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THE POTENTIAL USE OF RADIOACTIVE DECAY PRODUCTS FOR DATING GROUNDWATER

by

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ABSTRACT*

The accumulation in groundwater of products from the radioactive decay of elements naturally found in rocks offers a potential for measuring the time that the groundwater has been in contact with the rock. This method of dating groundwater has an advantage over using decay products from the atmosphere in that the amount of decay product becomes greater with increasing age rather than less. However, different decay products accumulate at different rates and, thus, have a different potential usefulness in age determinations.

The most useful decay product is helium, produced from uranium and thorium. Argon produced from potassium is marginally useful for very old water. Neon, xenon, and krypton are probably not useful because they are produced in extremely small quantities. In general, the potential for error increases when a long time to produce a small quantity is required.

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INTRODUCTION

The "age" of groundwater can be defined as the length of time that the water has been out of contact with the atmosphere. On March 16-18, 1978, a workshop was held in Tucson, Arizona, on methods which might be used to date very old groundwater (Davis, 1978). This workshop was sponsored by the U.S. Department of Energy, whose interest was in methods to evaluate the safety of proposed subsurface repositories for nuclear waste. The age of groundwater is a critical aspect of such an evaluation because it gives an indication of past rates of water movement, which in turn will help evaluate the likelihood of future migration of radionuclides from a given repository.

At this conference six methods of estimating the age were enumerated.

1. Hydraulic Methods use the hydraulic gradient, fluid conductivities, effective porosities, and Darcy's Law and related equations to estimate the velocity and, thus, the total travel time.
2. Geologic History such as previous stands of the ocean or a hot, cold, dry, or wet climate may leave a trace on the groundwater such as distinctive isotopic ratios or dissolved solids content.

3. Atmospheric Radionuclides that decay after entering the ground include tritium and carbon-14, isotopes commonly used in today's

dating methods. Other possibilities exist for determining much older ages by using chlorine-36 or krypton-81.

4. Decay Products of some radionuclides begin to accumulate after the water comes in contact with rocks. These accumulated decay products increase in concentration as the water becomes older as opposed to atmospheric radionuclides which decrease as the water becomes older.
5. Structural Molecular Changes of dissolved material, such as amino acids, in the groundwater might be useful indicators of water age.
6. Radionuclide Disequilibrium between parent and daughter elements, as has been applied to uranium-234/uranium-238, may be an index to groundwater age.

This paper focuses on Decay Products (4) and carries out one recommendation of the Tucson conference, namely to evaluate the potential usefulness of the noble gases for dating groundwater.

PRINCIPLES

Natural precipitation is virtually devoid of the decay products of uranium, thorium, or potassium. This water recharges the ground and flows with the groundwater. Because uranium, thorium, and potassium are nearly ubiquitous in rocks and undergo continual radioactive decay, the decay products are generated continuously within the rock. Some of the decay products will be retained by the rock, but some will enter the groundwater. If the generation rate of the decay product and the parent radionuclide element content of the rock are known, then a minimum residence time for the water to be in contact with this type of rock can be calculated from the amount of decay product present in the water.

The principal assumption involved in this calculation is that the transfer rate of the decay product from the rock to the water is the same as the generation rate. For a hydrologic system subject to new conditions, such as initial saturation or a radical change in salinity, this assumption may be suspect. However, if the hydrogeological history of the region shows that the groundwater system has not undergone significant change, the release rate of the decay products from the rock to the water may have reached a steady state that is proportional to its generation rate.

To the extent that the decay product continues to accumulate in the rock-forming minerals or diffuses through the rock and is lost to the atmosphere, the water may be older than the age calculated. To the extent that the decay product migrates into the aquifer of interest from deeper zones in the earth, the calculated age may be too old. Independent hydrogeological knowledge of the groundwater system is obviously required for this method of dating, as it is with all other methods.

Another assumption required for using decay product dating of groundwater is that the parent element content of the rock be known along the entire flow path. To the extent that the geology is relatively homogeneous over the flow path, this is not a complicating assumption. Even if the geology is unknown, minimum ages can be calculated from literature on assumed parent element contents of rock.

Helium, a decay product from uranium and thorium, has been used to date water in crystalline rock beneath the Coastal Plain (Marine, 1976, 1979), but other decay products are not known to have been used.

