

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 volatility. 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 volatility, 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. Geologi-

cal 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} , $\text{Zn}(\text{HS})_3^{-}$, and HgS_7^{-2} , that increase the metal's volatility. For other conditions the anions do the opposite and form insoluble compounds, such as CaCO_3 , MgSO_4 , HgCl , or $\text{Th}_3(\text{PO}_4)_4$.

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 be-

cause 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 results 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 Cambrian 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 Cambrian 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 Cambrian 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-