Migration of Radioisotopes in the Earth's Crust

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Radioisotopes trace out mechanisms important both to underground nuclear waste storage and to our planet's geology.

Water moves steadily in the earth beneath our feet, flowing in aquifers through the pores, fractures, and grain boundaries of rocks and minerals. This ubiquitous "universal solvent" interacts with the rock, helping gradually to reshape the geology of our planet's crust; it is the fluid most commonly associated with an important process called geochemical migration, that is, the selective movement of chemical elements in rock. A better understanding of the nature of this process has implications for a variety of human activities.

For example, burial of hazardous materials has often been chosen in the past as the safest method of disposal. But this choice sometimes ignored the pervasive nature of geochemical migration, leading to a number of serious cases in which hazardous material resurfaced in drinking water. A particularly important disposal problem is what to do with nuclear reactor waste. Storage in deep geologic sites is being considered, but it is imperative to evaluate the potential for migration of long-lived, highly radioactive waste away from the site and into the accessible environment.

There are also implications for locating ore deposits. A wide variety of ore bodies are thought to be formed as the result of selective dissociation of elements from a large body of rock followed by transport in water and eventual concentration and precipitation at another site. What conditions favor the dissolved forms of the elements, what favor the precipitated forms? A full understanding of such processes would serve as a rational basis for predicting the location of ore bodies in different geologic settings.

The complex phenomena that constitute geochemical migration have long intrigued and challenged geochemists. Much relevant information has come from studies of volcanism, of the processes that alter a rock's mineral composition, and of age determination techniques. Much remains to be learned if we are to understand the complexities of geochemical migration and its relationship to all the other geologic processes that shape our planet.

Radioisotopes

At Los Alamos we draw upon the Laboratory's background in nuclear physics and radiochemistry to study geochemical migration using radioisotopes. These methods have much to recommend them, starting with the fact that even trace amounts of radioisotopes are easily detectable. This is important because elements are frequently present in water only to the extent of parts per billion. The ease of detection is due, of course, to the radiation emitted by these isotopes. This radiation, characterized by type and energy, also helps establish a unique signature for any source of radioisotopes, especially when coupled with mass spectrometric measurements that give the relative isotopic abundances of both the radioactive and nonradioactive isotopes in a sample. The signature can then be used not only to identify the source of an element but also to follow its migration through the environment.

For example, the atmospheric nuclear weapons tests that took place over the ocean in the fifties injected large quantities of chlorine-36, a long-lived beta emitter, into the environment. This isotope is normally produced by cosmic rays in the atmosphere and had already been of use as a tracer in hydrology. The much larger quantities, however, could be uniquely associated with tests detonated in proximity to seawater: chlorine-36 is not a direct fission or fusion product but is generated by thermal neutron activation of the chlorine-35 isotope abundant in seawater. A recent study by researchers at the University of Arizona, New Mexico Institute of Mining and Technology, and the University of Rochester has shown that these tests caused a global "pulse" of chlorine-36 to be injected into the environment. This pulse lasted from 1953 to 1976 and, at its peak, rose to 1000 times the natural background level of chlorine-36 in the mid latitudes. In contrast to carbon-14 and tritium, which are still being generated by China's atmospheric testing, fallout rates for chlorine-36 have returned to natural background levels, making this isotope ideal for use as an environmental tracer. Because its long half-life eliminates ambiguities associated with loss of the isotope through radioactive decay, chlorine-36 should be especially valuable for studies of hydraulic flow and dispersive mixing as it incorporates itself into the water and geology of the earth's crust. Although these processes continuously reduce the concentrations of the tracer, recent advances in analytical chemistry, namely accelerator-based mass spectrometry, make possible its detection in amounts of 10^7 atoms per liter or less.

There are further advantages in the use of radioisotopes. As is well known from radioactive dating, individual radioisotopes decay at specific rates characterized by their half-lives; ages are determined using the ratio of the amount of radioisotope, or parent, to that of the decay product, or daughter. But because the daughter is usually a different element that is chemically distinct from the parent, fractionation processes can occur that physically separate the two. For example, conditions may have been such that the two elements had considerably different solubilities in the groundwater moving through the rock and one was transported away while the other remained in place. Deficiencies of parent or daughter elements in geologic samples compared to amounts predicted from nuclear physics may thus indicate geochemical migration. Samples from other geologic locations may reveal the destination of the transported element. Even more important, the chemical nature of the elements sheds light on the chemical nature of the fractionation process that took place in the sample. And comparison of parent to daughter ratios helps determine the geologic time at which the fractionation occurred (Fig. 1).

A particular advantage of analytical techniques based on mass spectrometry stems from the fact that amounts of both unstable and stable isotopes are measured. Even billions of years after a particular geological or nuclear event, stable isotopes and long-lived radioisotopes remain. Depending on the history of a sample, the relative abundances of these isotopes differ, providing the researcher a unique signature of the source. For example, the products of a uranium fission chain reaction can be distinguished easily from chemically identical products found naturally.

Initial motivations for much of the radioisotope migration research at the Laboratory have been related to nuclear weapons testing and nuclear energy. For example, how much, if any, of the radioactive material generated in the underground testing at the Nevada Test Site will be carried away by the groundwater? Or if radioactive nuclear wastes are stored underground, what mechanisms may cause migration of the radioisotopes and how fast would this happen? Yet, because geochemical migration is actually a complex group of interacting phenomena, answers to these particular questions also shed light on more general questions important to geology. (See "Mechanisms of Migration" for highlights of this broad picture.)

Migration from Underground Tests

From 1957 to the present there have been over five hundred underground nuclear tests at the Nevada Test Site, of which at least ninety-five were detonated at or below the

