaolin deposits showed very slight to no radioactivity. Rothe reported that clays found in a quarry of rhyolite had an exceptional activity. He also noticed a concentration of radioactivity associated with "wad" deposits.

It is interesting to note that kaolinite, which has almost no base exchange capacity, also showed negligible radioactivity. Other clays, however, such as the montmorillonite, which develop from volcanic ash and basic flows, have a large base exchange capacity. While Rothe did not specifically state the type of clay associated with the Permian rhyolite that was so highly radioactive, it is almost certain that it was a clay with high base exchange capacity. This leads to the obvious conclusion: If the source rocks containing uranium are weathered to clays with a high base exchange capacity, these clays should show high radioactivity.

A world-wide association of certain types of carbonaceous[3] material with vanadium and uranium materials has been observed. This close association must be due to some unique feature of the chemistry of carbon, the principal characteristic of which is its four tetrahedral electron pair bonds and the remarkable stability of these bonds with hydrogen, oxygen, nitrogen, sulfur, the halogens, and especially with other carbon atoms. All forms of so-called amorphous carbon, from lampblack and coke to charcoal, are graphitic in character. They are composed of portions of the graphite structure without, however, the regular 3-dimensional periodicity characteristic of crystalline graphite. Because of its structure, with its extensive internal surfaces and unsatisfied valencies, charcoal (and similar forms of carbon) possesses the property of adsorbing ions to a remarkable extent. The layer structure of graphitic material behaves in much the same manner as do certain of the layer-lattice clay minerals. Oxygen atoms may attach themselves to the graphite sheets and cause them to swell, forming the so-called graphitic oxides. Water may then be adsorbed until two layers of water molecules are between successive layers of graphite.

It is important to note that the unique $UO_2^{++}$ ion consists of two oxygen atoms located at opposite sides of the uranium atom. It is quite possible that this $UO_2^{++}$ ion is adsorbed between the graphite layers of carbonaceous material, forming a strong structure due to the stable $UO_2^{++}$ ion holding the two layers together. In this manner uranium may be concentrated to a remarkable degree in carbonaceous materials.

A possible method of concentration of uranium in sedimentary deposits containing carbon may then be as follows:

Uranium ions are released, on weathering, from the granitic, rhyolitic, etc. rocks in which they occur in relatively large amount and are then adsorbed by base exchange phenomena on layer-lattice minerals such as cer-

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[1] Ionic potential $=\frac{Z}{r}$, where Z = valence of the ion and r = the ionic radius.

[2] Evaporates are saline deposits such as salts found in desert basins, etc.

[3] The word "carbonaceous" is used to denote that type of material containing carbon of an organic source.

tain clays. This may be considered the first step in the process of concentration of the uranium.

Because of an increase in the thermal environment of the clays, aging of the material, or the introduction of chemically more active ions into the system, the uranium is displaced and again put into solution. Carbonaceous material, in the path of the displaced ions, would act as a "filter" and again concentrate, and this time fix, the uranium ions.

For the concentration of uranium according to the above suggestions it is probably important that an oxidizing environment prevail. Alkaline solutions cause the graphite layers to expand to such an extent that they may be converted into a colloidal suspension, leading to a final breakdown of the graphite structure. Colloids containing uranium would then be adsorbed again on clays and similar minerals.[4]

The above discussion does not, however, account for the uranium in the bauxite core. The clay mineral in the core is kaolinite, a clay with very little base exchange capacity. The drill core contained siderite distributed throughout its entire length. The carbonate solutions of high pH should disperse or leach the uranium from the core. When tested in the beta counter, the siderite-rich material showed almost no radioactivity.

The drill core contained large amounts of titanium and zirconium. These elements form ions similar to the uranyl ion:

$$UO_2(OH)_2 \rightarrow TiO^{++} + 2OH$$
$$ZrO(OH)_2 \rightarrow ZrO^{++} + 2OH$$
$$UO_2(OH)_2 \rightarrow UO_2^{++} + 2OH$$

Certain portions of the drill core that contained no titanium or zirconium minerals showed high assays for these two elements. The elements must have been present in the form of adsorbed ions on one of the minerals in the core. The writer believes that the uranium was introduced into the deposit in the form of the uranyl ion, concentrated along with the titanates and zirconates which were in the form of the above ions, and was adsorbed on the aluminum mineral gibbsite, thus giving rise to the relatively high radioactivity found. The radioactivity of some of the samples from the drill core are listed in Table 1.

TABLE 1

RADIOACTIVITY OF SOME OF THE MINERALS IN THE DRILL CORE

| Samples from the drill core | $10^{-12}$ gm/gm Ra equivalent |
|---|---|
| Ilmenite and brookite ...... | 8.1 |
| Sample 1 (92% kaolinite) .. | 9.6 |
| " 2 (74% gibbsite) ... | 13.1 |
| " 3 (54% siderite) ... | 8.6 |

Miss Geraldine Sullivan, working on a program sponsored by the Geological Society of America at the Geochemical Laboratory of Massachusetts Institute of Technology, found that the average β-radioactivity for 233 shales was $9 \times 10^{-12}$ gm/gm Ra equivalent. This figure can be used as a basis of comparison for the radioactivity of the samples listed in the above table. Almost all of the uranium is located in the sample containing a large amount of gibbsite, whereas the kaolinite specimen shows very little radioactivity.

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[4] Could a process such as this account for the high radioactivity of certain carbonaceous shales or have something to do with the formation of oil by the polymerization of the highly active carbon into hydrocarbons by radioactive processes?

#### References

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## Penicillin Blood and Milk Concentrations in the Normal Cow Following Parenteral Administration

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The question of whether or not penicillin can be demonstrated in the milk of the dairy cow following parenteral administration has been undergoing considerable study. Seeley, *et al.* (*6*) tested milk of a normal cow for penicillin activity following intravenous administration. A total of 500,000 units was injected in two portions of 15 ml each about 1 min apart. No measureable amounts of penicillin were present when samples of milk were taken at frequent intervals for 24 hrs after dosing. Watts and McLeod (*7*) injected doses up to 1,000,000 units of penicillin intramuscularly into normal heifers and were unable to detect the drug in the milk. Barker and Dussault (*1*) treated a cow infected with mastitis streptococci with a total dosage of 2,681,000 units of penicillin, administered intramuscularly at 8-hr intervals over a period of 4 days and, on the basis of their results, stated that the lactating bovine mammary gland appears to be nonpermeable to penicillin.

When high, persisting blood concentrations were obtained following parenteral administration of Sulfamethazine in the dairy cow, significant amounts of the drug in the milk were demonstrated (*4*). When low blood levels were obtained after sulfathiazole administration and the

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