USEFUL DECAY PRODUCTS

One of the suggestions of the Tucson meeting (Davis, 1978) was that the usefulness of various decay products should be evaluated in terms of their generation rates. The noble gases are particularly useful for this purpose in that they are nonreactive with earth materials. A preliminary list of isotopes that might be useful includes helium, xenon, krypton, neon, and argon. The purpose of the present paper is to evaluate the potential usefulness of these decay products in terms of quantity produced. No discussion is presented on the transfer of the accumulated products to the surrounding groundwater.

Uranium and thorium are nearly always present in rocks. ^{238}U, ^{235}U, and ^{232}Th decay by α-emission leading to the formation of ^{4}He.

A very small fraction of the uranium and thorium disintegrations occurs by spontaneous fissions that yield fission products including neutrons. The neutrons are absorbed by certain constituents of the rocks to form activation products. In a relatively small fraction of the alpha decays, the α-particle interacts (α, n) with light elements such as ^{18}O and ^{19}F to for additional neutrons and two isotopes of neon. ^{40}Ar is formed by decay of the long-lived radioisotope ^{40}K, a minor constituent of natural potassium.

Production of ^{4}He

The present composition of natural uranium is 99.3% ^{238}U and 0.7% ^{235}U. Eventually, ^{238}U decays to stable ^{206}Pb with a half life ($T_{1/2}$) of 4.51×10^9 yr (Lederer and others, 1967) and the emission of eight alpha particles; ^{235}U decays to stable ^{207}Pb with a $T_{1/2}$ of 7.1×10^8 yr and the emission of seven α-particles. ^{232}Th decays to stable ^{208}Pb with a $T_{1/2}$ of 1.41×10^{10} yr with the emission of six α-particles. The ultimate fate of the vast majority of the α-particles (He^{++} ions) is conversion to neutral ^{4}He atoms by the capture of two electrons. ^{4}He is formed continually from the time of original formation of the rock.

The number of ^{4}He atoms formed as a function of time can be expressed as follows:

For ^{232}Th: ^{4}He atoms = $6\ N_o\ (1-e^{-\lambda_{232}t})$

^{235}U: ^{4}He atoms = $7\ N_o\ (1-e^{-\lambda_{235}t})$

^{238}U: ^{4}He atoms = $8\ N_o\ (1-e^{-\lambda_{238}t})$

Where N_o is the original number of atoms and the λ's are the radioactive decay constants (4.91×10^{-11}/yr for ^{232}Th, 9.76×10^{-10}/yr for ^{235}U, and 1.54×10^{-10}/yr for ^{238}U). Time t is in years. Under the assumption that the time of decay (perhaps up to 3×10^8 yr) is short compared with the half-lives involved, the $(1-e^{-\lambda t})$ term can be replaced by λt. This assumption is strictly valid for ^{232}Th and ^{238}U, but a small correction would be necessary for ^{235}U at long decay times. Because of the low abundance of ^{235}U in natural uranium, however, the correction can be ignored without any significant error being introduced.

Conversion of the He atoms to microliters (μL) of ^{4}He gas at STP yields the following rates of formation of ^{4}He:

^{232}Th: 2.84×10^{-5} μL/(yr)(g Th)

Natural U: 1.20×10^{-4} μL/(yr)(g U)

Accumulation of ^{4}He from decay of natural uranium and ^{232}Th is plotted in Figure 1 as a function of decay time. The quantity of ^{4}He produced would be the sum from both sources. Actual quantities expected from a given rock can be calculated from the percent of uranium or thorium in the rock.

Production of ^{21}Ne and ^{22}Ne

One of about every 10^6 α-particles interacts with light elements in the rock matrix to form another isotope with the emission of a neutron. Two such reactions that produce ^{21}Ne and ^{22}Ne are

$^{18}O\ (\alpha,\ n)^{21}Ne$ and

$^{19}F\ (\alpha,\ n)^{22}Na \xrightarrow{\beta+} {}^{22}Ne$

The neon isotopes are stable and are produced in quantities of about one millionth of the ^{4}He formed. The principal isotope of atmospheric neon is ^{20}Ne (90.5%) (Chart of the Nuclides, 1972). The significant aspect of neon produced as the result of radioactive decay is that no ^{20}Ne should be formed. (The absence of ^{20}Ne would indicate no atmospheric contamination of the neon sample from the rock.) Estimated quantities of neon accumulated as a function of time are plotted also in Figure 1 (per g U).

