URANIUM AND TRITIUM AS NATURAL TRACERS IN THE FLORIDAN AQUIFER

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PUBLICATION NO. 14

FLORIDA WATER RESOURCES RESEARCH CENTER

RESEARCH PROJECT TECHNICAL COMPLETION REPORT

OWRR Project Number A-011-FLA

Annual Allotment Agreement Numbers

14-01-0001-1628 (1969)
14-31-0001-3009 (1970)
14-31-0001-3209 (1971)

Report Submitted: August, 1971

The work upon which this report is based was supported in part by funds provided by the United States Department of the Interior, Office of Water Resources Research as Authorized under the Water Resources Act of 1964.

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ABSTRACT

URANIUM AND TRITIUM AS NATURAL TRACERS IN THE FLORIDAN AQUIFER

Naturally occurring radioisotopes serve as hydrologic tracers in the study of ground water movement and aquifer recharge.

A benzene synthesis method of tritium analysis involving no isotopic enrichment has been developed which permits analysis of samples at a level of 10 or more tritium units (10+ H-3 per 10^{18} H-1). In the North Florida study area sharp boundaries separate young and old waters in the aquifer according to their tritium content.

Uranium in ground water exhibits extreme variability in isotopic distribution and the combination of isotopic ratio (U-234/U-238) and total uranium concentration (0.0X to X parts per billion) serves as the tag with which to trace aquifer water. The sources of water flowing from Wakulla Springs and Silver Springs is calculated quantitatively; the results agree well with conclusions based on standard hydrologic methods of analysis. Uranium analysis requires one to four gallons of water per sample, and involves isotopic spiking with U-232, iron hydroxide co-precipitation, ion exchange separation, electrodeposition, vacuum counting, and alpha pulse height analysis.

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URANIUM AND TRITIUM AS NATURAL TRACERS IN THE FLORIDAN AQUIFER
Completion Report to the Office of Water Resources Research, Department of the Interior, August, 1971, Washington, D.C. 20240.
KEYWORDS: tritium*, uranium isotopes*, ground water recharge*, aquifers*, tracers, ground water movement, springs.

1. INTRODUCTION

The use of naturally occurring radioisotopes to study the movement of ground water has been the subject of study by researchers at the Florida State University Department of Geology for several years. From April 1, 1966 to June 30, 1971 this research has been supported by the U.S. Department of Interior Office of Water Resources Research under its Title I program (A-005-FLA and A-011-FLA).

This report covers the activity from July 1, 1968 through June 30, 1971 (A-011-FLA). Some of the work described herein, especially that concerned with analytical techniques, had its inception under the previous grant (A-005-FLA). Conversely, some of the sub-projects begun under A-011-FLA are not complete. Work on these will continue and separate reports will be issued. One of these, a PhD Dissertation by L. I. Briel, will require several months of analysis and data reduction before completion. It will be concerned with the application of uranium isotopes to analysis of the sources and mixing patterns of the Santa Fe River System of north central Florida. The second, an MS Thesis by Ivan Wilson, will be completed soon. It deals with the application of non-isotopically enriched tritium analyses to the study of the Floridan Aquifer of north central Florida, between Tallahassee and Lake City. The following quotation from a preliminary report by Wilson illustrates the direction of this research:

> "In the eastern part of the study area the Floridan aquifer receives little or no local recharge during below normal rainfall periods. Some recharge in the upper portions of the Floridan aquifer occurs where the overlying Hawthorn Formation thins. Where the Hawthorn thickens or a well taps a deeper portion of the Floridan aquifer no local recharge was indicated. The Floridan aquifer is nearer the surface in the central part of the study area, west of Live Oak, Suwannee County. Here the low tritium content of the shallow wells and a sinkhole indicate that the aquifer is discharging during the drier periods. The western part of the study area appears to have a greater local recharge. A possible flow direction to the southwest in Madison and Jefferson Counties is indicated by the decrease in the tritium content down the piezometric gradient. Local recharge over the entire area can not be entirely ruled out since the overall low tritium content may be a reflection of the dry period."

Because of the interesting possibilities of the uranium isotopic approach to ground water studies, as developed under the Office of Water Resources Research Title I funding, continued support has recently been granted under the OWRR

Title II program, so that some of the approaches herein described will receive continued attention and development.

Most of the data and conclusions of this report have been published elsewhere and a list of publications and theses supported entirely or in part by A-011-FLA is appended. Those researchers, students, and technicians, other than the authors of this report, who have participated in the research program are acknowledged in the separate publications, and are listed in the annual reports to the Office of Water Resources Research.

2. URANIUM ISOTOPES IN NATURE: BACKGROUND AND ANALYTICAL PROCEDURE

Previous Studies

In closed geologic systems older than about 10^6 years, U-234 is in equilibrium with its parent U-238 (U-234/U-238 alpha activity ratio = 1.00). At secular equilibrium, by definition: $N_1\lambda_1 = N_2\lambda_2 = A$; and $AU^{234}/AU^{238} = 1.00$, where N_1 and N_2 = number of atoms of U-238 and U-234 respectively, λ_1 and λ_2 = decay constant of U-238 and U-234 respectively, and A = alpha activity. In open systems such as those exposed to weathering and ground-water circulation, separation of these two isotopes can occur, giving rise to a state of radioactive disequilibrium.

An increased interest in radioactive disequilibrium within the natural U-238 series in hydrologic systems has developed in recent years, especially with respect to geochemical, geochronological and hydrogeological studies. Rosholt (1958) suggested that radioactive disequilibrium studies could aid in understanding the natural migration of uranium and its decay products and also provide an insight into the geological and geochemical history of deposits. Until recently, the magnitude and frequency of disequilibria have been generally underestimated. The fractionation of U-234 with respect to its radiogenic parent U-238 was first discovered in 1953 by Russian investigators working with ground waters and secondary minerals (Cherdyntsev, et al, 1955).

Detailed studies in both the United States and Russia of natural waters, carbonates, sandstones, uranium ore deposits, soils, secondary minerals and peats have confirmed and extended these initial observations and have shown that preferential leaching of U-234 from a variety of rock types occurs, that differing isotopic ratios are characteristic of various source areas, and that for most natural waters, a relative enrichment of U-234 over U-238 is observed (Chalov, 1959; Isabaev, et al, 1960; Thurber, 1962; Cherdyntsev, et al, 1963; Rosholt, et al, 1963, 1965, 1966; Dooley et al, 1966).

The greatest deviations from equilibrium of the isotopes of the radioelements are observed in natural waters. The large reservoir of uranium, the oceans, reflects the magnitude of isotopic disequilibrium of uranium in nature (U-234/U-238 activity ratio = 1.14) (Thurber, 1962; Koide and Goldberg, 1965). Successful applications of U-234/U-238 activity ratios to Pleistocene geochronology have been made (Chalov, et al, 1964). By noting that U-234/U-238 activity ratios in natural waters draining specific source areas remained constant with time, in spite of considerable change in uranium content,

discharge, and salinity, Chalov, et al (1964) were able to utilize the isotopic ratios to arrive at absolute age determinations of closed drainage basins.

Decay Scheme and U-234 Fractionation Mechanism

The decay scheme of the natural U-238 series is shown in part in Figure 1. The two isotopes, U-234 and U-238, are separated in the decay chain by two short-lived daughter nuclides, Th-234 and Pa-234. It has been suggested that the physicochemical reason for the U-234 fractionation is a change in the valence electron configuration from the U-238 parent to the radiogenically produced U-234 daughter for a time long enough to permit fractionation (Cherdyntsev, et al, 1955; Chalov, 1959; Rosholt, et al, 1963).

Possible mechanisms for the U-234 fractionation have been presented by Rosholt, et al (1963) and Dooley, et al (1966). In the three-step decay of U-238 to U-234, chemical bonds holding the decaying tetravalent U-238 are broken by the nuclear recoil from the decay. As a result of the U-238 alpha decay and Th-234 and Pa-234 beta decay, the daughter atom (U-234) is both displaced within the crystal structure and stripped of some of its electrons thus attaining an excited electronic state. According to Dooley, et al (1966, p. 1373),

> "At the time of decay and recoil the transformed nucleus is stripped of some of its electrons and momentarily is in a chemically uncombined state as a charged particle within the mineral lattice, or within a microfissure perhaps beyond the crystal boundary or in solution. Chemical recombining of U-234, except in a highly reducing environment, probably favors the electron-deficient hexavalent or oxidized state either as UO_2^{++} in a compound, or as an ion in solution."

Thus, as noted by Rosholt, et al (1963), U-234 would differ from much of the U-238 in oxidation state, in location in interstitial spaces (unstable site?), and in type of chemical bonds, and is therefore potentially more mobile than its parent U-238.

Chalov and Merkulova (1966), in studying comparative oxidation rates of U-234 and U-238, concluded that on the natural dissolution of uranium from minerals a partial separation of U-234 and U-238 may occur as a result of the greater ease of oxidation of U-234 atoms. They also considered radioactive recoil to be of great importance. In addition, according to Rosholt, et al (1965), the differing chemical affinities between uranium and the intermediate daughter products may result in differential migration of the Th-234 and Pa-234 with respect to U-238.