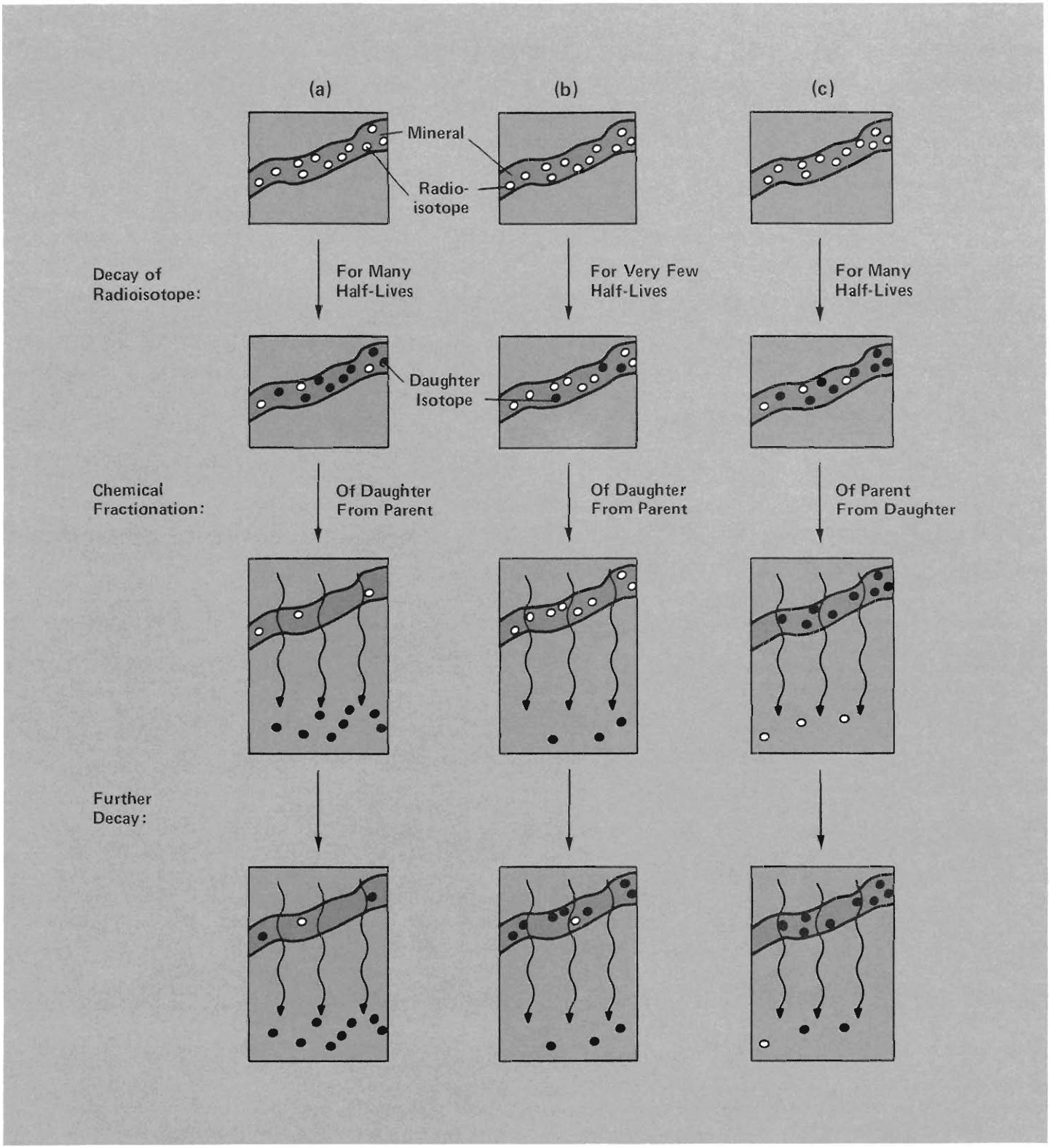


Fig. 1. Simple examples of fractionation of radioisotopes. Because the daughter isotope (solid circles) of a radioactive decay process is a different element than the original radioisotope (open circles), chemical and physical processes may eventually separate the two. The figure depicts a radioisotope-containing mineral in the same state at the top of each column. In (a) considerable decay occurs before fractionation, whereas in (b) only a small amount of decay occurs first. The fractionation process for these two columns is identical, say dissolution and transport of the daughter isotope by groundwater. The result of the difference in the time when fractionation occurs is seen at the bottom of each column. Column (a) has a high depletion of daughter in the mineral, whereas in (b) the depletion is much less. In (c) there is again considerable decay, but the fractionation process transports the original radioisotope, leaving an excess of daughter in the mineral.

Mechanisms of Migration

Most people are aware that rainfall, as it seeps into the earth, becomes laden with dissolved material or solutes. What they may not realize as fully is that the composition of the solutes can change drastically as the water passes from one geochemical environment to another, causing significant relocation of particular elements in relatively short geologic times.

Consider granite, a rock with a very low permeability to water. If a cube of such rock, 1 kilometer on a side and without fractures, has a typical hydraulic pressure gradient along one axis of 10 meters per kilometer, then 30 billion liters of water will flow through the rock in only 10 million years. If the water picks up uranium from the rock to the extent of 5 parts per billion, which is only 5 milligrams per 1000 liters, then a total of 150 kilograms of uranium will be transported out of the block. Although the degree of permeability and the strength of the driving forces determine how fast water flows, we see that large volumes can move through even very impermeable rocks, transporting significant quantities of trace elements.

The forces that act to produce migration are gravitational, chemical, and thermal. Gravity is the force responsible for hydraulic gradients. The rate of flow of groundwater is determined by this gradient, which, in turn, is generally a function of the topographic relief. A totally flat plain at sea level has a zero hydraulic gradient and zero flow.

For a given hydraulic gradient, flow is a function of permeability, which reflects texture and structure. Fractures may provide relatively low-resistance pathways through rock while a fine-grained or plastic rock may be relatively impermeable. In sedimentary and volcanic ash sequences, the permeability of individual strata may differ widely.

Another factor affecting flow is porosity, a measure of the space available in the rock for water. Porosity is generally related to permeability so that highly permeable rocks tend to be quite porous and vice versa. But for geochemical migration it is *connected* porosity that is important. This parameter determines the degree to which the entire bulk of the rock, as opposed to the surfaces of fractures, is exposed to flowing groundwater. Highly porous, permeable rock, such as some tuffs, are totally exposed, allowing elements to be leached from all minerals in the rock.

Above the water table, rock is unsaturated, and flow is limited although not stopped. As air replaces water, flow is gradually restricted to surface films that must be connected for liquid flow to occur. When the film becomes discontinuous, water movement is restricted to vapor transport in the air-filled pores, and transport in water becomes negligible.

A thermodynamic measure of the chemical force is the chemical potential, which, in aqueous systems, is directly related to solubility. For a given element, the chemical potential varies with the element's concentration and the environmental conditions such as temperature and pressure, acidity, the tendency for reduction or oxidation reactions, and the presence or absence of complexing ions or molecules in the water. In general, elements move from higher to lower potentials. For example, if the amount of dissolved mineral is less than the equilibrium concentration, then dissolution will take place, albeit often very slowly; if the amount exceeds the equilibrium solubility, then precipitation occurs.

The chemical processes contributing to

water table (Fig. 2). Considerable thought went into the engineering of the tests to insure that no radioactivity escaped into the environment, not even by way of underground water. However, it was realized that aspects of this latter path, such as the complex chemical partitioning of a radioisotope between the liquid, gaseous, and solid phases, were poorly understood. Hard data were needed.

Starting in 1972, an AEC (now DOE) program evolved that included the Los Alamos and Lawrence Livermore National Laboratories, the Desert Research Institute of the University of Nevada, the U.S. Geological Survey, and the Reynolds Electrical and Engineering Company. The program's mission was to gather and interpret data necessary for an understanding of radioisotope migration at the Test Site. Studies were eventually conducted at eight areas, including seven nuclear test sites and one area in which tritium was detected several hundred meters from the nearest underground test cavity. One of the most informative of these projects, and the one we will discuss here, measured migration by imposing an artificial hydraulic gradient on the normal underground water flow from a nuclear test cavity.

The cavity, the result of a test shot called Cambric, was located 73 meters below the water table within a Test Site water-supply aquifer. Since the detonation had occurred in 1965, nine years before the start of the study, it was predicted that the cavity, and the chimney resulting from later collapse above the cavity, had long since filled with water to the preshot level of the water table. Any radioisotopes present would constitute a potential source for transport, and it was felt that the postshot debris would contain sufficient amounts of radioisotopes to compare concentrations between rubble and groundwater. Table I gives the Cambric source

geochemical migration can be very complex. A specific element can, in fact, move upstream against its potential treated as an isolated system if there is a net zero or negative potential change for the total system of interacting elements. It is quite possible in complex systems for one or more minerals in a rock to be dissolving while others are forming.

An illustration of this complexity is the variety of possible associations between metal cations in the minerals and the anions that may be available in groundwater, such as chloride, fluoride, carbonate, sulfate, or phosphate. For some conditions anions form stable complexes with cations, such as $PbCl_4^{-2}$, $Zn(HS)_3^-$, and HgS_2^{-2}, that increase the metal's solubility. For other conditions the anions do the opposite and form insoluble compounds, such as $CaCO_3$, $MgSO_4$, HgCl, or $Th_3(PO_4)_4$.

Temperature has a major effect on chemical potential. A mineral stable at 200 degrees Celsius may be unstable at 300 degrees. Solubilities typically increase with temperature but may be retrograde and decrease instead. Geothermal systems are particularly active zones for geochemical migration because thermal gradients combine with gravitational forces to produce convective groundwater circulation that exposes the minerals to a wide range of chemical environments.

Important chemical processes take place even in solid or crystalline materials. Trace elements such as the rare earths are frequently found as dissolved components in solid solution. These impurities can either be incorporated into the solid when it forms or diffuse into the lattice later. Conversely, diffusion out of the solid can release trace element impurities into the groundwater.

One of the most important aspects of geochemistry is the role of surfaces. For example, silicates tend to have a negative surface charge, due to exposed oxygen atoms, that attracts cations. Depending on the mineral, the cation, and the chemical environment, this attraction can cause a particular cation to spend most of its time sorbed on a surface, retarding its transport by moving water. Van der Waals forces, due to dipole interaction, and chemisorption, in which one or more chemical bonds are formed between the solute species and the surface atoms, also play an important role.

Because sorption is a surface effect, the crystal structure of a mineral is very important. With densely packed structures, only the external surface of the crystals can sorb species from solution. However, other minerals, such as zeolites, have a very open lattice structure that permits relatively easy access to interior passages. These show preferential sorption for species whose size matches the openings most closely.

Because the surfaces of the mineral in the pores are predominantly negatively charged, anions are typically repelled and cannot enter a small pore as readily as a neutral molecule or a cation. (Only a few minerals sorb anions, and then not very strongly.) This repulsion leads to the surprising result that anions can migrate through the rock more rapidly even than the water. The water molecules exchange with the stationary fluid in small water-filled pores, while the anions continue moving in the flowing stream.

The task, then, of the geochemist trying to understand migration in a given geologic setting is complicated. He must sort from a variety of factors those particular ones that apparently caused the equilibria to shift in one direction or another. ■

term, that is, the expected activity of selected radioisotopes if radioactive decay but no migration had occurred during the ten years before re-entry into the cavity. One important feature of this source term was the amount of tritium—enough to act as an easily measurable tracer for water from the cavity.

The geologic medium surrounding the Cambric cavity is tuffaceous alluvium, a deposit of gravel-like or sand-like debris that was originally volcanic material. This material was believed to constitute a good medium for hydrologic studies because it is quite permeable and does not have large fissures or cracks through which the water might flow selectively. Because the yield of Cambric was relatively low (about 0.75 kilotons), the test was expected to have had little effect on the local hydrology.