Production of Isotopes of Xe and Kr

Several isotopes of Xe (^{131}Xe, ^{132}Xe, ^{134}Xe, and ^{136}Xe) and Kr (^{85}Kr, ^{86}Kr, and ^{86}Kr) are formed as fission products in the spontaneous fissioning of ^{238}U, ^{235}U, and ^{232}Th. Spontaneous fission half-lives are 1.9×10^{17} yr for ^{235}U, 6.8×10^{15} yr for ^{238}U, and $>10^{21}$ yr for ^{232}Th. Significant amounts of fission thus would occur only in ^{238}U, and fissioning of ^{235}U and ^{232}Th can essentially be ignored.

Fission yields for the isotopes of xenon and krypton were estimated (Argonne National Laboratory, 1963) and volumes of xenon and krypton per gram of uranium were calculated. Results are plotted on Figure 1. Quantities are very small compared with quantities of ^{4}He. It should be noted that all the xenon and krypton isotopes are stable and that in each case natural xenon and natural krypton contain stable isotopes that are not formed as fission products and thus would not be formed in rocks.

Production of ^{40}Ar

^{40}Ar is the principal constituent (99.59%) of natural argon but is also formed by the decay of ^{40}K, a minor constituent (0.012%) of natural potassium. ^{40}K decays with a half-life of 1.26×10^{9} yr; in 11% of its disintegrations, it decays by electron capture to form ^{40}Ar.

The volume (STP) of ^{40}Ar at STP formed per gram of ^{40}K can be expressed as follows:

$$\mu L\ ^{40}Ar/g\ ^{40}K = (6.16 \times 10^{4})\ (e^{\lambda kt}-1)$$

where λ_k is the decay constant of $^{40}K = 5.50 \times 10^{-10}$/yr.

This ratio of argon produced to potassium present is reduced by a factor of 0.00012 if the amount of ^{40}Ar is expressed as per gram of natural potassium ($^{39}K + {}^{40}K + {}^{41}K$).

Estimates of the amounts of ^{40}Ar as a function of time are shown on Figure 1.

Although the $^{40}Ar/^{40}K$ method is quite useful in dating rocks and minerals, it does not appear useful in dating water. A mineral date by this method requires a closed system, i.e., a mineral grain for which the assumption is valid that no parent nor daughter product has been added or lost. Obviously, where the argon is collected from the water, a closed system cannot be assumed. Because of the very small quantity of ^{40}K in natural potassium (0.012%) and the great abundance of ^{40}Ar in natural argon (99.59%), the amount of ^{40}Ar that originated from decay of ^{40}K is almost impossible to determine.

Production of ^{3}He

Small amounts of ^{3}He can be produced in rocks as an indirect result of radioactive decay. It has been estimated (Rankama, 1963, p. 92) that about 6% of the neutrons liberated in rocks as the result of spontaneous fission or (α, n) reactions result in the formation of ^{3}T which decays to ^{3}He. The amounts of ^{3}He formed are probably insignificant. Calculated ^{3}He to ^{4}He ratios formed from natural uranium and thorium are about 1.2×10^{-7} in each case. The $^{3}He/^{4}He$ ratio in atmospheric helium is about 1.3×10^{-6}.

$^{3}He/^{4}He$ ratios from 10 to 15 times the atmospheric ratio have been found in oceanic basalts and in volcanic gases from Lassen and Yellowstone Parks (Lupton and Craig, 1975; Craig and Lupton, 1976; Craig, Lupton, et al., 1978).

Conclusions

The decay product that appears most promising for dating groundwater is ^{4}He. This element is formed in reasonable quantities by direct α-decay of uranium and thorium. Use of other isotopes for groundwater dating does not appear promising.

Methods using argon, xenon, krypton, and neon entail significant difficulties. All of these elements are formed in smaller quantities than corresponding quantities of ^{4}He. Spontaneous fission half-lives which determine the production of xenon and krypton are very long. Considerable uncertainty in the calculation of ages by use of neon isotopes is introduced because of inaccuracy in predicting how many α-particles react to produce the neon isotopes. Meaningful utilization of any of the decay products discussed here as indicators of age would require the assumption that the elements involved either be absent or their compositions be known at the start of the period of decay. This is not a valid assumption for ^{40}Ar.