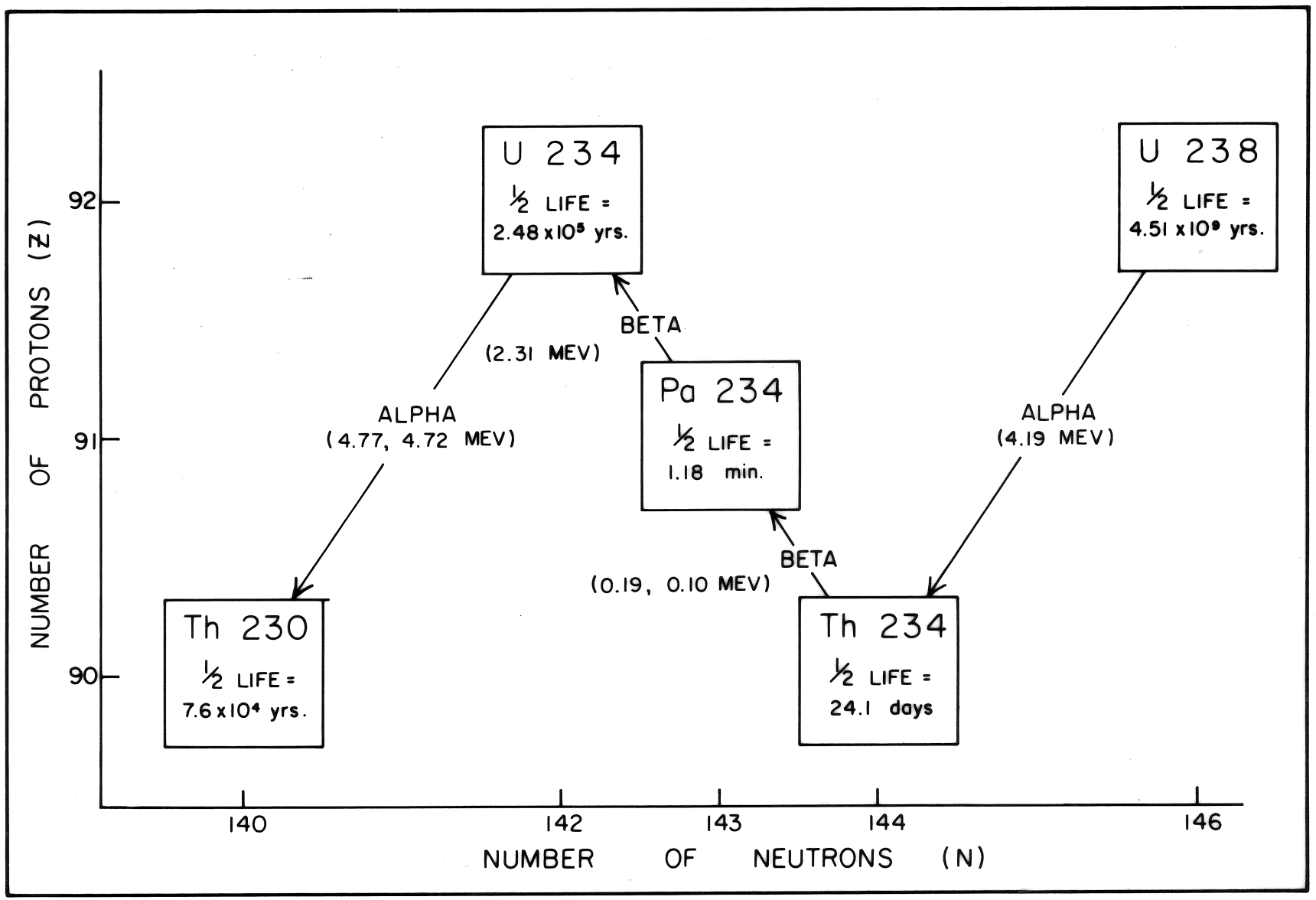


Figure 1. Decay scheme of the natural U-238 series showing isotopes of interest, half-life, mode and energy of decay.

It is pertinent to note that the transition from the +4 to the +6 state has an oxidation potential within the normal range for geologic environments:

$$U^{+4} + 2H_2O \leftrightarrows UO_2^{+2} + 4H^+ + 2e^-;\ E^\circ = +0.33 \text{ volt}$$

so compounds of both valences would be expected in nature (Krauskopf, 1967, p. 527). Thus the oxidation potential of the environment, in addition to the electronic effects of decay, may be a major control on the separation of uranium isotopes, once decay and recoil of the daughter isotope into solution occurs. It has been observed (Rosholt, et al, 1965) that slightly oxidizing environments appear to result in large magnitudes of isotopic disequilibrium, whereas in reducing environments U-234 does not appear to be preferentially leached. Both U-238 and U-234 are leached in more equal proportions from an environment having a strong oxidizing potential.

The leaching solutions preferentially pick up the oxidized U-234 as the stable divalent uranyl ion UO_2^{++}. The greater solubility of uranyl compounds (hexavalent uranium) relative to those of tetravalent uranium has been documented (Adams, et al, 1959). Although noting that in aqueous solutions the uranyl ion forms a somewhat soluble series of hydroxides or hydrates ($UO_2(OH)_2$, HUO_4^-, UO^{-2}), Krauskopf (1967, p. 527, 528) reported that the solubilities of the latter two ions became appreciable only in strongly alkaline solutions. In solutions containing carbonate ion, the solubility of compounds of hexavalent uranium is greatly increased by the formation of carbonate complexes such as the uranyl dicarbonate and uranyl tri-carbonate anionic species, hence carbonate-bearing solutions are excellent solvents for uranium (Scott and Barker, 1958; Garrels and Christ, 1965, p. 253; Krauskopf, 1967, p. 528). The solubility of uranyl compounds is strongly pH dependent, thus the pH of the environment plays a major role in the mobility of uranium. Serebryakova (1964), utilizing physico-chemical methods, determined that in oxygenated ground waters uranium is present as anionic complexes such as $(UO_2(CO_3)_2(H_2O)_2)^{-2}$ (86%) and $(UO_2(CO_3)_3)^{-4}$ (12%), consistent with earlier results. No colloidal uranium was detected.

Dooley, et al (1966), in studying U-234 fractionation in sandstone-type uranium ore deposits, noted that greater U-234 deficiencies and range of disequilibrium in ore samples appeared to be related to zones of higher permeability and greater circulation of ground water. A water saturated, slightly oxidizing, environment appears to be the primary medium for continuous fractionation and differential solution of uranium isotopes; consequently, the hydrologic system exerts a major control on the patterns of environmental disequilibrium.

Methods and Procedures

Sampling sites, consisting of wells, springs, streams, and lakes were selected so as to adequately represent the regional geohydrologic environment within the study area. Determinations were made of the total uranium content and of the U-234/U-238 activity ratios, using the analytical procedures of isotope dilution and alpha-particle spectrometry.

In brief, the field sampling and analytical procedures were as follows:

Samples were collected from each source in duplicate to serve as a check on analytical variability. The radioactive isotope U-232, which served as the isotopic yield tracer, and sufficient nitric acid to attain a pH of 1.0 were added in the field. The recovery procedure for uranium consisted of co-precipitation with ferric hydroxide, and purification using solvent extraction and ion-exchange. Following ion-exchange, the uranium samples were plated onto stainless steel planchets by electrodeposition for isotopic analysis using a high resolution solid state alpha-particle spectrometer. Figure 2 illustrates a typical alpha-particle spectrum of uranium isotopes.

Blank solutions were run through the entire chemical separation and electrodeposition procedure and analyzed on the alpha spectrometer. These blanks provided a correction factor for background as well as for any contaminants which may have been introduced during the chemical processing. Chemical yields ranged from 15 percent to greater than 50 percent. The above methods and procedures resulted in determinations of uranium isotopes in trace amounts of less than .04 micrograms per liter and of U-234/U-238 activity ratios to within $\pm$.003. Average errors for uranium content and activity ratio at the 0.95 confidence level were $\pm$5 and $\pm$3 percent, respectively, for water with a uranium content greater than 0.1 micrograms per liter.

For a more complete description of technique, see the discussion under "Detailed Methods and Analytical Procedures" in Appendix A.

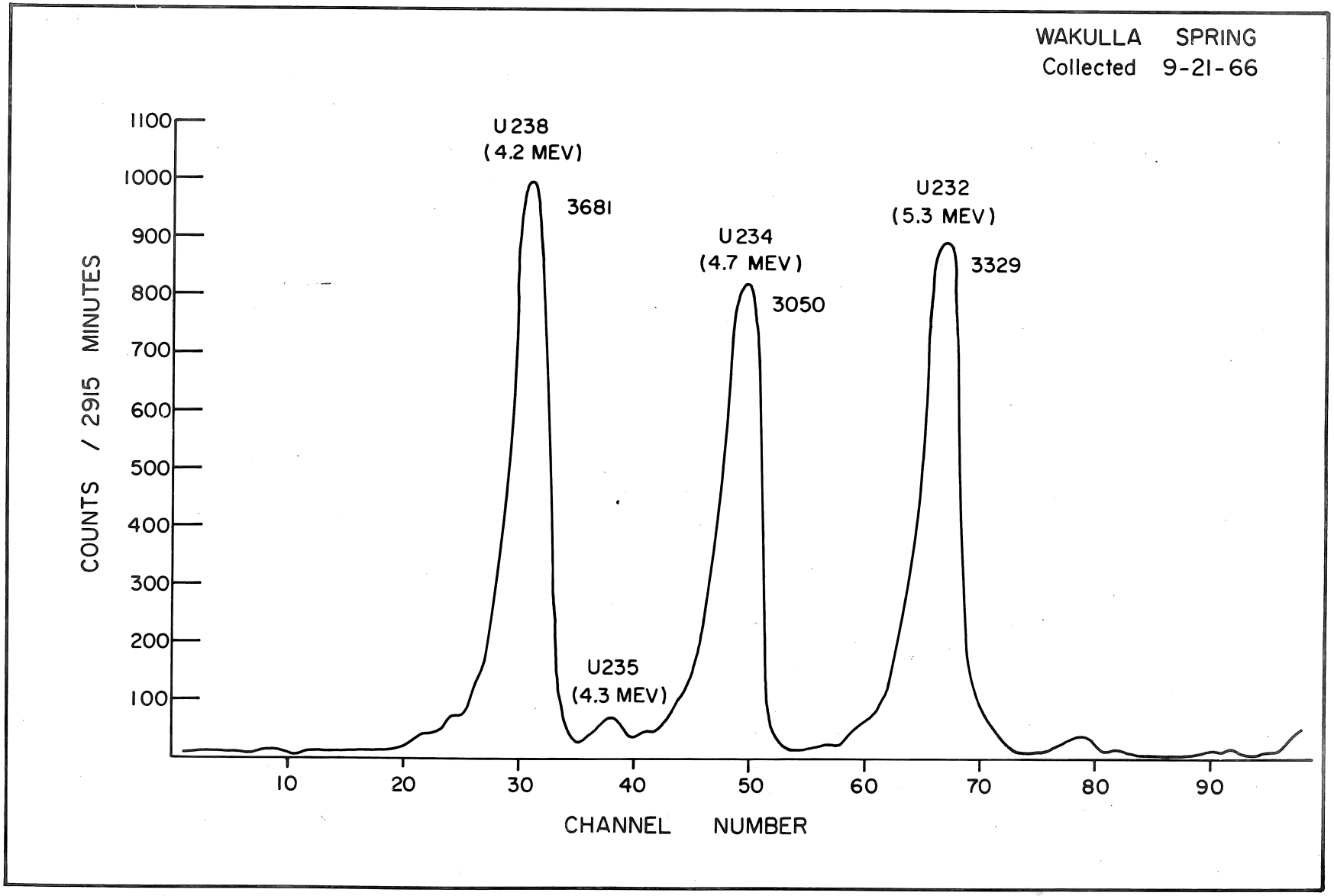


Figure 2. Alpha-particle spectrum of uranium isotopes; alpha energy in million electron volts (MeV).

3. URANIUM ISOTOPES AS AN AID TO HYDROLOGIC STUDY OF THE FLORIDAN AQUIFER

Purpose and Significance

One of the purposes of this study is to investigate uranium isotope disequilibrium conditions within the Floridan aquifer and related natural waters of north Florida with a view towards evaluating the potential applicability of uranium isotope studies to hydrology. By studying the occurrence, distribution, and environmental disequilibrium patterns of naturally occurring uranium isotopes in selected Florida waters, it may be possible to determine the suitability of these isotopes as natural tracers or as other aids to hydrologic investigations, and to determine whether variations in radioisotope ratios and concentrations in natural waters can be used to indicate sources and/or history of waters from various parts of the geohydrologic environment. An analysis of the relations between the isotopic distribution patterns and the hydrologic-flow system may permit interpretation in terms of regional permeability characteristics, ground-water circulation, and areas of extensive Pleistocene leaching within the Floridan aquifer.

