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THE POTENTIAL FOR DATING GROUND WATER USING RADIOGENIC NOBLE GASES^a

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ABSTRACT

The accumulation in ground water of products from the radioactive decay of elements naturally found in rocks offers a potential for measuring the time that the ground water has been in contact with the rock. This dating method has an advantage over using decay products from the atmosphere in that the amount of decay product increases with age rather than decreases. 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. The use of Ar-40 produced from potassium is limited because Ar-40 is abundant in meteoric water. Neon, xenon, and krypton are useful with great difficulty because they are produced in extremely small quantities. In general, the potential for error increases when a long time is required to produce a small quantity of the dating nuclide.

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INTRODUCTION

The "age" of ground water 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 ground water (Davis, 1978). This workshop was sponsored by the United States Department of Energy, whose interest was in methods to evaluate the safety of proposed subsurface repositories for nuclear waste. The age of ground water 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 ground water, such as distinctive isotopic ratios or dissolved solids content.
3. Atmospheric Radionuclides that decay after entering the ground include tritium and C-14, isotopes commonly used in today's dating methods. Other possibilities exist for determining much older ages by using Cl-36 or Kr-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 ground water might be useful indicators of water age.
6. Radionuclide Disequilibrium between parent and daughter elements, as has been applied to U-234/U-238 may be an index to ground water 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 ground water.

PRINCIPLES

Natural precipitation is virtually devoid of the decay products of uranium, thorium, or potassium. This water recharges the ground and flows with the ground water. 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 ground water. 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 ground-water 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 ground-water 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 ground water 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 the literature based on assumed parent element content of the rock.

Helium, a decay product from uranium and thorium, has been used to date water in crystalline rock beneath the Atlantic Coastal Plain (Marine, 1976, 1979), in outcropping crystalline rock (Fritz and others, 1979) and in Sandstone (Andrews and Lee, 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 dating purposes in that they are non-reactive with earth materials. A preliminary list of elements 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 radiogenic noble gases in terms of the quantity produced. No discussion is presented on the transfer of the accumulated gases from the rock minerals to the surrounding ground water.

Uranium and thorium are nearly always present in rocks. Uranium-238, U-235, and Th-232 decay by alpha emission leading to the formation of He-4. A very small fraction of the uranium and thorium disintegrations occurs by spontaneous fission that yields fission products including isotopes of xenon and krypton. In addition, neutrons are produced which are absorbed by certain constituents of the rocks to form activation products. In a relatively small fraction of the alpha decays, the alpha-particle interacts (α, n) with light elements such as O-18 and F-19 to form

additional neutrons and two isotopes of neon. Argon-40 is formed by decay of the long-lived radioisotope K-40, a minor constituent of natural potassium.

Production of Helium-4

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

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

$$\text{For Th-232: He-4 atoms} = 6 N_0 (1 - e^{-\lambda_{232}t})$$

$$\text{U-235: He-4 atoms} = 7 N_0 (1 - e^{-\lambda_{235}t})$$

$$\text{U-238: He-4 atoms} = 8 N_0 (1 - e^{-\lambda_{238}t})$$

Where N_0 is the original number of atoms and the λ is the radioactive decay constant ($4.91 \times 10^{-11}/\text{yr}$ for Th-232, $9.76 \times 10^{-10}/\text{yr}$ for U-235, and $1.54 \times 10^{-10}/\text{yr}$ for U-238). 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 Th-232 and U-238, but a small correction would be necessary for U-235 at long decay times. Because of the low abundance of U-235 in natural uranium, however, the correction can be ignored without any significant error being introduced.

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

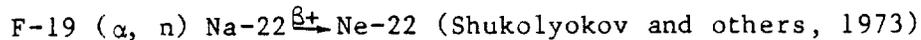
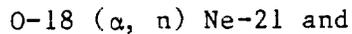
$$\text{Th-232:} \quad 2.84 \times 10^{-5} \mu\text{L}/(\text{yr})(\text{g Th})$$

$$\text{Natural U:} \quad 1.20 \times 10^{-4} \mu\text{L}/(\text{yr})(\text{g U})$$

Accumulation of He-4 from decay of natural uranium and Th-232 is plotted in Figure 1 as a function of decay time. The quantity of He-4 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 Neon-21 and Neon-22

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



The neon isotopes are stable and are produced in quantities of about one millionth of the He-4 formed. The principal isotope of atmospheric neon is Ne-20 (90.5%) (Chart of the Nuclides, 1972).

The significant aspect of neon produced as the result of

radioactive decay is that no Ne-20 should be formed. The absence of Ne-20 would indicate no atmospheric contamination of the neon sample from the rock. On the other hand, the presence of Ne-20 would indicate meteoric water. Estimated quantities of neon accumulated as a function of time are plotted also in Figure 1 (per g U).

Production of Isotopes of Xenon and Krypton

Several isotopes of Xe (Xe-131, Xe-132, Xe-134, and Xe-136) and Kr (Kr-83, Kr-84, and Kr-86) are formed as fission products in the spontaneous fissioning of U-238, U-235, and Th-232. Spontaneous fission half-lives are 1.9×10^{17} yr for U-235, 6.8×10^{15} yr for U-238, and $>10^{21}$ yr for Th-232. Significant amounts of fission thus would occur only in U-238, and fissioning of U-235 and Th-232 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 shown on Figure 1. Quantities are very small compared with quantities of He-4. 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 Argon-40

Argon-40 is the principal constituent (99.59%) of natural argon but is also formed by the decay of K-40, a minor constituent (0.012%) of natural potassium. Potassium-40 decays with a

half-life of 1.26×10^9 yr; in 11% of its disintegrations, it decays by electron capture to form Ar-40.