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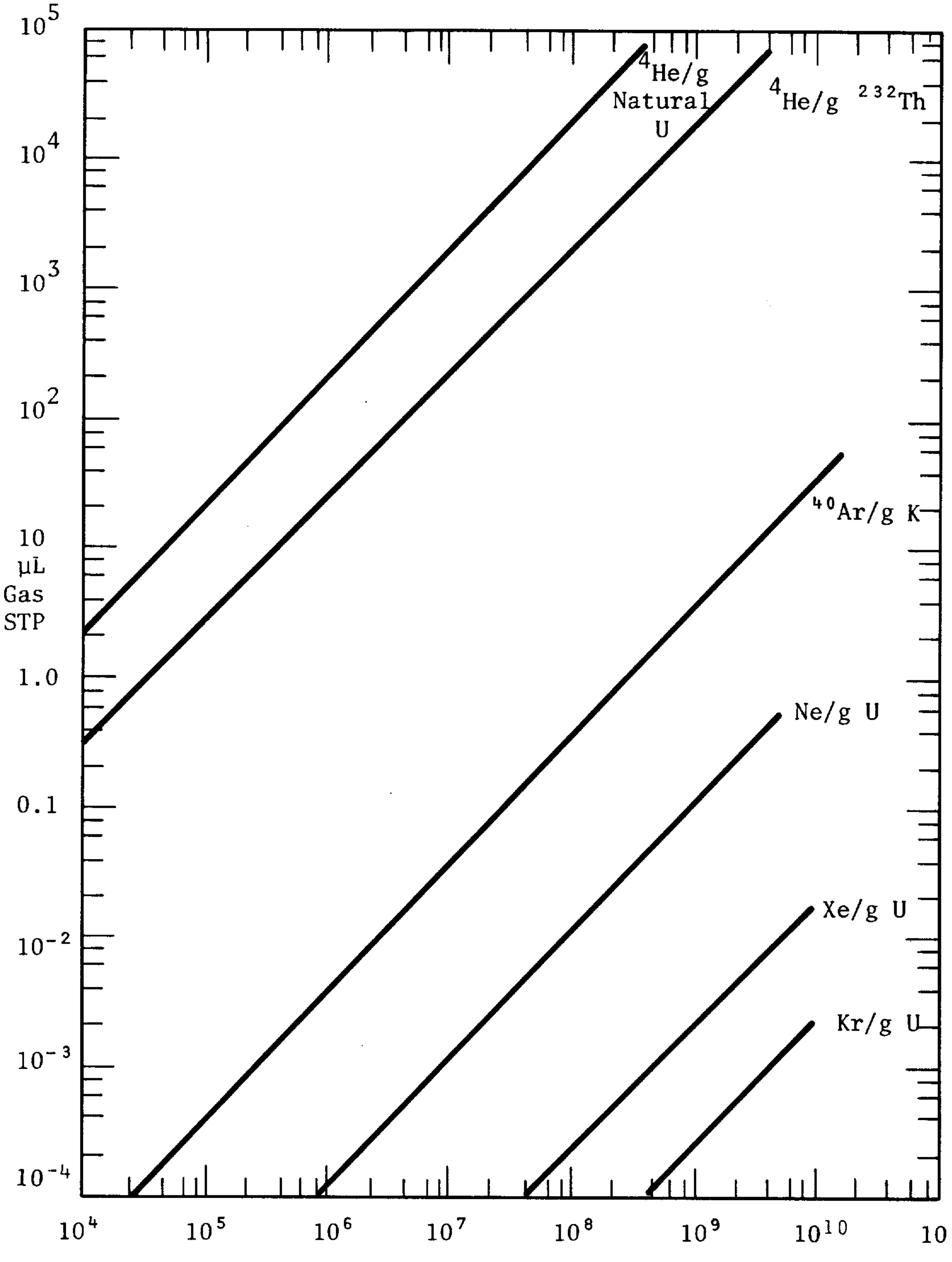

FIGURE 1. Generation of Stable Decay Products as a Function of Time