Furthermore, although detailed discussions are beyond the scope of this investigation, in order to utilize uranium isotopes in geochemical and geochronological studies, an extensive knowledge of the fundamental physicochemical behavior of the U-234 daughter product in relation to parent U-238 in hydrologic environments, as well as an understanding of the hydrologic-flow system, is needed (Rosholt, et al, 1966; Thurber, 1962). As pointed out by Osmond (1964), a more comprehensive study of the heavy radioelements in the waters of Florida may lead to new concepts in the mobility of these elements. In addition, a knowledge of the isotopic distribution patterns may contribute to a better understanding of the hydrogeochemistry of uranium in natural aqueous systems.

Results and Discussion

The results of the analyses (Table 1) show that in natural waters within the study area (refer to Table 2) both the U-234/U-238 activity ratio and the uranium content are quite variable, indicative of extensive disequilibrium within the hydrogeologic environment. The errors given are based on counting statistics of samples and do not include consideration of systematic errors. The artesian Floridan aquifer, part of the main Tertiary limestone aquifer system in the southeastern United States, is the major source of ground water and the most

Table 1

URANIUM CONCENTRATIONS AND ISOTOPIC ACTIVITY RATIOS
OF NATURAL WATERS OF FLORIDA

Sample Number	Uranium Content in Parts Per Billion	U-234/U-238 Activity Ratio
FAW 010	0.363 ± 0.028	2.116 ± 0.138
FAW 011	0.080 ± 0.013	0.999 ± 0.213
FAW 012	0.019 ± 0.006	3.327 ± 1.149
FAW 013	0.016 ± 0.005	4.070 ± 1.301
FAW 014	0.662 ± 0.080	1.145 ± 0.124
FAW 015	0.013 ± 0.009	1.580 ± 1.343
FAW 020	0.514 ± 0.021	0.953 ± 0.020
FAW 021	0.584 ± 0.024	0.878 ± 0.020
FAW 023	0.154 ± 0.008	1.021 ± 0.053
FAW 024	0.036 ± 0.005	1.230 ± 0.207
FAW 025	0.007 ± 0.002	1.468 ± 0.572
FAW 026	0.209 ± 0.010	1.012 ± 0.045
FAW 027	0.038 ± 0.003	1.121 ± 0.108
FAW 029	18.484 ± 0.954	0.523 ± 0.006
FAW 030	1.968 ± 0.104	0.941 ± 0.019
FAW 033	0.608 ± 0.029	0.854 ± 0.028
FAW 034	2.631 ± 0.101	0.686 ± 0.007
FAW 035	0.604 ± 0.027	0.852 ± 0.025
FAW 036	25.912 ± 1.450	0.503 ± 0.005
FAW 039	0.050 ± 0.007	1.588 ± 0.264
FAW 040	0.135 ± 0.009	0.841 ± 0.063
FAW 041	1.552 ± 0.081	1.073 ± 0.022
FAW 042	0.079 ± 0.007	2.938 ± 0.237
FAW 043	0.691 ± 0.037	0.687 ± 0.023
FAW 044	0.014 ± 0.004	1.343 ± 0.455
FAW 045	0.134 ± 0.100	0.803 ± 0.724
FAW 046	11.015 ± 0.661	0.925 ± 0.010
FAW 049	0.488 ± 0.027	0.899 ± 0.032
FAW 050	0.008 ± 0.003	1.972 ± 0.896
FAW 051	0.340 ± 0.017	0.963 ± 0.032
FAW 052	1.140 ± 0.059	1.021 ± 0.024
FAW 053	0.481 ± 0.027	1.002 ± 0.037
FAW 054	0.191 ± 0.056	1.001 ± 0.275
FAW 056	2.673 ± 0.151	0.710 ± 0.029
FAW 057	0.687 ± 0.042	0.836 ± 0.044
FAW 060	0.696 ± 0.050	0.762 ± 0.033
FAW 061	0.532 ± 0.030	0.896 ± 0.030
FAW 063	3.422 ± 0.166	1.116 ± 0.012
FAW 065	0.008 ± 0.004	0.618 ± 0.613
FAW 066	0.314 ± 0.025	0.935 ± 0.059
FAW 067	0.600 ± 0.037	0.840 ± 0.031
FAW 068	0.386 ± 0.026	0.928 ± 0.046
FAW 069	2.649 ± 0.189	1.019 ± 0.023
FAW 070	0.082 ± 0.007	3.710 ± 0.297
FAW 071	0.042 ± 0.005	1.034 ± 0.149

Table 1 - Continued

Sample Number	Uranium Content in Parts Per Billion	U-234/U-238 Activity Ratio
FAW 072	1.343 ± 0.083	0.971 ± 0.026
FAW 073	0.276 ± 0.020	1.062 ± 0.062
FAW 074	0.674 ± 0.046	0.824 ± 0.033
FAW 075	0.119 ± 0.018	1.041 ± 0.160
FAW 076	0.858 ± 0.052	0.892 ± 0.028
FAW 077	0.376 ± 0.024	1.002 ± 0.045
FAW 078	0.628 ± 0.040	1.096 ± 0.039
FAW 079	0.702 ± 0.046	0.904 ± 0.034

Table 2

LOCATION AND DESCRIPTION OF WATER SAMPLES

Sample Number	Location	Description	Date Sampled	Aquifer or Source
FAW 010	T33S; R22E; Sec. 22 Hillsborough County	L. Taylor Well; well depth 11 ft., csg. 11 ft., sample slightly rusty	6-21-66	Water Table
FAW 011	T31S; R23E; Sec. 23 Polk County	R. Marsee Well; well depth 120 ft., csg. 80 ft.	6-21-66	Hawthorn Formation
FAW 012	T31S; R23E; Sec. 25 Polk County	American Cyanamid Co. Well; well depth 950 ft., csg. 337 ft.	6-21-66	Floridan Aquifer
FAW 013	T34S; R25E; Sec. 3 Hardee County	City of Wauchula Municipal Well; well depth 1,103 ft., csg. 404 ft.	6-21-66	Floridan Aquifer
FAW 014	T30S; R25E; Sec. 5 Polk County	Bartow City Well Number 10; well depth 663 ft., csg. 59 ft., possibly some fine pebble phosphate in sample	6-21-66	Floridan Aquifer
FAW 015	T28S; R26E; Sec. 21 Polk County	Winter Haven City Well Number 2; well depth 816 ft., csg. 138 ft.	6-21-66	Floridan Aquifer
FAW 020	T1N; R1E; Sec. 30 Leon County	Tallahassee City Well Number 6; well depth 414 ft., csg. 170 ft.	9-21-66	Floridan Aquifer
FAW 021	T3S; R1W; Sec. 11 Wakulla County	Wakulla Spring, southwest of Woodville; discharge 560 cfs.	9-22-66	Floridan Aquifer
FAW 023	T1S; R1E; Sec. 6 Leon County	Unnamed spring in Myers Park, Tallahassee; flow issuing from hillslope above clay layer	11-16-66	Hawthorn Formation

Table 2 - Continued

Sample Number	Location	Description	Date Sampled	Aquifer or Source
FAW 024	T1S; R5E; Sec. 15 Jefferson County	Beasleys Creek, nr. Lamont; brown color due to organics	11-17-66	Surface Water
FAW 025	T2N; R1W; Sec. 33 Leon County	Lake Jackson, nr. Tallahassee	11-18-66	Surface Water
FAW 026	T5N; R9W; Sec. 33 Jackson County	Blue Springs, nr. Marianna	11-26-66	Floridan Aquifer
FAW 027	T3N; R5W; Sec. 14 Gadsden County	Glen Julia Springs, nr. Mt. Pleasant	11-26-66	Water Table Aquifer
FAW 029	T2S; R1E; Sec. 8 Leon County	City of Woodville Municipal Well; well depth 183 ft., csg. 32 ft.	1-27-67	Floridan Aquifer
FAW 030	T2S; R1E; Sec. 8 Leon County	Well at Ice House in Woodville; well depth 21 ft., csg. 15 ft.	1-28-67	Floridan Aquifer
FAW 033	T3S; R1W; Sec. 11 Wakulla County	Wakulla Spring, southwest of Woodville; discharge 255 cfs., clear, unfiltered	4-8-67	Floridan Aquifer
FAW 034	T1S; R1E; Sec. 19 Leon County	Well at Big Bend Truck Center South of Tallahassee; well depth 100 ft., csg. 70 ft.	4-10-67	Floridan Aquifer
FAW 035	T3S; R1W; Sec. 11	Wakulla Spring, southwest of Woodville; discharge 255 cfs.; clear	4-8-67	Floridan Aquifer
FAW 036	T2S; R1E; Sec. 8 Leon County	City of Woodville Municipal Well; well depth 183 ft., csg. 32 ft.	4-8-67	Floridan Aquifer

Table 2 - Continued

Sample Number	Location	Description	Date Sampled	Aquifer or Source
FAW 039	T38S; R38E; Sec. 1 Martin County	R. Carlton flowing artesian well; well depth 835 ft., csg. 373 ft.	5-24-67	Floridan Aquifer
FAW 040	T30S; R23E; Sec. 13 Polk County	Well at Kingsford Plant International Minerals & Chem. Corp. shallow well removing water from phosphate deposit	5-23-67	Water Table
FAW 041	T30S; R24E; Sec. 35	C. W. Shepard Well; well depth 50 ft., csg. 20 ft.	5-23-67	Water Table
FAW 042	T31S; R25E; Sec. 30 Polk County	A. L. McClellan Well; well depth 165 ft., csg. 42 ft.	5-23-67	Hawthorn Formation
FAW 043	T30S; R21E; Sec. 17 Hillsborough County	Lithia Springs, southwest of Plant City	5-22-67	Floridan Aquifer
FAW 044	T30S; R23E; Sec. 12 Polk County	City of Mulberry Municipal Well; well depth 833 ft., csg. 330 ft.	5-22-67	Floridan Aquifer
FAW 045	T28S; R25E; Sec. 12 Polk County	Eagle Lake, nr. Winter Haven	5-22-67	Surface Water
FAW 046	T30S; R24E; Sec. 25 Polk County	Seepage from mine face at Noralyn Plant International Minerals & Chem. Corp.	5-23-67	Bone Valley Formation
FAW 049	T2S; R2E; Sec. 9 Leon County	Horn Springs, east of Woodville	7-16-67	Floridan Aquifer

Table 2 - Continued

Sample Number	Location	Description	Date Sampled	Aquifer or Source
FAW 050	T1S; R4W; Sec. 11 Leon County	Flowing Well at Elk Horn Fish Camp; well depth 136 ft., csg. 127 ft.	7-16-67	Hawthorn Formation
FAW 051	T2N; R5E; Sec. 19 Jefferson County	City of Monticello Municipal Well; well depth 350 ft., csg. 155 ft.	7-19-67	Floridan Aquifer
FAW 052	T3N; R2W; Sec. 26	City of Havana Municipal Well; well depth 692 ft., csg. 418 ft.	7-19-67	Floridan Aquifer
FAW 053	T1N; R1W; Sec. 2 Leon County	R. O. Vernon Well, nr. Lake Jackson; well depth 236 ft., csg. 171 ft.	7-21-67	Floridan Aquifer
FAW 054	T1N; R2W; Sec. 23 Leon-Gadsden Line	Ochlockonee River	7-21-67	Surface Water
FAW 056	T1S; R1E; Sec. 19 Leon County	Well at Big Bend Truck Center, south of Tallahassee; well depth 100 ft., csg. 70 ft.	8-17-67	Floridan Aquifer
FAW 057	T3S; R1W; Sec. 11 Wakulla County	Wakulla Spring, southwest of Woodville; discharge 1100 cfs; brown color	8-18-67	Floridan Aquifer
FAW 060	T2S; R1W; Sec. 17 Leon County	Dismal Sink	2-27-68	Floridan Aquifer
FAW 061	T2S; R1E; Sec. 10 Leon County	Osgood Sink, 2 miles east of Rhodes Cemetery, Woodville	2-27-68	Floridan Aquifer
FAW 063	T3N; R4W; Sec. 32 Gadsden County	Well At Spring Hill Elementary School, Gretna	2-29-68	Floridan Aquifer