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

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

where

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

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

Estimates of the amounts of Ar-40 produced per gram of natural potassium as a function of time are shown on Figure 1. The other noble gases shown on Figure 1 are all the results of uranium decay. Thus, the total quantity of each noble gas is in the same ratio as shown on Figure 1 irrespective of the amount of uranium present. Argon, however, is produced from potassium which is about 10,000 times more abundant than uranium (Clark, 1966). Zartman and Wasserberg (1961) estimate that the ratio of radiogenic produced He-4 to Ar-40 is about 7.

Although the Ar-40/K-40 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 K-40 in natural potassium (0.012%) and the great abundance of Ar-40 in natural argon (99.59%), the amount of Ar-40 that originated from decay of K-40 is almost impossible to determine.

Production of Helium-3

Small amounts of He-3 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 tritium which decays to He-3. The amounts of He-3 formed are probably insignificant. Calculated He-3 to He-4 ratios formed from natural uranium and thorium are about 1.2×10^{-7} in each case. The He-3/He-4 ratio in atmospheric helium is about 1.3×10^{-6} .

Helium-3/Helium-4 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 ground water is He-4. This isotope is formed in reasonable quantities by direct alpha-decay of uranium and thorium. Use of other isotopes for ground water dating does not appear promising.

Methods using argon, xenon, krypton, and neon entail significant difficulties. All of these elements except argon are formed in smaller quantities than corresponding quantities of He-4. 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 alpha-particles react to produce the neon isotopes. In general, the potential for error increases when a long time is required to produce a small quantity of the isotope. Meaningful utilization of any of the decay products discussed here as indicators of age would require the assumption that the isotopes involved either be absent or their compositions be known at the start of the period of decay. This is not a valid assumption for Ar-40, which limits the usefulness of Ar-40 for ground water dating.

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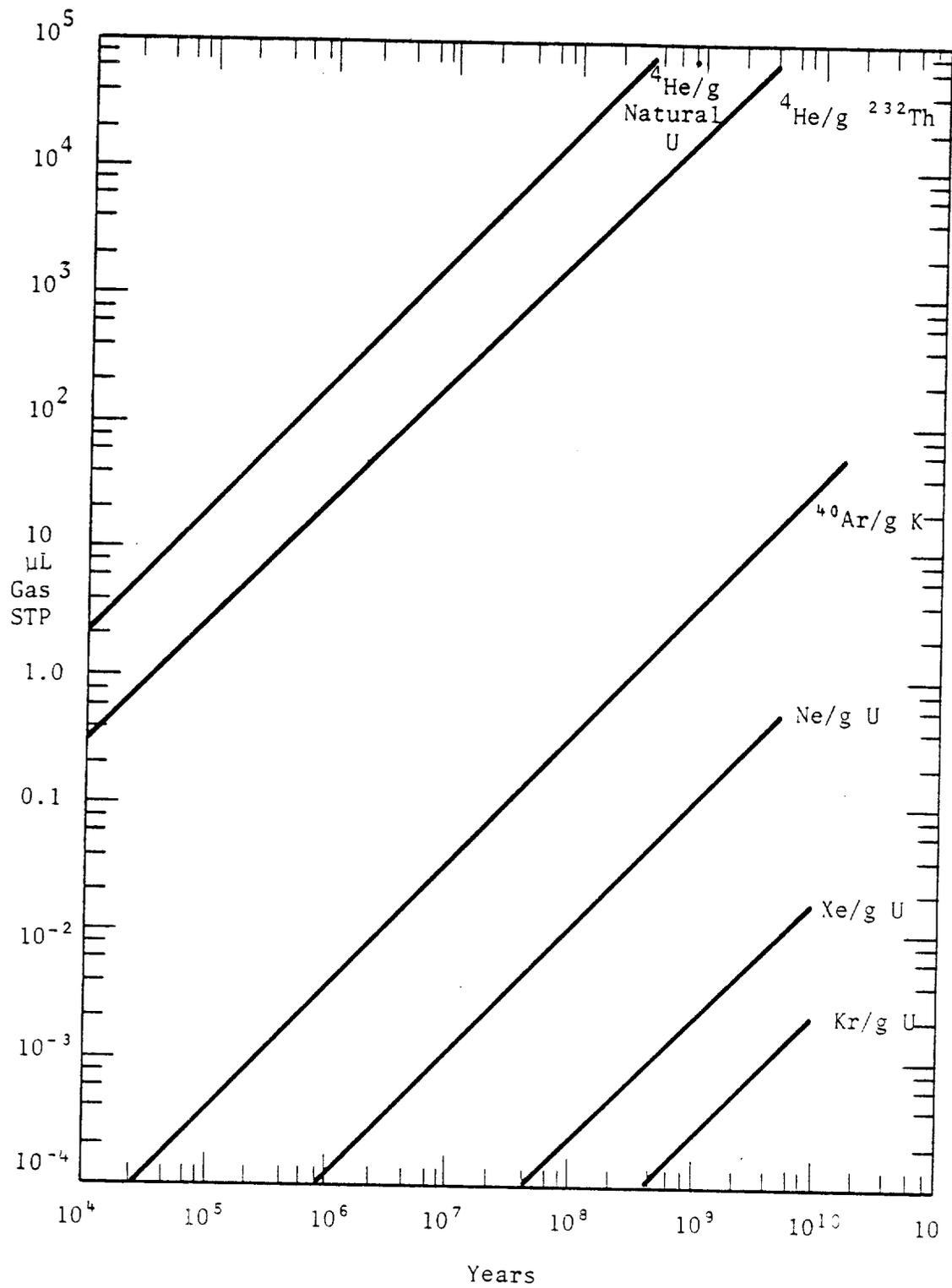


Fig. 1. Generation of Stable Radiogenic Noble Gases as a Function of Time