NATURAL MIGRATION. Two wells were drilled: the first, the satellite well, 91 meters from the cavity in the direction of normal water flow for the aquifer; the second, the re-entry well, at an angle through the lower chimney and cavity of the Cambric test (Fig. 3). The first question addressed was the extent of natural radioisotope migration since the detonation. To answer it, core samples were taken from the walls of the re-entry well starting just below the ground surface and continuing to 50 meters below the detonation point. Then, by using inflatable packers to isolate a zone in the well and perforating the casing in that zone, water samples were taken from five levels that ranged from just above the chimney to below the cavity.

Several interesting facts were determined about the distribution of the radioactive material. Ten years after the test, most of the radioactivity was still in the cavity region. No activity above background was found 50 meters below the point of detonation. Al-

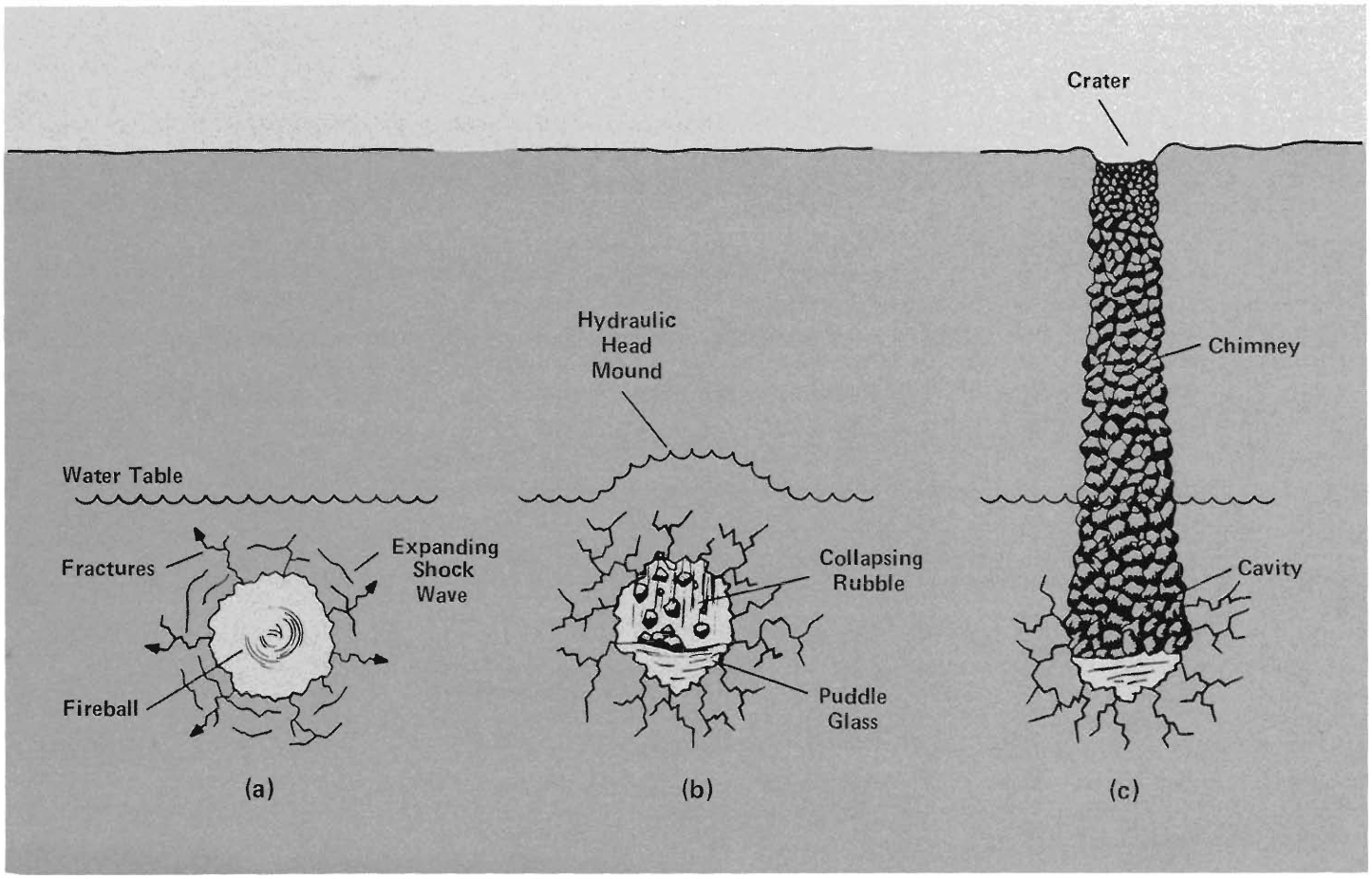


Fig. 2. Sequence of events in an underground nuclear explosion. (a) The explosion vaporizes the rock immediately surrounding the weapon, melts and spalls rock somewhat further away, and generates a compressional shock wave that creates a cavity and may fracture rock for several hundred meters. (b) After the explosion the gases cool and condense, forming puddle glass, or resolidified rock, at the bottom of the cavity that incorporates a significant fraction of the refractory radioisotopes, such as the rare earths, plutonium, zirconium, and the alkaline earths. At this point the cavity begins to collapse, and volatile radioactive species, such as the inert gases, move upward. Partly volatile species, such as the alkali metals, uranium, antimony, and iodine, may condense on rubble surfaces in the lower chimney. Also note that the shock wave has perturbed the water table, generating a mound in the hydraulic head. (c) A chimney of rubble forms above the collapsed cavity and, if it reaches ground level, forms the crater typical of underground tests. Eventually, the cavity and part of the chimney refill with water, dissipating the hydraulic head mound. The time for this last process ranges from days to years.

though some krypton-85 and tritium were found in the collapsed zone above the cavity, these two isotopes were concentrated in the cavity region. More than 99.9 per cent of the tritium was in the form of tritiated water (HTO), and the krypton-85 was dissolved in the water. In the lower cavity region, where the puddle glass was concentrated, strontium-90, cesium-137, and plutonium-239 were almost entirely incorporated into the solid material. As a result, only strontium-90 and tritium were present in the water from this region of highest radioactivity at concentrations above the federal guidelines for drinking water in uncontrolled areas.

TABLE I

SELECTED CAMBRIC RADIOISOTOPES TEN YEARS AFTER DETONATION

Calculated Source Term			Measured Distribution		
Isotope	Half-life (years)	Activity (curies)	Locations Detected	Form	Retention Factor on Solid in Cavity
$^{3}H(T)$	12.3	3.4×10^{4}	cavity, chimney	HTO	—
^{85}Kr	10.7	4.4	cavity, chimney	dissolved in water	—
^{90}Sr	29	34	cavity, chimney	retained with solids	2000
^{106}Ru	1.0	2.8	cavity	retained with solids	200
^{125}Sb	2.8	3.2	cavity	retained with solids	300
^{129}I	1.6×10^{7}	6.7×10^{-5}	cavity	dissolved in water	—
^{137}Cs	30	99	cavity, chimney	retained with solids	20,000
^{144}Ce	0.78	0.4	—	—	—
^{147}Pm	2.6	33	cavity	retained with solids	$>10^{6}$
^{155}Eu	5.0	6.4	—	—	—
^{239}Pu	2.4×10^{4}	classified	cavity	retained with solids	$>10^{7}$