Table 2 - Continued

Sample Number	Location	Description	Date Sampled	Aquifer or Source
FAW 065	T1S; R4W; Sec. 11 Leon County	Flowing Well at Elk Horn Fish Camp; well depth 136 ft., csg 127 ft.	8-6-68	Hawthorn Formation
FAW 066	T1S; R2W; Sec. 11 Leon County	Well at Silver Lake, Southwest of Tallahassee, depth unknown	8-6-68	Floridan Aquifer
FAW 067	T1S; R1W; Sec. 31 Leon County	Well at Lost Lake; well depth 154 ft., csg. 100 ft.	8-6-68	Floridan Aquifer
FAW 068	T1N; R1E; Sec. 23 Leon County	J. Sessions Well, east of Tallahassee; well depth 155 ft., csg. 85 ft.	8-6-68	Floridan Aquifer
FAW 069	T1S; R2E; Sec. 3 Leon County	Well at Hollis Motor Court, Chaires; well depth 120 ft., csg. 64 ft.	8-6-68	Hawthorn Formation
FAW 070	T2N; R3W; Sec. 24 Gadsden County	Well at Hav-a-Tampa Cigar Co.; well depth 411 ft., csg. 261 ft.	8-6-68	Floridan Aquifer
FAW 071	T1N; R3W; Sec. 14 Gadsden County	E. Tennell Well, nr. Midway; well depth 10 ft., csg. 10 ft.	8-8-68	Hawthorn Formation
FAW 072	T1N; R1W; Sec. 29 Leon County	Well at Floridan Company, Tallahassee; well depth 170 ft., csg. 105 ft.	8-8-68	Floridan Aquifer
FAW 073	T2S; R2E; Sec. 29 Leon County	Well at Natural Bridge Monument, southeast of Woodville; well depth 175 ft.	8-10-68	Floridan Aquifer
FAW 074	T2S; R1W; Sec. 28 Wakulla County	River Sink Spring, Southwest of Woodville	8-9-68	Floridan Aquifer

Table 2 - Continued

Sample Number	Location	Description	Date Sampled	Aquifer or Source
FAW 075	T3S; R2W; Sec. 26 Wakulla County	Lost Creek, nr. Arran	8-9-68	Surface Water
FAW 076	T2S; R1W; Sec. 22 Wakulla County	M. L. Huntley Well, southwest of Woodville; well depth 43 ft.	8-9-68	Floridan Aquifer
FAW 077	T1N; R1W; Sec. 5 Leon County	Well nr. Lake Jackson; well depth 194 ft., csg. 140 ft.	8-15-68	Floridan Aquifer
FAW 078	T1N; R1E; Sec. 5 Leon County	Well at Maclay Gardens, north of Tallahassee; depth unknown	8-15-68	Floridan Aquifer
FAW 079	T1S; R1W; Sec. 4 Leon County	Tallahassee City Well at Ridgeway & Arnold Sts.; well depth 254 ft., csg. 156 ft.	8-15-68	Floridan Aquifer

important hydrologic unit within the study area (Hendry and Sproul, 1966; Stringfield, 1966). The generalized potentiometric surface is shown in Figure 3 (Healy, 1962) with the direction of ground-water movement being southeasterly to southerly along section A-A'.

The cross-sectional distribution of the uranium content and the U-234/U-238 activity ratios is given in Figure 4. The data show that surface waters and ground waters above the Hawthorn Formation have a relatively low uranium content and a high U-234/U-238 activity ratio. Water from the Hawthorn, which contains phosphatic material and clays, has a slightly increased uranium content. The artesian waters from the underlying Floridan aquifer exhibit the highest and most variable uranium content, probably due to a variable uranium distribution within the sediments (Kaufman, 1968). U-234/U-238 activity ratios approaching equilibrium occur in waters from the Hawthorn Formation and from the Floridan aquifer where it is overlain by thick younger deposits. Waters from the Floridan aquifer exhibiting activity ratios less than unity ($^{234}U/^{238}U$ = 0.50 to 0.90) underlie the Woodville Karst Plain.

Figures 5 and 6 portray the areal distribution of the U-234/U-238 activity ratios of water in the Floridan aquifer and the regional structural and physiographic setting within the report area. The data indicate definitive distribution patterns, the most notable being a deficiency of U-234 in the waters underlying the Woodville Karst Plain and the southern and eastern parts of the sinkhole-riddled Tallahassee Hills (area B, Figure 5). Activity ratios near equilibrium underlie the Gulf Trough, the Marianna Lowlands, and the northwestern part of the Tallahassee Hills (areas A and C, Figure 5). Consequently, a close interrelation between uranium isotope disequilibrium and the hydrogeologic framework is suggested.

Within area B (Figure 5) the karstic topography results in a well-developed subterranean drainage system, including several first-magnitude springs (Figure 6), suggestive of high permeability and active circulation. Sellards (1917) concluded that a structural ridge (upthrown fault block?) existed within this area which elevated the limestone nearer the surface. This resulted in a thin, easily breached overburden, and permitted increased ground-water circulation with concomitant increased solution and development of secondary permeability. Hydrologic data, including large seasonal fluctuations of Wakulla Spring discharge correlative with local precipitation suggest the occurrence of extensive local recharge (Kaufman, 1968).

To account for the low activity ratios observed in these waters, it is hypothesized that during periods of lowered Pleistocene sea levels, extensive leaching within the Floridan

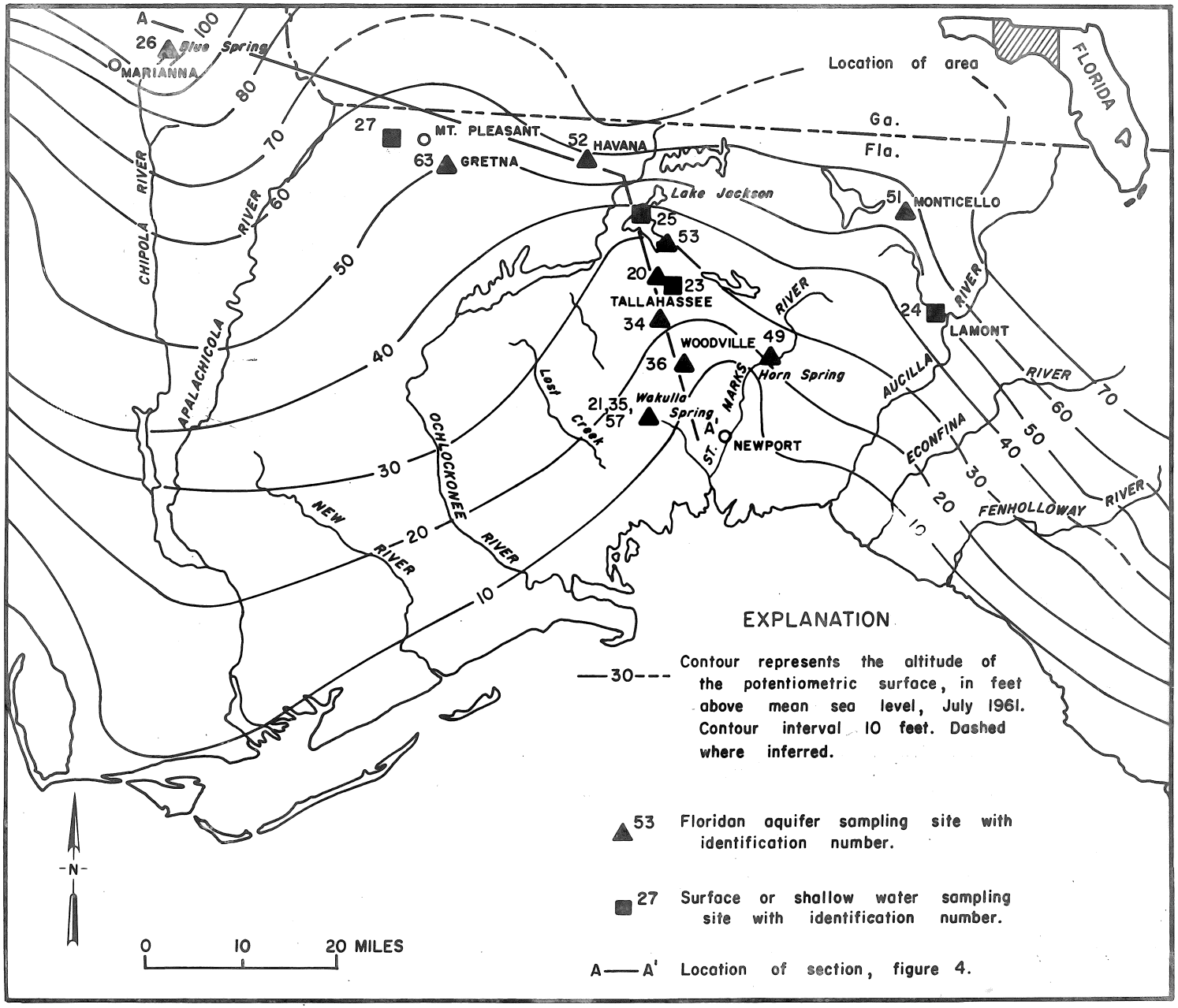


Figure 3. Location of sampling sites and potentiometric surface of the Floridan aquifer in North Florida.

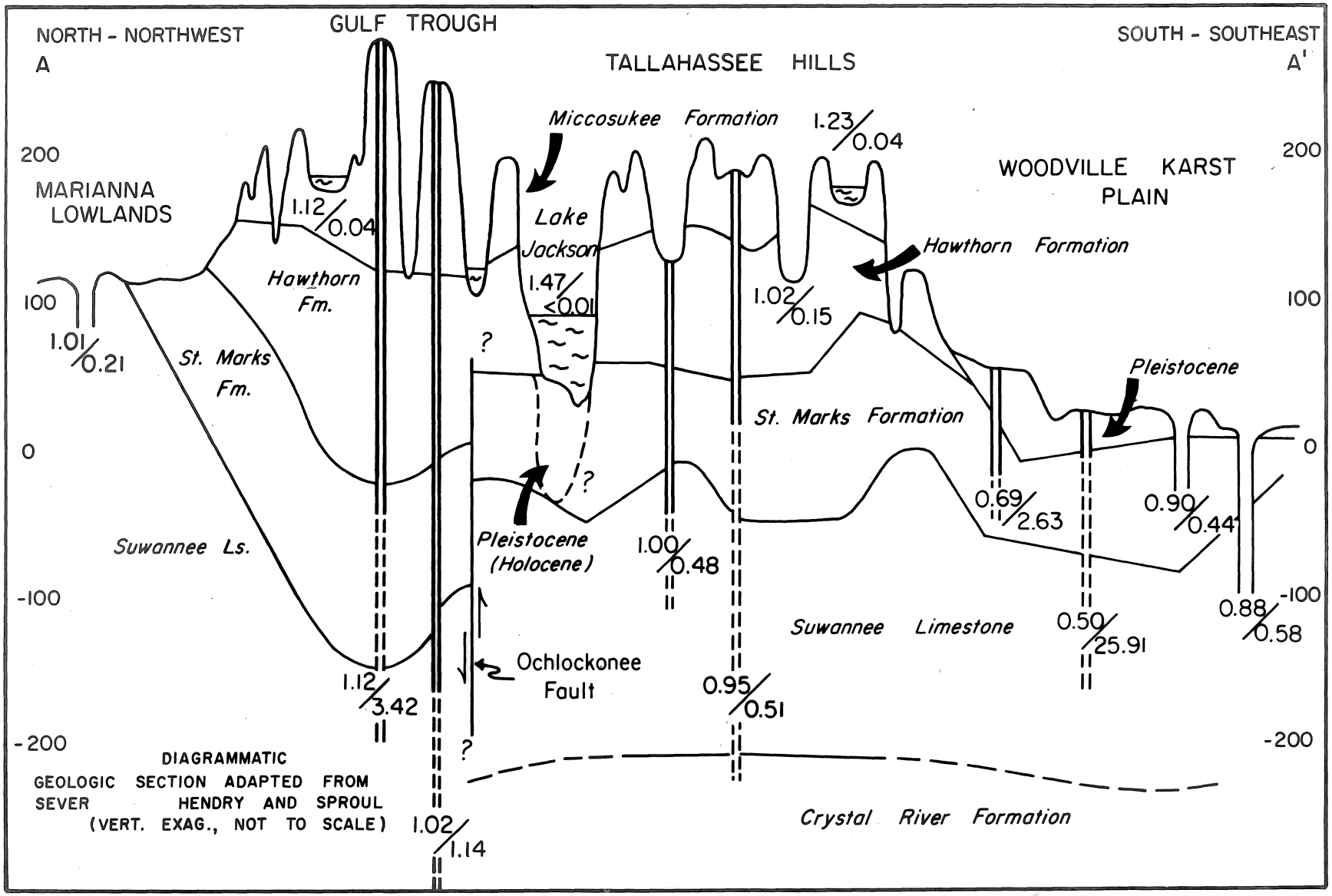


Figure 4. Geologic section and distribution of the U-234/U-238 activity ratios (upper number) and uranium content in micrograms per liter (lower number) in the waters of North Florida.

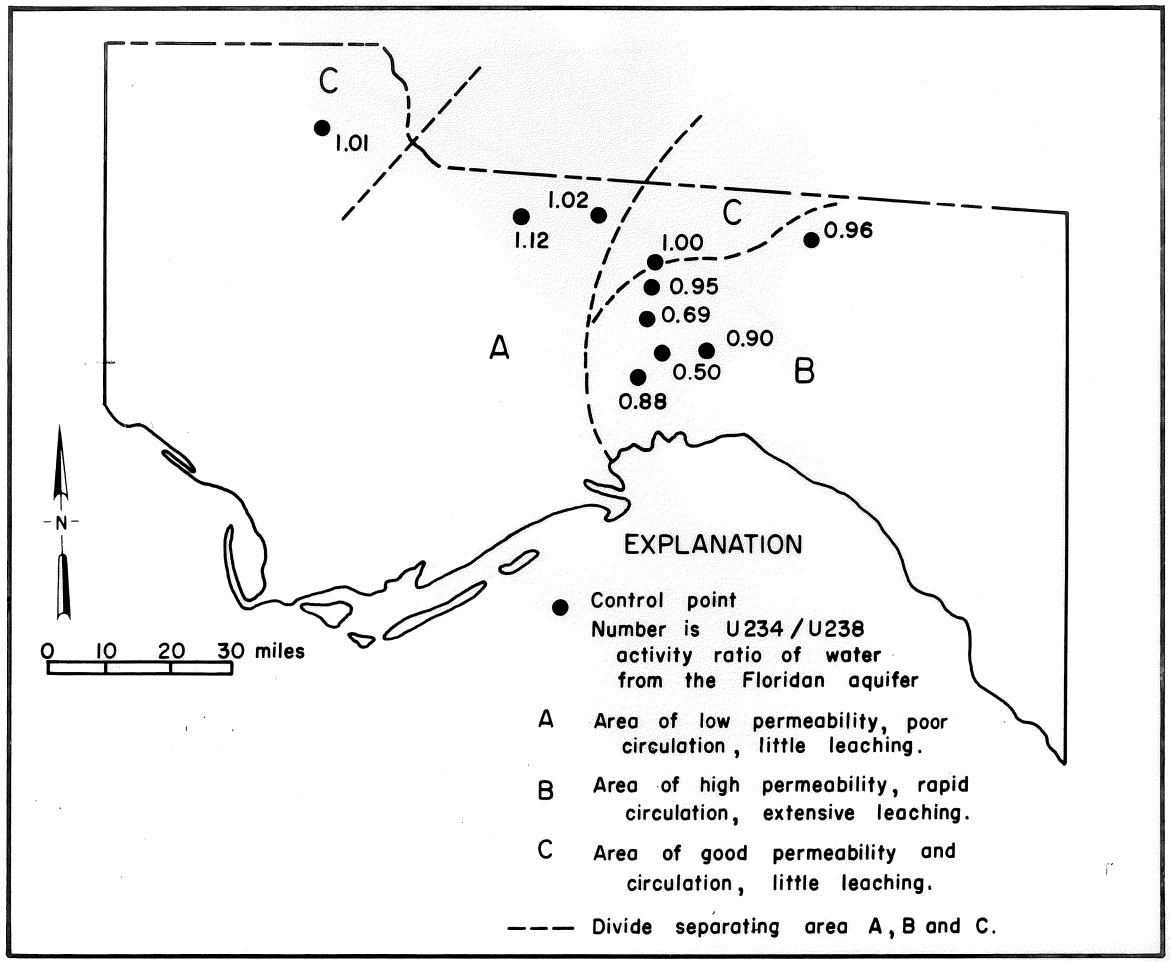


Figure 5. Areal distribution of the U-234/U-238 activity ratios of waters from the Floridan aquifer in North Florida.

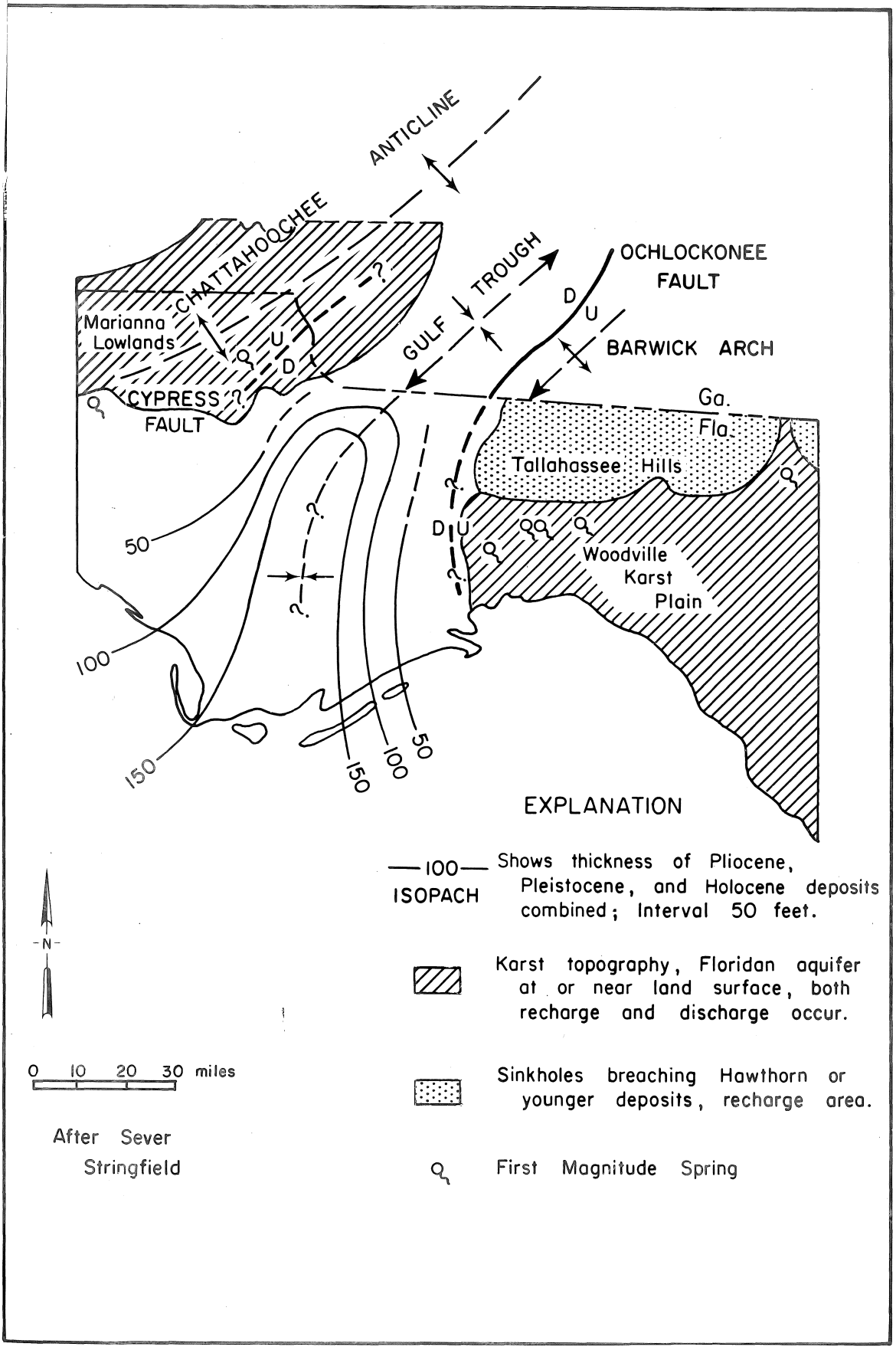


Figure 6. Regional structure and physiographic map of North Florida depicting recharge areas.

aquifer occurred, associated with an active ground-water flow system and favorable environmental oxidation potentials. This resulted in preferential leaching of U-234, leaving behind rocks deficient in U-234 with respect to U-238. The physicochemical processes responsible for the low activity ratios, utilizing geochemical and paleohydrologic models has been evaluated by Rydell (1969).