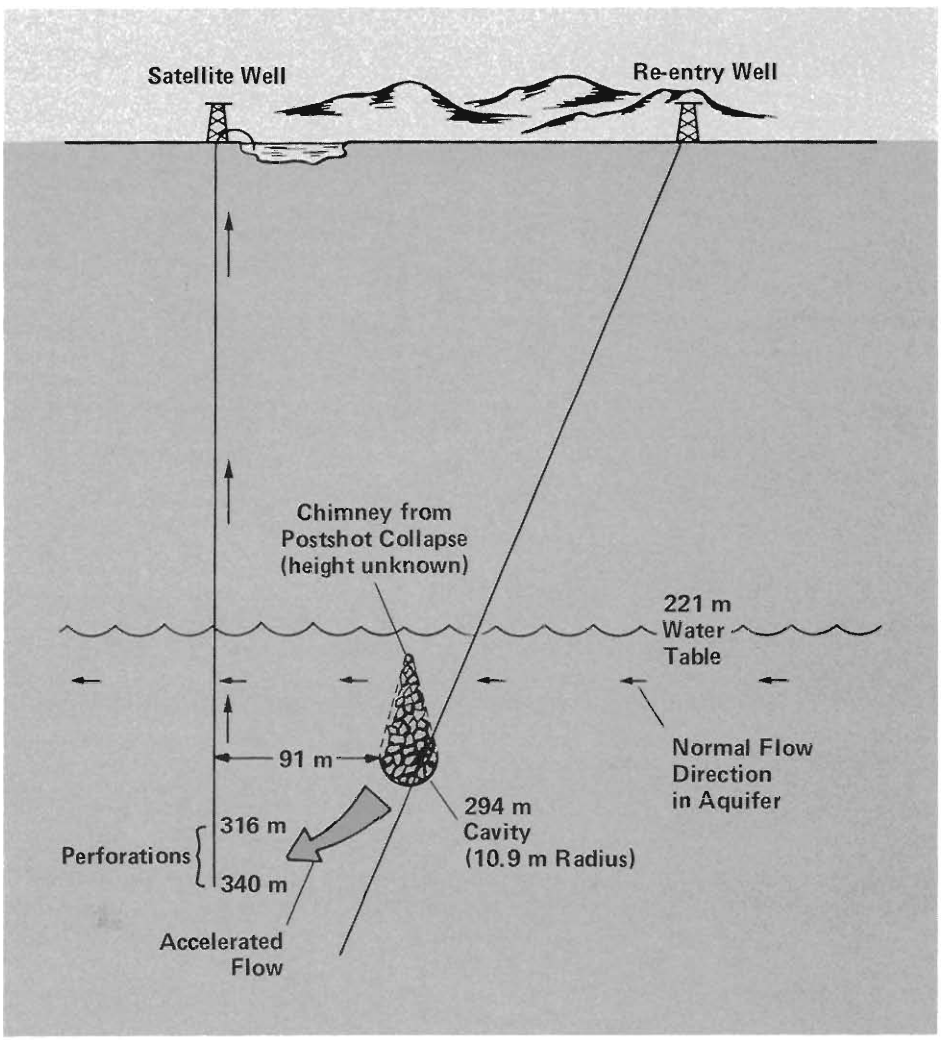


Fig. 3. The Cambric radioisotope migration study. The Cambric underground test was detonated about 9 years earlier at a depth of 73 meters below the water table. Accelerated flow of radioisotopes from the cavity (large arrow) was induced by pumping water from a satellite well 91 meters away in the direction of the normal flow of groundwater.

Retention factors were calculated to measure how effectively strontium-90, for example, had been retained in solid material. The ratio of strontium-90 activity in a solid sample to tritium activity in a water sample from the same location was compared to the same ratio for the Cambric source term. The high retention factors for strontium-90, ruthenium-106, antimony-125, cesium-137, promethium-147, and plutonium-239 (Table I) indicate that these isotopes were either fused into or highly sorbed on the solid material, or both.

ACCELERATED MIGRATION. The next step was to generate an artificial hydraulic gradient by pumping water from the satellite well. It was planned that pumping would draw water from the cavity and permit the study of radioisotope migration under field conditions. Pumping began in October 1975 at a rate of 1 cubic meter per minute; two years later the rate was increased to 2.3 cubic meters per minute. Early in 1978, after a total of 1.4 million cubic meters had been pumped, significant amounts of tritium were detected, signaling the arrival of water from the cavity region.

The tritium concentration grew, peaked at just below the maximum permissible concentration for drinking water in controlled areas (3 nanocuries per milliliter), and is now decreasing. By October 1982, 42 per cent of the tritium available from Cambric had been removed by this pumping. The concentration data are shown in Fig. 4 along with a theoretical fit to the data of a typical model for fluid flow through a dispersive medium.

Neutron-activated chlorine-36 produced

by the Cambric explosion was also detected by mass spectrometry in water pumped from the satellite well. The same flow model also fit these data. The major difference between the migrations of tritiated water and chlorine was that the chlorine arrived and peaked 20 per cent sooner. This difference was felt to be due to the anion exclusion effect in which anions are repelled by the negative surface charge in the small pores of the aluminosilicates. As a result, anions cannot enter these pores as readily as cations or neutral water molecules. The net result is that the anions migrate on a more direct path than the water.

Another radioisotope of great interest was iodine-129. Because of its biological activity and lack of sorption on most minerals, this radioisotope is considered a particular hazard. A method was devised, using neutron activation followed by counting of the iodine-130 product, that measured the aqueous concentration of iodine-129. Significantly, water from the cavity region had an iodine-129 concentration that was at least a factor of five lower than that recommended for drinking water in uncontrolled areas.

Iodine-129 was also detected in water drawn to the satellite well—at concentrations 5000 times lower than in the cavity water. These data are also plotted in Fig. 4. Fluctuations in the low concentrations make it difficult to determine a maximum; however, iodine-129 appeared to arrive at the satellite well at about the same time as the tritium. If iodine was present as an anionic species, its arrival and peak, like those of chlorine-36, should have preceded tritium's. Examination of the complex behavior of iodine in dilute solutions offers a possible explanation: for the pH and oxygen content of Cambric water, iodine may exist predominantly as the neutral molecule HIO and thus experience little or no anion exclusion effect.

The only other radioisotopes detected at the satellite well have been krypton-85 and, possibly, minute amounts of ruthenium-106.

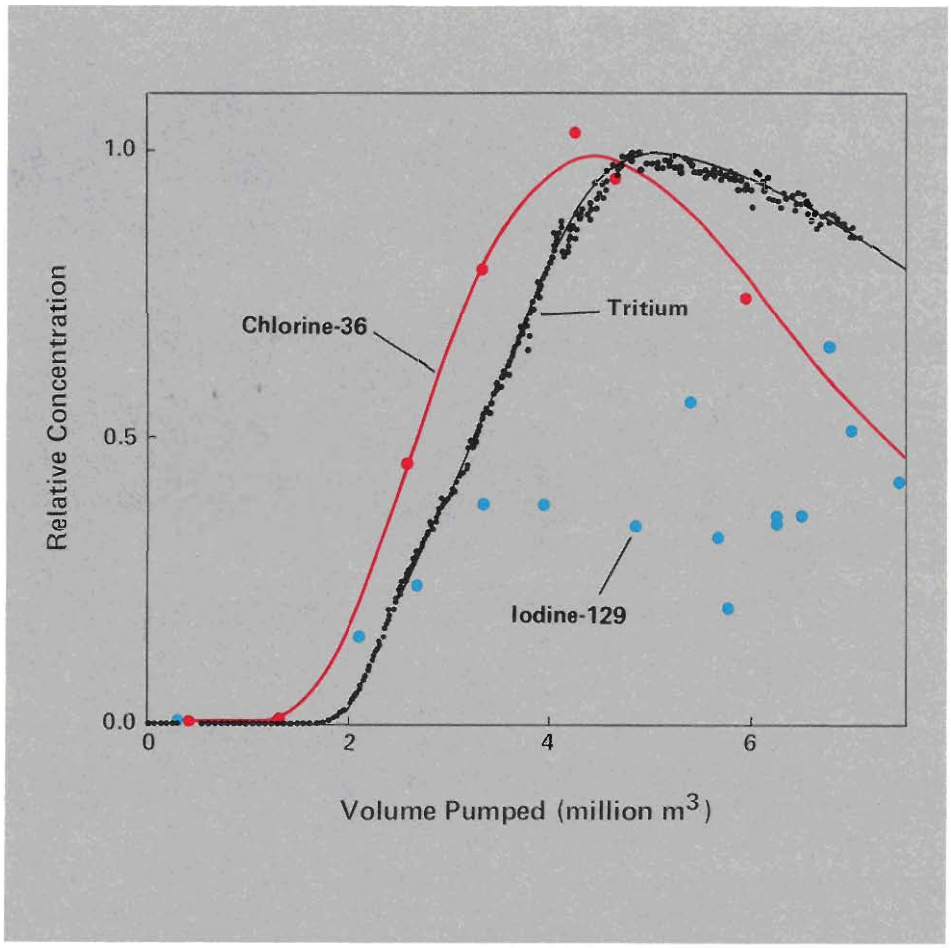


Fig. 4. Migration of radioisotopes from the Cambric cavity. The detection of tritium (black) signaled the arrival of water from the cavity. Concentrations of chlorine-36 (red) arrived earlier and peaked sooner than the tritium, most likely because of repulsion between the negative chloride ions and the negatively charged pore surfaces of the rock. On the other hand, iodine-129 (blue) appeared not to be accelerated by this effect, probably because its dominant species in the groundwater was the neutral molecule HIO. The solid curves are calculated from a model of dispersive fluid flow.

The krypton, dissolved in water, has been arriving with concentrations about one-third as great as expected based on tritium. Because ruthenium-106 has the lowest retention factor (Table I) and a very complex chemistry, it might be expected to migrate in minute amounts.

The main conclusion from the accelerated migration study is that, in general, the sorption of radioisotopes is sufficiently high to preclude the accelerated migration of most radioactive material, particularly cationic species, in the near future. However, pumping and analysis of the water will be continued to investigate the possible arrival of other poorly retarded species.