An apparent relation between the magnitude of the U-234 deficiency and the uranium content is indicated for most of the waters sampled (Figure 7). The increased U-234 deficiency may define areas of greater ground-water circulation and solution during Pleistocene time with concurrent development of secondary aquifer permeability and preferential leaching of U-234. Waters with a higher uranium content may define zones of greater leaching of uranium. Thus, points falling on or near the plotted line in Figure 7 suggest the waters are part of an active flow system. As one moves up the curve, the higher uranium content and increased magnitude of the U-234 deficiency indicate progressively greater permeability and ground-water circulation. This concept is consistent with the results of Dooley et al (1966) who noted that greater U-234 deficiencies and range of disequilibrium in sandstone-type uranium ore deposits appear to be related to zones of higher permeability and greater circulation of ground water.

Area A (Figure 5) coincides with the Gulf Trough (Figure 6), a northeast-southwest trending downfaulted syncline containing thick Hawthorn and post-Miocene deposits (Sever, 1964, 1966; Hendry and Sproul, 1966). Drainage is for the most part by surface streams, flowing over poorly drained materials of low permeability. Hendry and Sproul (1966) report that limestone cores from within the trough show little evidence of solution or development of secondary permeability. This, plus the low yield of wells in the area, suggests a limited ground-water circulation system, negligible recharge, and no significant Pleistocene leaching of the sediments.

Data presented by Wait (1960) suggest the influence of structural features upon the hydrologic system and ground-water quality in southwestern Georgia. Water from wells located within the Gulf Trough, adjacent to the Ochlockonee Fault, trending northeast-southwest is poorer in quality (high dissolved solids and sulfate) and higher in temperature than water from wells located away from these structural features. These physical and chemical differences suggest low aquifer permeability and restricted circulation. Olds (1961) concluded that the Ochlockonee Fault may restrict the flow of artesian water, a conclusion supported by the later results of Hendry and Sproul (1966) and Kaufman (1968).

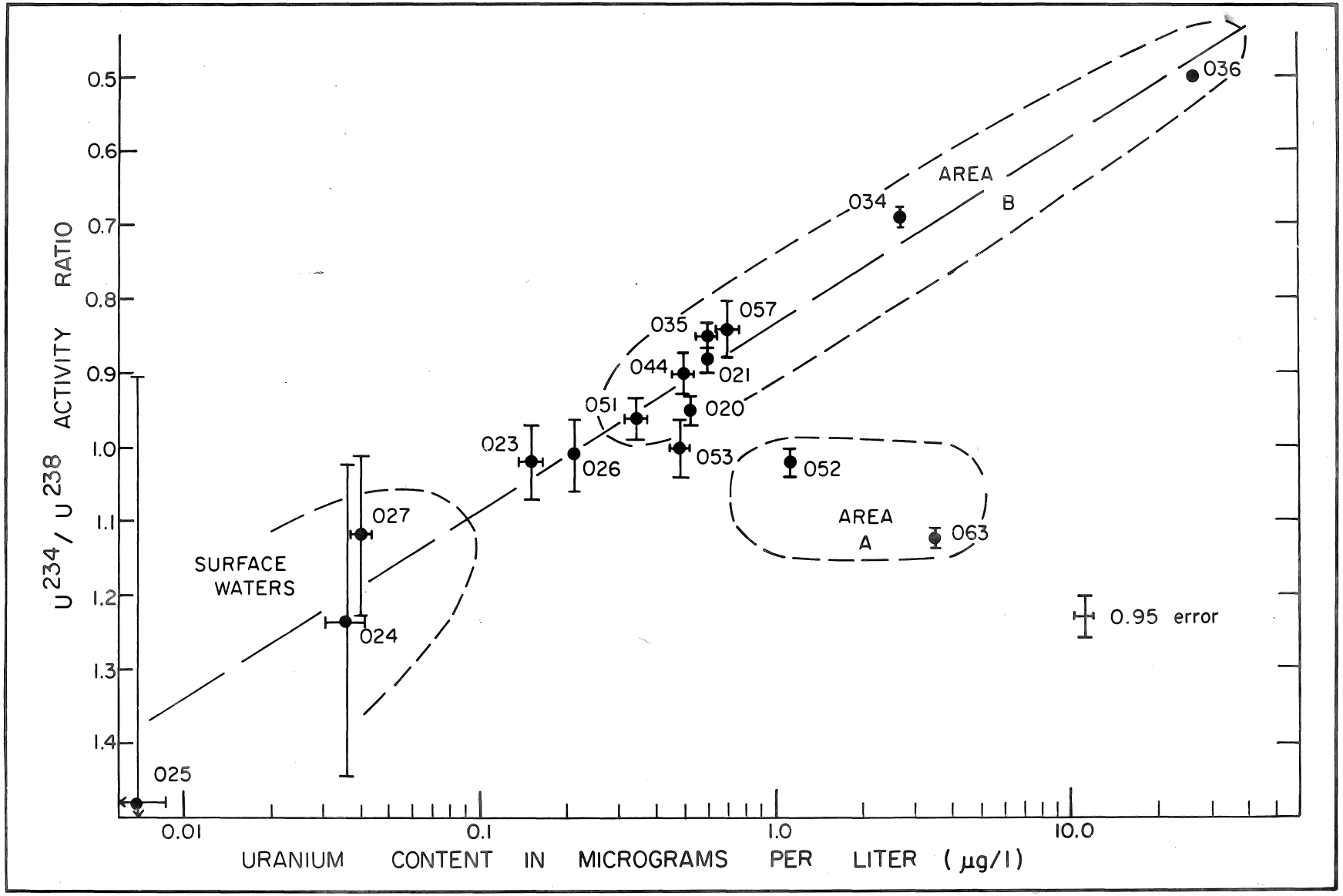


Figure 7. Relation between the U-234/U-238 activity ratio and uranium content in the waters of North Florida.

Artesian waters from within area A depart considerably from the plotted line in Figure 7, indicating waters that are not part of the active hydraulic flow system, consistent with the concept of low permeability and restricted circulation in this region.

Area C is interpreted as one of active circulation and high permeability today with little preferential leaching of U-234 during the Pleistocene. The region may have been shielded somewhat from the Pleistocene circulation, solution and leaching by its thick cover of overlying sediments and/or environmental oxidation potentials may not have been favorable.

Conclusions

Artesian waters deficient in U-234 are associated with a karst terrane - an area of extensive recharge, high permeability and active ground-water circulation. The magnitude of the U-234 deficiency appears to be related to the degree of circulation, leaching, and permeability, as well as the oxidation potential of the environment and infiltrating waters. Artesian waters with U-234/U-238 ratios at, or slightly greater than, equilibrium are associated with a downfaulted syncline - an area of negligible recharge, low permeability and little ground-water circulation, with limited preferential leaching of U-234 during the Pleistocene. The data suggest that waters within the faulted syncline are isolated from Pleistocene and present-day active hydraulic flow systems.

As the activity ratios should reflect ratios in the source materials, the U-234 deficient waters sampled from the karst terrane appear to reflect a different source or history than waters updip to the northwest. The Gulf Trough and Ochlockonee Fault act as a hydraulic barrier that prevents any significant southeastward flow of groundwater.

4. URANIUM ISOTOPES AS QUANTITATIVE INDICATORS OF GROUND WATER SOURCES

The Isotope Dilution Approach to Hydrologic Problems

Investigation of the distribution and environmental disequilibrium patterns of naturally occurring uranium isotopes (U-234 and U-238) in waters of the Floridan aquifer (Table 1) suggests that variations in isotopic activity ratios and concentrations can be used to quantitatively evaluate mixing proportions of waters from differing sources.

Quantitative evaluation of mixing proportions may be achieved by treating the uranium disequilibrium of ground waters as a natural experiment in isotope dilution analysis (Osmond, et al, 1968).

A. Wakulla Springs

This approach may be illustrated by an example from the Tallahassee area where the karstic nature of the topography results in a well-developed subterranean drainage system and, toward the south, several first magnitude springs. Wakulla Spring, one of the largest in Florida, has an average discharge of 10.3 cubic meters (365 cubic feet) per second (U. S. Geologic Survey, 1966). Hydrologic data, including large seasonal fluctuations of spring discharge correlative with local precipitation, suggest that a large portion of the water is derived from local recharge in the karst area (Kaufman, 1968). An alternative, in part, is that the source is to the north, with flow down the gradient of the piezometric surface.

Natural waters may be considered an isotope dilution system inasmuch as variations in the U-234/U-238 activity ratio can occur only at the time uranium is added to the system through leaching of enclosing rock or by mixing with other uranium-bearing waters; once uranium is in solution, the activity ratio is unaffected by dilution, precipitation, or changes in chemical state.

If an amount of water #1 is mixed with water #2 (each with its dissolved uranium) to produce a mixture, water #3, the following relationships hold;

$$(1) \quad V_1 + V_2 = V_3$$
$$(2) \quad M_1 + M_2 = M_3$$
$$(3) \quad M_1A_1 + M_2A_2 = M_3A_3$$
$$(4) \quad M_1 = C_1V_1$$

Where V is volume in liters; M is the amount of uranium in micrograms; C is concentration in µg/l; and A is the activity ratio, U-234/U-238. From these relationships, and letting V_1 be unity, the following two equations are derived:

$$(5)\quad M_2 = C_1 \frac{A_1 - A_3}{A_3 - A_2}$$

$$(6)\quad V_2 = \frac{C_1 + M_2}{C_3} - 1$$

These expressions can be used in two ways: (1) in the calculation of the relative mixing volumes of two waters when C and A values for the two source waters (#1 and #2) and the resultant mixed water (#3) have been determined, and (2) in deducing the amount of uranium and water (#2) that have been added to an initial water (#1) to produce a resultant water (#3). In the latter case, there are three unknowns, M_2, A_2, and V_2, in the two equations (5) and (6), and one of these variables must be estimated.

As an example in which three waters are analyzed, we might ask: What volume of water like that from Horn Spring (#2) must be mixed with a unit volume of water like that from Big Bend (#1) to produce water like that flowing from Wakulla Spring (#3) (Figure 8). Using equations (5) and (6), M_2 is 8.4 and V_2 is 17.4. Consequently, for every liter of Big Bend water, 17.4 liters of Horn Spring water would be required to yield 18.4 liters of Wakulla Spring water. As a check on the uranium balance, we can compute the necessary C_2 of Horn Spring water, obtaining 0.48 µg/l, almost precisely the value measured.

There are probably numerous hydrologic situations in which "closed system" assumptions can be made, the C and A values of three waters determined, and the mixing volumes calculated with confidence and accuracy. Requirements include: sufficient uranium (0.1 µg/l or more), diverse activity ratios, and a reasonable understanding of the hydrologic system--of which the latter probably contributes the greatest error to this approach.

Isotope dilution analysis cannot of course, define a mixing model; it does, however, set limits on possible models and develops the implications of these.

As an example of the second approach, again referring to Figure 8, successive aquifer points are compared and the additions of uranium and water between points deduced. This is useful because the aquifer system here is quite "open" in that rainwater is infiltrating from the surface and uranium is being leached from the aquifer rock. In this case, the observed variations in activity ratio of waters within the aquifer are

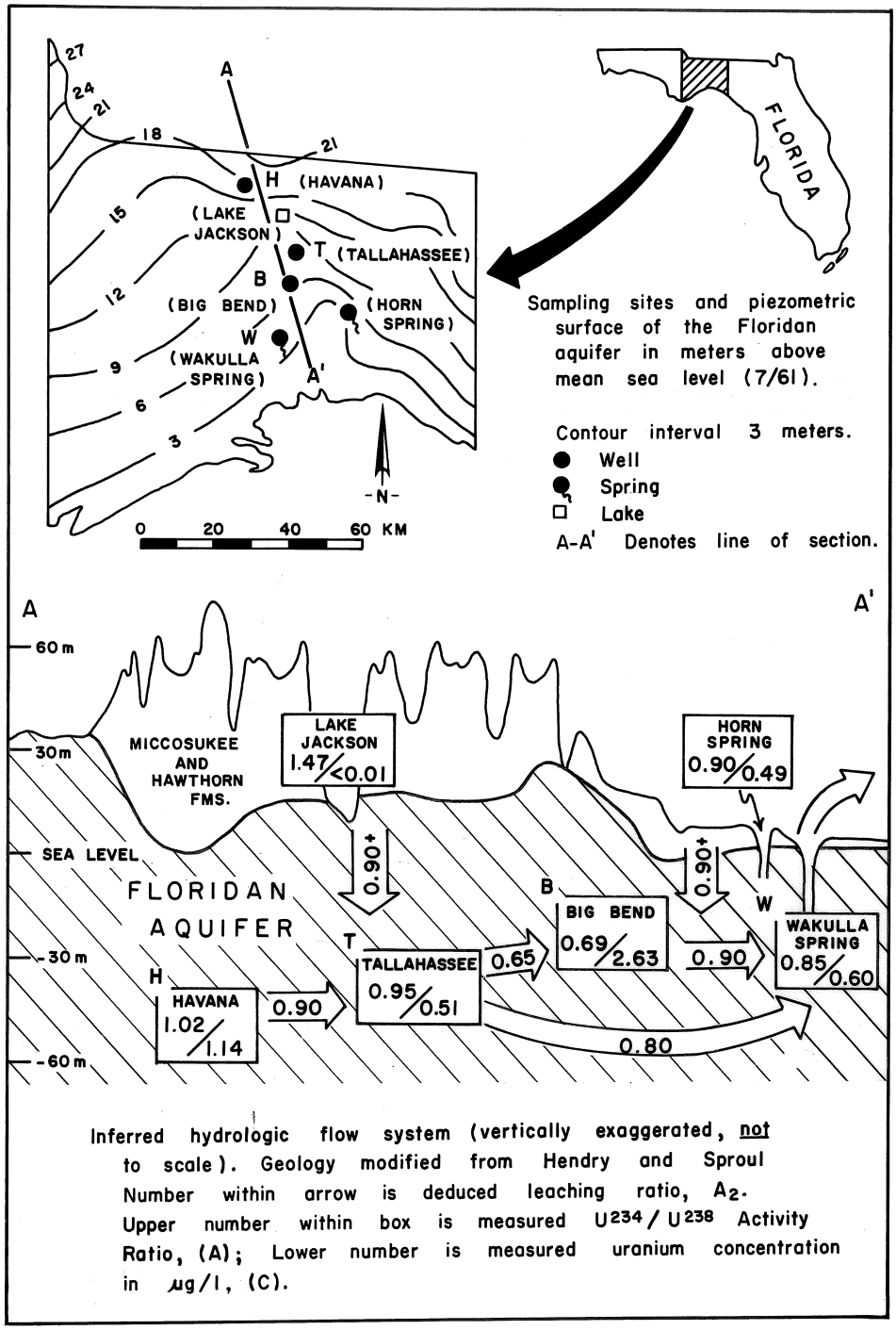


Figure 8. Composite hydrologic map and diagrammatic geologic cross section. Geology modified from Hendry and Sproul (1966). Composite portrays the inferred hydrologic flow system. Each box represents a sampling site showing activity ratio above and uranium concentration in µg/l below. The numbers within the arrows refer to inferred activity ratio of the uranium added to the water (leached from the rock) between sampling sites. All A and C values correspond to those used in Table 3.

systematic enough to permit "most probable" A_2 values to be assigned and thus M_2 and V_2 values to be calculated.

In estimating the A_2 value, the activity ratio, of the uranium leached between sampling points #1 and #3, the following aspects were considered: (1) aquifer waters here show a generally decreasing activity ratio for their dissolved uranium in the down-dip direction relative to the piezometric surface, (2) surface waters generally have activity ratios greater than 1.00, in agreement with the commonly observed isotope fractionation by leaching, (3) $A_2 - A_3$ must have the same sign as $A_3 - A_1$, and (4) whenever C_3 is significantly greater than C_1, $A_2 - A_3$ must be small. As a result of these considerations, all A_2 values were selected such that the range of $A_2 - A_3$ was .02 to .10, except for Tallahassee to Big Bend, where it was .01 to .06. Infiltrating waters were assumed to be contributing only small amounts of uranium; the activity ratio of these waters is indicated as being 0.90+ in Figure 8.

The results of these successive interval calculations based on the values of Tables 2 and 3 are shown in Table 4, in which the relative volumes, as well as the computed amounts of uranium which are added between Havana, Tallahassee, Big Bend, and Wakulla Spring, are also computed for comparison.

Since each V_2 is defined relative to each initial V_1, the total volume increment to the final water can be determined (last column of Table 4). Calculation shows that of the hypothesized sources for Wakulla Spring the more local sources predominate, and no more than about 8% could be contributed from as far away as Havana.

B. Silver Springs

The proposed Cross-Florida Barge Canal has precipitated considerable interest in the geohydrology of the Floridan aquifer in the area of Ocala and Silver Springs. Faulkner in a U.S.G.S. open file report (1970) summarizes the underground water flow pattern in this region, and has calculated the probable sources of water for the major effluence of the area, Silver Springs.

As a test of the utility of the uranium isotope technique for calculating water sources and mixing proportions, we chose this well documented system for sampling and analysis. We will accept Faulkner's conclusions as correct, and compare with them the isotopic results derived more or less independently of hydrologic data.

Table 3

Aquifer Interval (see Fig. 1)	Results of Analysis				Deduced Values	
	A_1 ratio	C_1 (µg/liter)	A_3 ratio	C_3 (µg/liter)	A_2 ratio	A_2 ratio range
H to T	1.02	1.14	0.95	0.51	0.90	0.85-0.93
T to B	0.95	0.51	0.69	2.63	0.65	0.63-0.68
B to W	0.69	2.63	0.85	0.60	0.90	0.87-0.95
T to W	0.95	0.51	0.85	0.60	0.80	0.75-0.83

Aquifer Interval (see Fig. 1)	Computed Values						
	M_2 (µg)	V_2 (liter)	V_2 range (liter)	C_2 (µg/liter)	Δ_M (percent)	Δ_V (percent)	Contrib. to Wakulla (percent)
H to T	1.60	4.37	2.8-9.1	0.37	140	440	8
T to B	3.31	0.45	<0.1-4.2	7.35	650	45	32
B to W	8.42	17.4	10.0-38.	.48	320	1740	60
T to W	1.02	1.55	0.7-4.1	.66	200	155	--

Additions of uranium and water between aquifer sampling points. The first row refers to the aquifer between Havana and Tallahassee, Florida, in which A_1 and C_1 are the activity ratio and concentration respectively, of the aquifer water at Havana, and A_3 and C_3 are the corresponding values at Tallahassee; A_2 is the estimated range of possible values for the activity ratio of uranium added between these two points. Values for M_2 V_2 and C_2 are calculated from Eqs. 5 and 6; M_2 is the amount of uranium added, V_2 is the volume of water added (the range of possible V_2 values is given, corresponding to the listed A_2 ranges), and C_2 is the resulting concentration of uranium if M_2 and V_2 describes a mixing water. The quantities Δ_M and Δ_V refer to the proportions M_2/C_1 and V_2/V_1, respectively. The last column follows from the various V_2 values calculated with respect to the flow model (Fig. 1).

Table 4

URANIUM CONCENTRATIONS AND URANIUM ISOTOPIC ACTIVITY RATIOS: SILVER SPRINGS REGION

Location or Well No.	U conc., ppb	U-234 / U-238
SCE 124	1.27 ± .04	0.84 ± .03
CE 47S	1.60 ± .02	0.96 ± .02
CE 48	0.57 ± .02	0.56 ± .02
CE 79	0.21 ± .03	1.09 ± .06
CE 39	0.13 ± .03	0.95 ± .10
CE 81	0.88 ± .04	0.94 ± .04
CE 33	0.47 ± .05	0.98 ± .07
BELLE VIEW	4.04 ± .03	0.56 ± .02
ORANGE LAKE	0.66 ± .12	1.04 ± .04
CE 30A	0.71 ± .03	1.47 ± .06
SCE 172	0.31 ± .04	1.05 ± .04
SCE 132	0.16 ± .02	1.42 ± .04
SCE 156	0.24 ± .03	1.27 ± .05
SCE 153	0.61 ± .03	1.26 ± .08
OCALA #3	1.08 ± .10	0.94 ± .02
OCALA:		
LIBBY MCNEIL	0.13 ± .02	2.43 ± .04
CE 42	0.01 ± .02	---- ± ---
LAKE WEIR	0.01 ± .02	---- ± ---
CE 61	0.10 ± .02	0.98 ± .04
CE 51	0.01 ± .02	---- ± ---
CE 55	0.01 ± .02	---- ± ---
CE 53	2.98 ± .26	0.85 ± .02
CE 131A	0.10 ± .04	1.19 ± .06
SALT SPRINGS	0.37 ± .03	1.30 ± .04
SILVER SPRINGS	0.71 ± .04	1.03 ± .02

The uranium data are listed in Table 4, and the sample sites are shown in Figure 9. The analytic data are also plotted on a graph of activity ratio versus reciprocal of concentration in Figure 10. (Several sample sites listed in Table 4 are not plotted in Figures 9 and 10. These samples contain too little uranium to analyze reliably, or were too far from the focus of the study area, or for other reasons were not considered to be important sources for Silver Springs water.)

The type of plot used (Figure 10) reveals unique and useful properties of the data. For example, the combining of two waters will produce a resulting water mixture whose activity ratio and reciprocal of concentration must fall on a straight line joining the plotted points of the two sources. The proportions of the two sources is a simple function (not linear) of the position of the resultant point on this line. This is, in effect, a graph of the mixing equations reported by Osmond, et al (1965) and discussed in an earlier portion of this chapter. In practice, one plots the possible sources to see if they do in fact, form a straight line relative to the resultant water, and if so, the equation is used to calculate the mixing proportions.

A simple extension of this procedure shows that a unique mixing proportions solution results when three possible sources are considered, provided that the plot of the resultant mixture falls within the triangle formed by the three plotted sources. For more than three sources, solutions are possible whenever the resultant water plots within the polygon formed by joining the proposed plotted sources. In the latter case however, a unique solution generally does not result; a certain range of possible mixing proportions can be calculated.

A straight-forward procedure for solving a complex source system, as in the case of Silver Springs, would be to select three proximal sources for the final resultant water (Silver Springs), and then select three sources for each of the proximal sources, etc., ultimately arriving at mixing proportions distributed among a number of primary sources.