Migration from a Natural Fission Reactor

A unique opportunity for the study of radioisotope migration presented itself in the mid '70s with the discovery of the remnants of natural fission reactors in the Oklo uranium mines in equatorial Africa. About two billion years ago—nearly half the age of the earth—thick lenses of uraninite were formed that were compact enough and had the right mix of neutron-moderating elements so that fission chain reactions started. The reactors operated for a few hundred thousand years, leaving behind a set of nuclear reaction products different from those normally present in uranium ore.

Several features made the study of these fossil reactors important. The migration or containment occurred over geologic time periods. Radioisotopes present at Oklo were identical to those of modern reactor waste products. The average thermal loading within the reactor zones during operation was estimated to be about 50 watts per square meter, several times greater than the local thermal loadings proposed for reactor waste repositories. Most important, this was an opportunity to quantitatively characterize the migration or retention of more than thirty elements, the products of nuclear fission, neutron capture, and radioactive decay.

Starting in 1974, samples from Oklo were sent to the Laboratory for geochemical and migration studies. It was hoped that by examining various decay-product signatures a fair amount could be learned about which elements migrated, when the migration occurred, and what mechanisms operated to cause the migration.

REACTOR CHARACTERISTICS. Natural uranium consists essentially of two isotopes: the abundant uranium-238 and the fissionable but less abundant uranium-235. The ratio of uranium-235 to uranium-238 has been found to be 0.0072 with only slight variations throughout the world. However, within the thirteen reactor zones so far discovered at Oklo, there were significant deficiencies of uranium-235. Based on the normal ratio of uranium isotopes, it was estimated that about 12,000 kilograms of uranium-235 had fissioned. In fact, the nuclear product inventory at Oklo corresponds to 1 to 2 per cent of the plutonium and fission products and 10 to 20 per cent of the uranium in the United States spent fuel inventory as of 1980.

The rock surrounding the reactor zones is generally pelitic sandstone, a fine-grained sedimentary rock. The uranium is uraninite, a crystalline uranium dioxide. Examination of this mineral revealed crystallites characteristic of those produced by radiation. A correlation between the abundance of these crystallites and the degree of uranium-235 depletion suggested that the grains of uraninite had been thermally and mechanically stable since the reactors started. Also, the discovery of uranium samples with quite different degrees of depletion located within a few tens of centimeters of each other clearly showed that the uranium had not been chemically homogenized in the 2 billion years since the reactor operated.

The two uranium isotopes decay ultimately to different stable lead isotopes at different rates. This fact is frequently used to date rocks, and in this case analysis of uranium and lead isotopes showed that uranium mineralization occurred 2 billion years ago. Likewise, analysis of the uranium fuel and the fission product neodymium indicated that the reactors became critical very soon after mineralization.

What were these zones like during the time of reactor criticality? Neutron fluences were as high as 10^{21} neutrons per square centimeter, a remarkably high fluence. Water in the rock was the most likely neutron moderator for the reactors, and this water, heated by the fission energy, generated hot aqueous solutions that circulated convectively through the rock. In fact, fluid inclusions in mineral grains formed at temperatures between 450 and 600 degrees Celsius have been found up to 30 meters from the reactor zones. Much of the unique physical character of the rock surrounding the reactors can be attributed to the dissolution and modification of minerals from heat and radiation and the chemical redistribution associated with circulating hydrothermal fluids.

FRACTIONATION. The isotopic composition in the reactor zones can be visualized as two components: a natural component found in materials throughout the earth and a nuclear component generated by the various nuclear processes. Total isotopic abundances were measured in the Oklo samples by mass spectrometric techniques and the natural component was then subtracted. The nuclear component remaining was compared to the predicted abundance resulting from nuclear reactions. Any difference, that is, any loss or gain for a given isotope, was indicative of migration.

Of particular interest was the evidence for fractionation between technetium and ruthenium. Technetium does not occur naturally on the earth in significant quantities, but the Oklo reactors generated approximately 730 kilograms of technetium-99. This isotope is of special concern in the storage of radioactive wastes because its 0.2 million year half-life implies storage times on the order of millions of years.

Natural ruthenium is composed of seven isotopes. These can be split into three groups depending on the relationship of each isotope to the fission process (Figs. 5 and 6). Three isotopes, the "natural-only" isotopes (96, 98, and 100), are not produced by fission. Knowing the amounts of these allows the natural component of all seven to be easily accounted for. Another three, the "instantaneous" isotopes of ruthenium (101, 102, and 104), are produced by the decay of short-lived technetium fission products. Amounts of these isotopes were generated while the reactors were operating. The last is

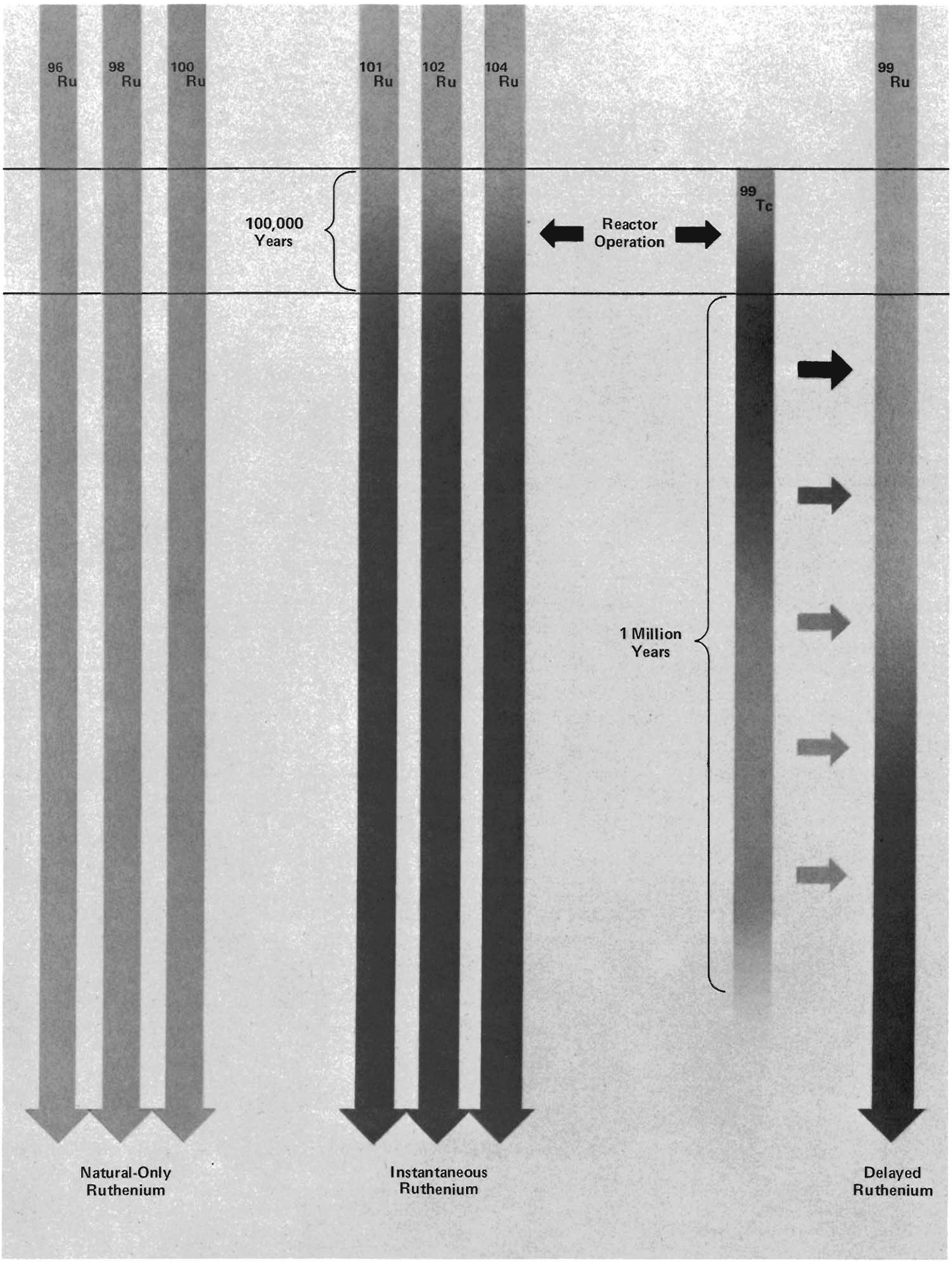

96 Ru
98 Ru
100 Ru
101 Ru
102 Ru
104 Ru
99 Ru
99 Tc
100,000 Years
Reactor Operation
1 Million Years
Natural-Only Ruthenium
Instantaneous Ruthenium
Delayed Ruthenium

Fig. 5. Ruthenium isotopes and their relationship to the Oklo reactor. The three "natural-only" isotopes on the left were not produced by any of the fission reactions and thus remained at their original concentrations except as modified by neutron-capture reactions. Fission reactions increased the concentrations of the three "instantaneous" isotopes during the 100,000 years of reactor operation. Because these isotopes are stable, their concentrations remained constant after reactor shutdown. Ruthenium-99, the "delayed" isotope, was produced by the gradual decay of reactor-generated technetium-99. The half-life of technetium-99 is 0.2 million years so that about 96 per cent changed to ruthenium-99 during the first million years after shutdown.

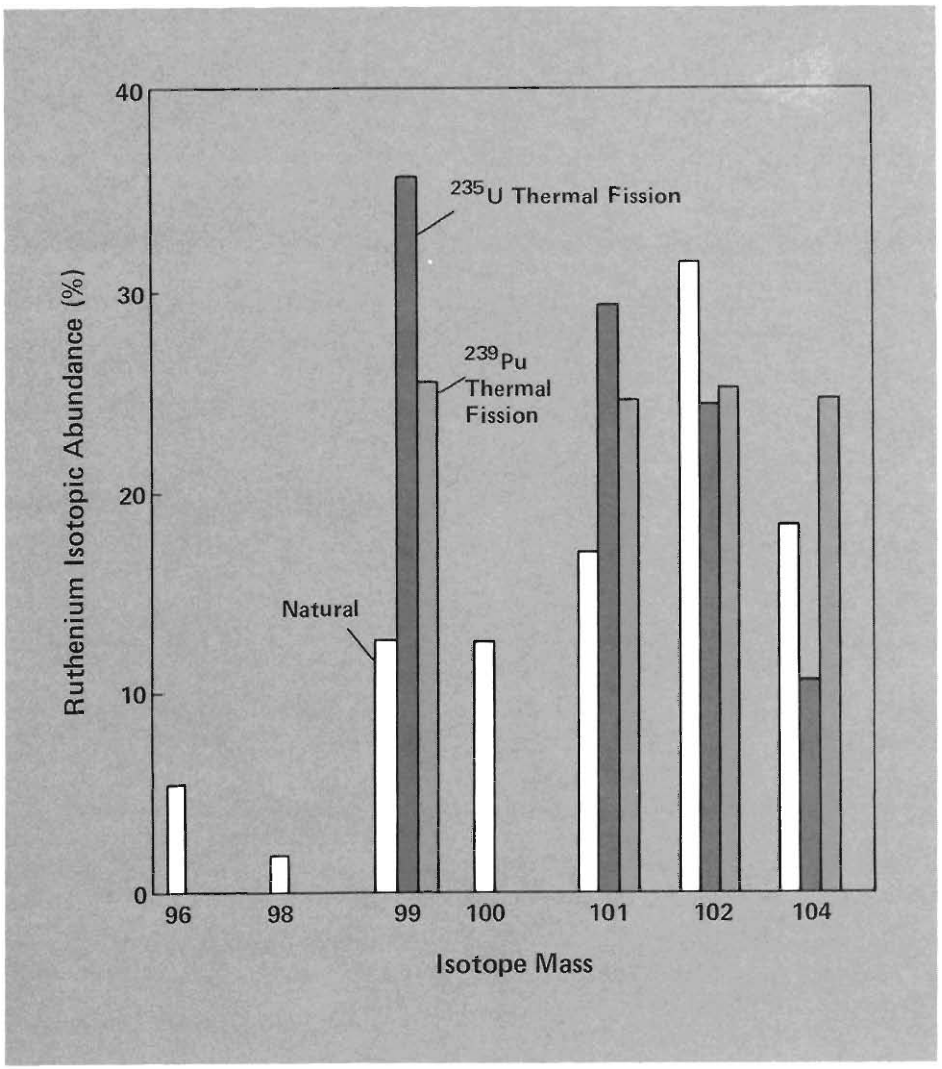


Fig. 6. Relative abundances of ruthenium isotopes in normal rock (white) and, likewise, as generated by the thermal-neutron-induced fission of uranium-235 (black) and of plutonium-239 (grey). Samples from the Oklo reactor zones usually contained ruthenium with the isotopic composition of the uranium-235 fission process; however, a few per cent of the fissions took place in plutonium-239 that had been produced from uranium-238 by neutron capture and subsequent beta decay. Samples from the periphery contained various proportions of natural and fission-generated ruthenium. Natural ruthenium was easily corrected for in a given sample using ratios based on abundances of the natural-only isotopes (96, 98, or 100).

the "delayed" isotope ruthenium-99, which, because it is the decay product of technetium-99, serves as a marker for fission-generated technetium. Any fractionation that separates ruthenium and technetium before technetium-99 decays would be observed today as a depletion or enrichment of delayed ruthenium relative to instantaneous ruthenium.

A detailed analysis based on the ideas only briefly outlined here showed that technetium-ruthenium fractionation had indeed occurred at the Oklo reactors. In fact, the half-life of technetium-99 places an upper limit on the time between reactor shutdown and fractionation. The basic conclusion was that chemical or physical processes caused technetium to be lost in greater abundance than ruthenium from the reactor zones at some time less than a million years after reactor shutdown. Analysis of samples from outside the reactor zones showed that the lost technetium (as well as other lost fission products) were contained within a few tens of meters of their source.

TRANSPORT MECHANISM. How were technetium and other elements carried out of the reactor zones? One clue was the physical distribution of technetium (now ruthenium-99). Generally, the direction of movement of this isotope was upward, consistent with convecting hydrothermal fluids as the carrier.

To examine this feature in more detail, it was postulated that the insoluble oxides of ruthenium and technetium were further oxidized to form soluble oxyion complexes (Table II). Because virtually nothing is known about the chemical conditions at Oklo during the thermal period, only this simple case of oxyions was considered. A pH and oxygen content typical of the reactor geology were assumed, and thermodynamic data were used to calculate the solubilities of the species as a function of temperature. As can be seen in Fig. 7, the solubilities vary

TABLE II

OXIDATION TO SOLUBLE OXYIONS

Insoluble		Soluble
RuO_2	→	RuO_4^{-2}
RuO_2	→	$Ru(OH)_2^{+2}$
TcO_2	→	TcO_4^-

widely (encompassing 50 orders of magnitude). The band in Fig. 7 around 10^{-10} moles per liter represents estimates of the concentrations of technetium, ruthenium, and neodymium in the aqueous fluid at Oklo. The width of the band is the uncertainty in the estimates. Also included is the solubility curve for the neodymium cation, which is retrograde.

Examination of Fig. 7 shows that at some temperature the thermodynamically controlled solubilities of neodymium, technetium, and ruthenium fall within the concentration band. Above the band, the solubility would cause the transport away of too much material, and below the band, of too little. However, this conjunction occurs at *different* temperatures for each species. RuO_4^{-2} will achieve the necessary solubility in the vicinity of 350 degrees Celsius, TcO_4^- around 150 degrees. Because of its retrograde solubility, neodymium achieves the necessary solubility *below* 25 degrees Celsius. The solubility temperature ranges for ruthenium and technetium agree with temperatures estimated for the reactor zone during its thermal period. Thus, the transport of ions by convecting hydrothermal fluids can account for the deficiency of these two elements but not for that of neodymium.

But there is a further complication. If the fluid temperature was 150 degrees Celsius, just hot enough to remove the appropriate quantity of technetium, then neither

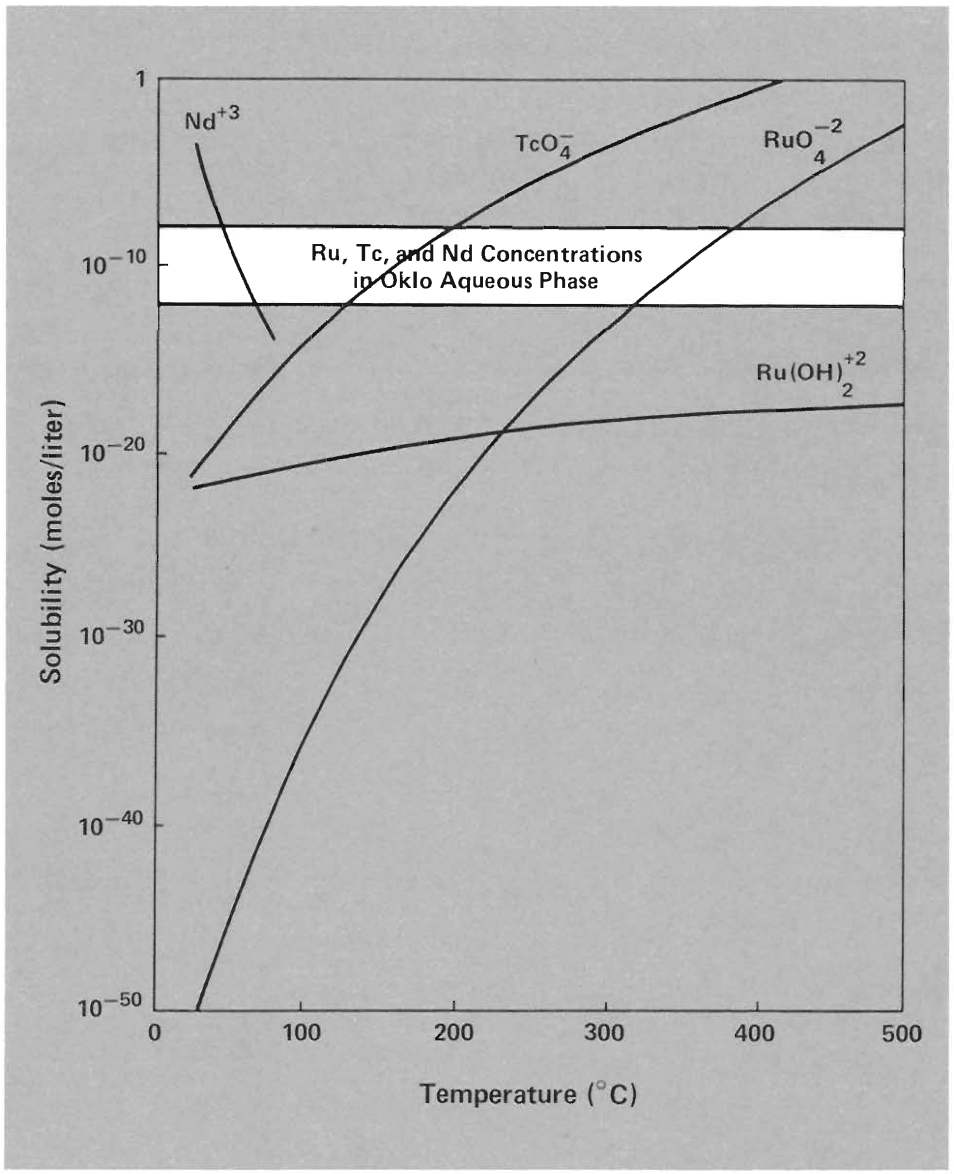


Fig. 7. The temperature dependence of the equilibrium solubilities for various ionic species of ruthenium, technetium, and neodymium. The range of estimated concentrations of these three elements in the groundwater at Oklo is superimposed on the diagram as the horizontal band centered at 10^{-10} moles per liter. Solubilities within this band indicate chemical processes and conditions that could have removed elements from the reactor zones at the appropriate rate. Solubilities above the band may have also occurred if other processes limited the rate of dissolution. The fact that $Ru(OH)_2^{+2}$ never intersects the estimated concentration band suggests that the dissolution of tetravalent RuO_2 was not a factor in the transport of ruthenium. (Uncertainty ranges for the solubility curves have been eliminated for clarity.)

ruthenium nor neodymium would have been transported away. On the other hand, if the fluid temperature was 350 degrees, hot enough to remove the necessary quantities of ruthenium, the solubility for TcO_4^- would have been so high that *all* the technetium would be gone. Since roughly equal quantities of each were removed from the reactor zone, it is likely that the rate of migration was controlled by diffusion of each element from the host mineral rather than by subsequent transport away from it as determined by the solubilities.

The retrograde solubility of neodymium suggests that it was redistributed after the thermal period. The fact that it appears to have been redistributed on a smaller scale than ruthenium or technetium agrees with this suggestion.

Although ruthenium and technetium migrated during the thermal period of the reactor, the overall transport was relatively insignificant. These elements were transported only a few tens of meters within a million years after reactor operation. Rates of transport were thus on the order of 10^{-5} meters per year whereas fluid movement could have been up to 5 meters per year. In other words, the pelitic sandstones surrounding the reactors had a remarkable ability to contain these nuclear products even after they were released from the uraninite. The extreme temperature dependence of the solubilities suggests a suitable mechanism for this retention capacity. As the fluids left the hot reactor zones and began to cool, they became supersaturated with respect to the ruthenium and technetium oxyions, and their reduced form could have been deposited in the rocks adjacent to the hot regions. If this mechanism is correct, aureoles reflecting temperature profiles around the hot zones should be found. That is, supersaturation for RuO_4^{-2} occurs around 200 degrees higher than for TcO_4^-, and ruthenium should be found closer to the reactors than technetium. This temperature dependence may also help explain the apparent fractionation of ruthenium and technetium during the thermal period.

In general, our studies have revealed the broad outline of a possible mechanism for the geochemistry of the Oklo reactors. Much work remains before the details are understood. However, the possibility of long-term storage of radioactive waste in underground sites has certainly been demonstrated by the existence of these natural reactors.

Nuclear Waste Storage

The National Waste Terminal program, initiated in 1976 and presently directed by DOE, is investigating several sites as potential repositories for high-level nuclear waste. One of these, Yucca Mountain, is located near the southwest corner of the Nevada Test Site and is being studied jointly by the Los Alamos, Sandia, and Lawrence Livermore National Laboratories and the U.S. Geological Survey. Our role in the research at this site is to develop part of the scientific base to be used in deciding whether Yucca Mountain will be appropriate as a repository.

Such a determination necessarily involves a wide range of studies. Rock samples at various depths to 6000 feet need to be analyzed for thermal and mechanical properties, porosity, permeability, extent of fractures, mineral composition, sorption properties for different elements, and so forth. The water there is very mild, containing mostly low concentrations of sodium and bicarbonate ions. Nevertheless, its physical and chemical properties, such as the amounts of dissolved oxygen, organic material, microorganisms, and other constituents that might effect migration, must be evaluated. One of the most important tasks is the realistic modeling of the geochemistry so that predictions can be made with confidence. Here we will discuss only a couple of examples to illustrate the link between laboratory or field experiments and model development.

RETARDATION. The rock underlying Yucca Mountain is primarily welded and nonwelded tuff, which are volcanic materials. Welded tuff is hard, dense, and has excellent thermal properties. Nonwelded tuff below the water table there contains large amounts of clay and zeolitic minerals, and the rock is highly porous but impermeable. In fact, this latter rock can hold an average of 25 per cent water by volume. Radioisotopes in the flowing water in fractures can diffuse into the rock matrix and be trapped in the static water or be sorbed on pore walls. Retardation describes the group of processes that, through interactions with rock, remove elements from solution in moving water and is an important parameter to measure and model.

A variety of experimental techniques have been used on Yucca Mountain tuff to measure sorption, an important process in retardation. They include the batch process on either crushed rock or tablets of whole rock, flow through columns of crushed material, continuous circulation of groundwater through crushed material, and radioisotope transport through cylinders or blocks of rock that contain real or artificial features. Quite similar sorption parameters are obtained for all these techniques if care is taken in both experimental procedure and in proper mathematical interpretation of the measurements.

For example, Fig. 8 shows batch sorption data for cesium as a function of depth in a series of layered volcanic materials. Although the sorption ratio can easily be experimentally reproduced within a range of 20 per cent, it varies with depth by more than two orders of magnitude, depending on the mineral composition of each sample.

The principal phases that aid in sorption and cause the dramatic changes in Fig. 8 include hydrated volcanic glasses, smectite clays, and zeolites. The glasses are the least important for sorption, but they are very reactive and can alter to other minerals with changes in hydration if heated in the presence of water. Smectite clays are reversibly

expandable with highly sorptive properties, although the properties can be modified in a detrimental way by prolonged exposure to heat. Zeolites, with their open lattice structure, are the most highly sorptive minerals.

Because tuff samples may be composed of several sorbing minerals, we are currently developing ways to predict sorption ratios by combining the effects of several minerals. One approach uses the sorptive mineral content, or *SMC*, a weighted sum defined by

$$SMC = \sum W_i X_i \ ,$$

where W_i is the weighting factor for each mineral phase and X_i is the per cent abundance of each phase.

Figure 9 demonstrates the results of this approach for the cesium sorption data. Weighting factors were determined relative to a zeolite, clinoptilolite, by directly measuring the sorption of cesium on pure minerals or by inferring it from measurements with mixtures. The resulting values are plotted in Fig. 9 along with the theoretical relationship (solid line) based on thermodynamic data. Note that almost all the data lie within the envelope (dashed lines) for an uncertainty factor of 3. Procedures similar to this should eventually allow us to predict sorptive properties for the tuffs along pathways to the environment. However, sorption of cesium is probably the simplest test of this concept. Any such procedure is critically dependent upon accurate determination of the mineral phases available to the groundwater.

KINETICS OF SORPTION. Another aspect that must be understood before an adequate transport model can be developed is the kinetics of sorption. This is especially true of tuff because its high porosity makes diffusion of waste elements into the rock matrix a very significant retardation process for radioisotopes.

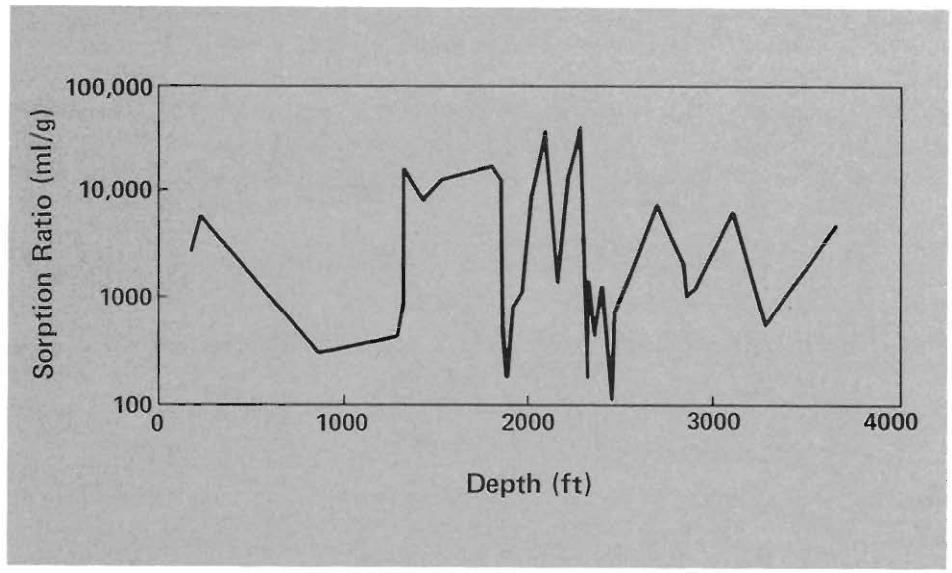


Fig. 8. The sorption ratio for cesium as a function of depth into earth. Because the rock at the Yucca Mountain site is made up of series of layers of volcanic material, each with its own mix of minerals, the sorption of cesium varies dramatically. Experimental reproducibility of the data shown here is about 20 per cent.

Figure 10 shows the sorption of strontium onto a sample of tuff as a function of time (circles). Three types of fits were made to the data. The first and least successful, labeled simple diffusion, is based on diffusion into a plane sheet. In this case the equilibrium concentration of strontium between the grain surfaces and the pore water, defined by the sorption parameters, is reached instantaneously and sorption is treated as being linear with concentration. However, the number of available sorption sites may be limited so that at higher concentrations sorption eventually drops below the linear curve. This nonlinearity complicates the diffusion equations by giving the diffusion coefficient a concentration dependence. A finite-difference solution of the nonlinear diffusion problem was made and is also plotted in Fig. 10. The agreement with experimental data is better in this case but still does not reproduce the early time points. Attempts to adjust the

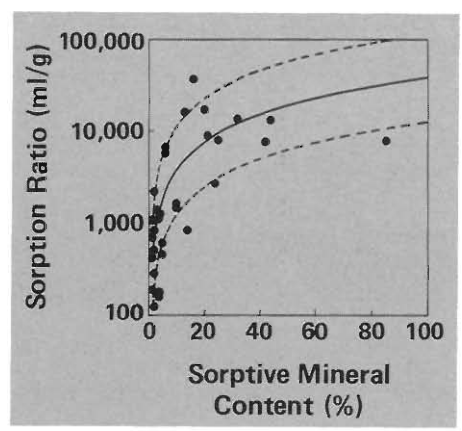
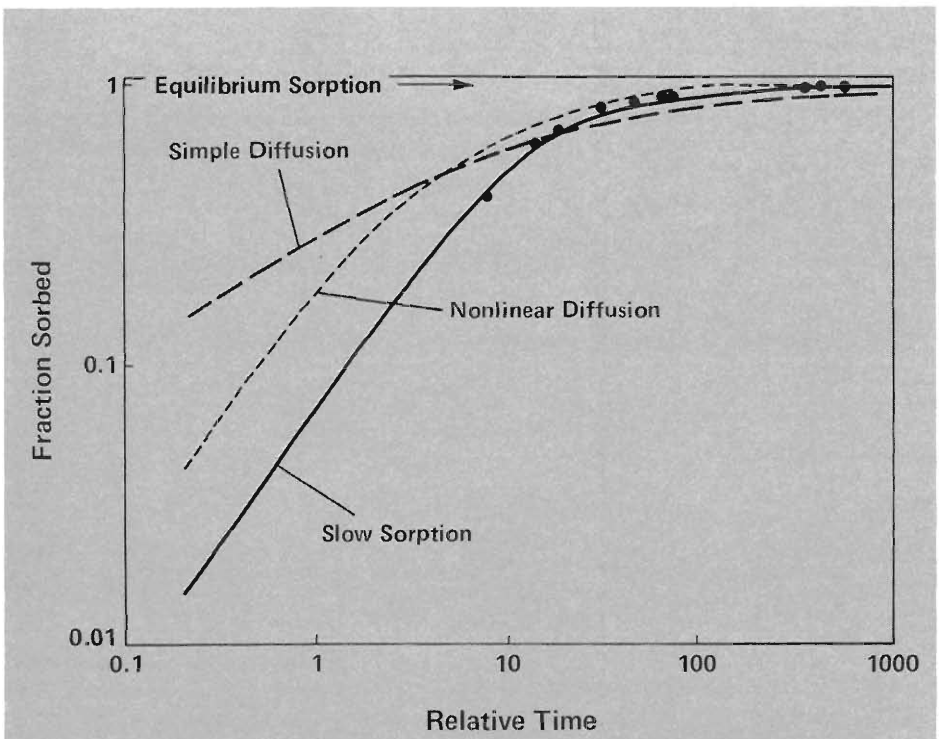


Fig. 9. Sorption ratios for cesium are here plotted as a function of sorptive mineral content (SMC), a parameter that weights the sorptive qualities of each mineral in a sample. The solid line is calculated from thermodynamic parameters; the dashed lines indicate an uncertainty factor of ±3.



MODEL EQUATIONS

Simple Diffusion

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \qquad D = \text{constant}$$

Nonlinear Diffusion

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \qquad D = f(C)$$

Slow Sorption

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - \frac{\partial S}{\partial t}, \quad \frac{\partial S}{\partial t} = \lambda C - \mu S$$

C = concentration in solution
D = apparent diffusion coefficient
S = concentration of immobilized solute
λ, μ = rate constants

Fig. 10. Modeling the kinetics of sorption of strontium on tuff. The fraction of strontium sorbed on the rock approaches equilibrium amounts as relative time increases (relative time is Dt/L^2 *where* D *is the apparent diffusion coefficient for the material and* L *equals half the sample thickness). Simple diffusion involves a constant diffusion coefficient, whereas nonlinear diffusion involves a concentration-dependent coefficient. The best fit is achieved with a slow sorption model that includes a reversible immobilization of part of the material in the rock matrix.*

fit led to values for the adjustable parameters that were not consistent with other data.

The third type of fit, labeled slow sorption in Fig. 10, is like the first model except that the equilibrium concentration between grain surfaces and pore water is not reached instantaneously. The process was considered to be a reversible reaction with the solid tuff in which part of the dissolved species is free to diffuse within the material and part is immobilized in the tuff. Mathematically, a term representing the rate of removal of the immobolized component was subtracted from the simple diffusion equation. The agreement between the data and the shape of the curve based on this approach was quite good. Moreover, the parameters determined from the best fit agreed with other data.

The consequences of these kinetic studies may be profound for migration of waste in which the radioisotopes are carried by rapidly moving water in fractures. The sorption rate constants determined by us will be used in calculations with the nonequilibrium version of our three-dimensional transport code (TRACR3D) to model the results of flow in fractured rock. Our models are becoming detailed enough so that we can extrapolate from the short time scales of laboratory experiments to the long time scales required for storage of nuclear waste.

In general, our studies of the geochemistry of the Yucca Mountain site, although far from complete, so far indicate that the geochemical properties and setting of the site will strongly inhibit the movement of radioisotopes by flowing groundwater to the accessible environment.

We have discussed examples from three areas in the study of radioisotope migration. There are many more published examples of such Los Alamos studies, and there are considerable possibilities for future investigations. The field remains vital and exciting because these radioisotopes act as tracers, illuminating processes generally hidden from us by complexity and by time in the earth's crust. ■

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Many people from the Isotope and Nuclear Chemistry Division have contributed to the work described in this article. Those pictured above are: Tim Benjamin, Ernie Bryant, John Cappis, Dave Curtis, Clarence Duffy, Alex Gancarz, Darleane Hoffman, Ed Norris, Al Ogard, Jim Sattizahn, and Kurt Wolfsberg. Others, who weren't available for the photograph, are Bill Daniels, Bruce Erdal, Bob Rundberg, and Rosemary Vidale.