Table 5 shows the results of a partial and tentative calculation of assignable proportions for sources for Silver Springs water. The resulting flow net is shown by arrows on the map of Figure 9, and also on the diagram of Figure 10. For this very rudimentary application of the isotopic analysis, the only selection rules for possible sources were: among the nearest (radially oriented) possible sources for a resultant water, choose three which plot as a relatively compact triangle and thus yield a unique mixing solution. On the diagrams, the dotted lines show inferred but not calculated contributions; except for one or two wells, these are excluded from the calculations summarized in Table 6.

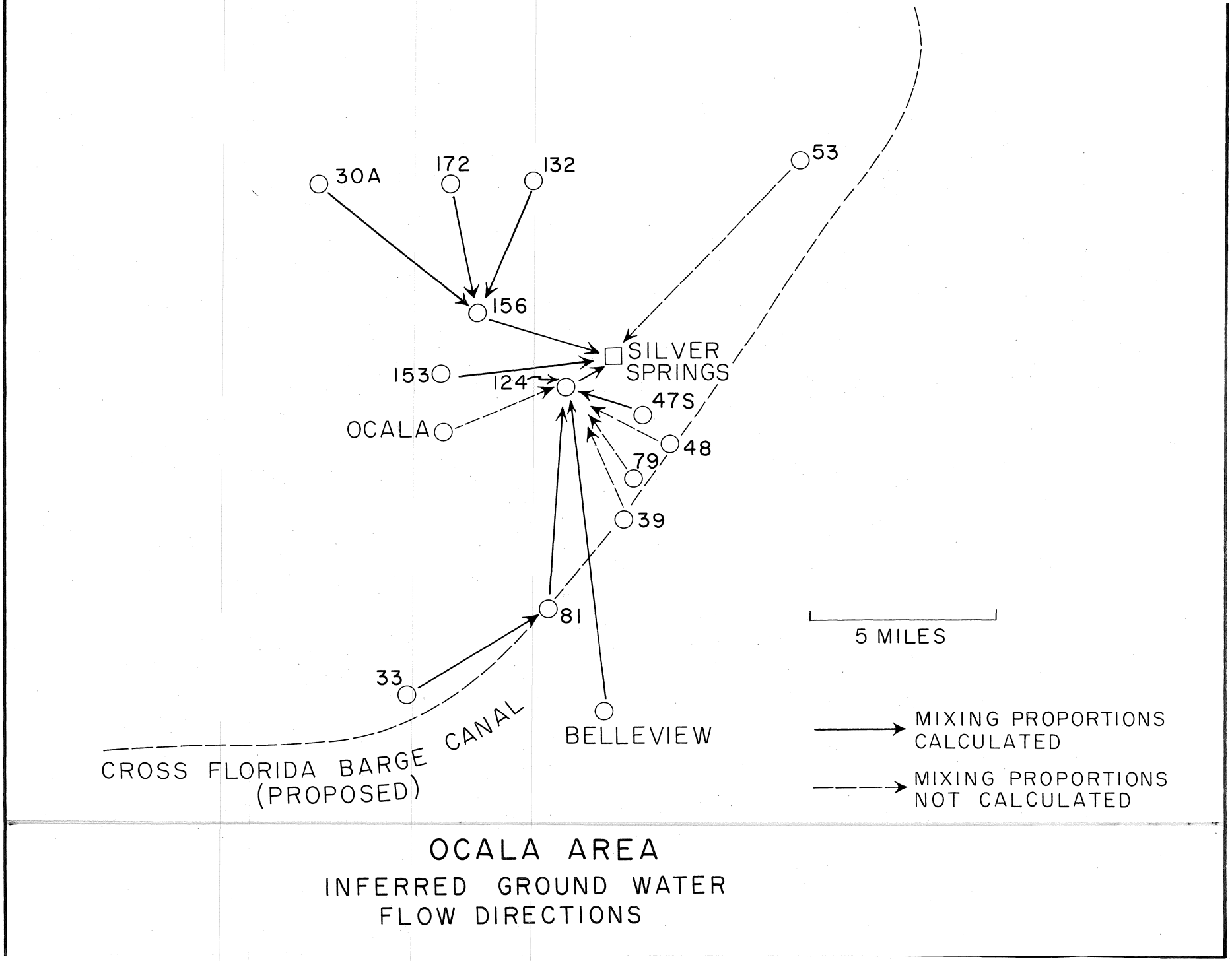


Figure 9. Ocala Area: Inferred ground water flow directions. Numbered circles are sampled well localities which satisfy the selection rules for the mixing calculations. Pattern of arrows from number to number matches that of Figure 10. In this diagram, geographic locations of sample points is only approximate.

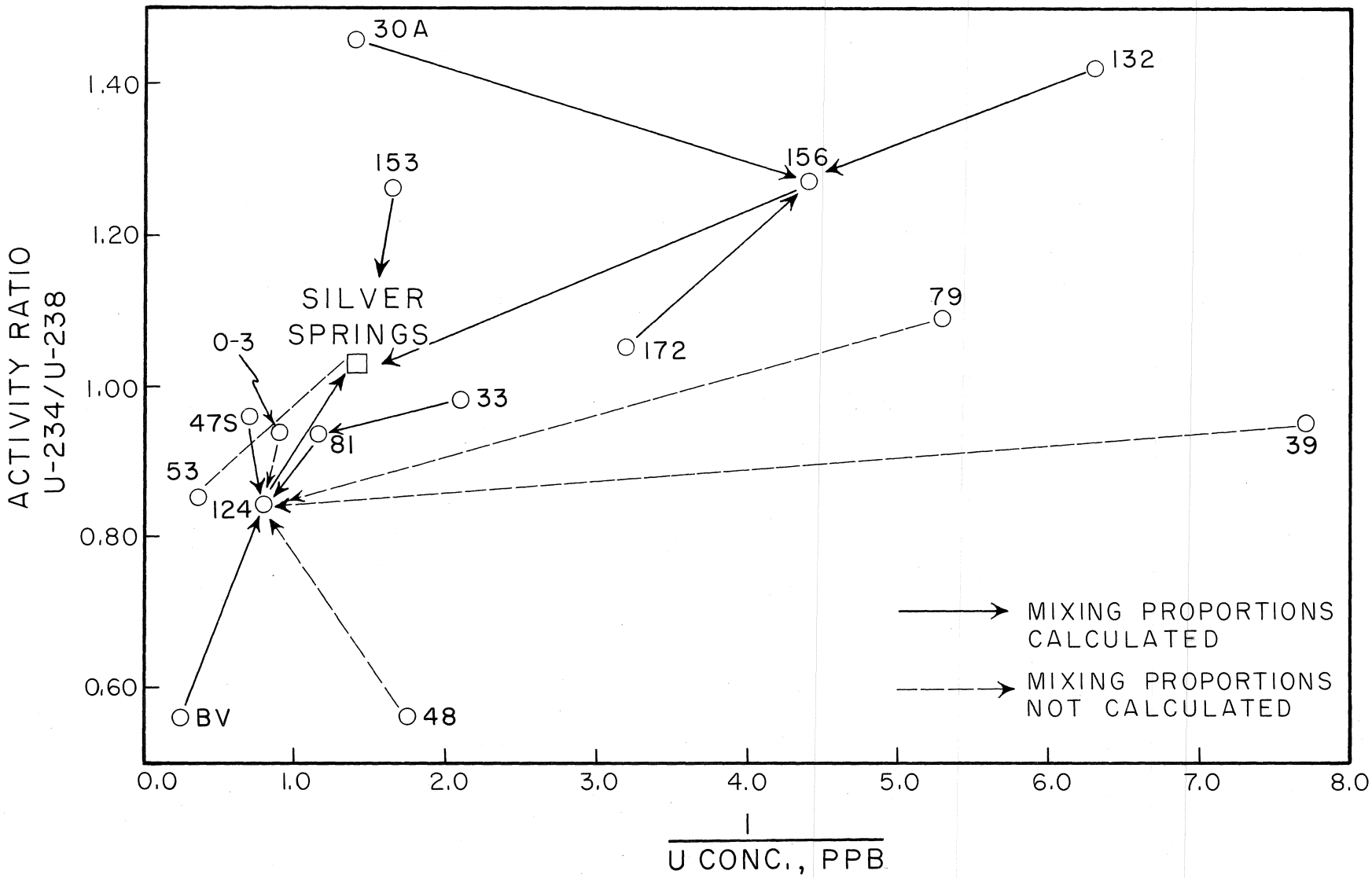


Figure 10. Activity ratio vs. reciprocal of concentration diagram of Ocala area samples. Numbered circles are plots of samples which satisfy the selection rules for the mixing calculations. Pattern of arrows from number to number matches that of Figure 9. This type of diagram permits immediate recognition of possible solutions to the mixing formula; however, exact mixing proportions must be calculated.

Table 5

MIXING PROPORTIONS

Resulting Mixture As In ----	Possible Sources As In ----	Proportions of Sources
A. SILVER SPRINGS	SCE 124	45%
	SCE 153	29%
	SCE 156	26%
B. SCE 156	CE 30A	6%
	SCE 172	33%
	SCE 132	61%
C. SCE 124	CE 47S	16%
	BELLEVIEW	8%
	CE 81	76%
D. SILVER SPRINGS	PRIMARY SOURCES	
	SCE 153	29%
	CE 30A	2%
	SCE 172	9%
	SCE 132	16%
	CE 47S	7%
	CE 81	33%
	BELLEVIEW	4%

Table 6

SOURCE OF SILVER SPRINGS WATER:
HYDROLOGIC vs ISOTOPIC CALCULATIONS

Source Zones (Faulkner)	Representative Sources (This Report)	Percent Contribution to Silver Springs (Faulkner)	(This Report) *	(This Report) **
1-5	33,81,BV	27%	37%	28
8-10	0-3	4%	5%	4
14-17	30A,132,172,153	45%	51%	49
22-25	47S	1%	7%	5
All others	-----	23%	---	23

*As calculated
**Corrected for 23% "others"

Table 6 compares the results of this calculation with that of Faulkner. The wells which were computed to be 'primary sources' according to the selection rules are grouped according to the corresponding radial geographic zones of Faulkner, and the percent contributions of source zones compared. As initially calculated the isotopically computed sources necessarily add up to 100%. However because the data points are limited and the calculation only partially completed, the figures are arbitrarily reduced by 23% in the last column to allow for the source zones of Faulkner.

The resulting percent contributions as computed here show a truly remarkable agreement with those of Faulkner, in fact, the agreement must be in part fortuitous. Among the factors which might have adversely affected the comparisons, but did not or else did so in a compensating way are; appreciable infiltration of ground water near the spring, appreciable solution of uranium within the aquifer flow system, seasonal variations in well sample uranium or in hydrologic flow pattern, strong depth dependence of flow pattern, etc. It should be noted that a more sophisticated treatment of the procedures would allow the computation of increments of surface recharge by low activity water (points at the extreme right of the ratio-concentration diagram) and also increments of newly dissolved uranium within the aquifer (points at extreme left in the diagram).

The point to be emphasized is that the isotopic flow pattern was deduced from a relatively small number of data points, whose geographic position was the only hydrologic factor considered. Even if other systems should prove to be less favorable with respect to uranium geochemistry, e.g., low uranium concentration or small isotopic variability, it seems that a combination of uranium-isotopic and standard hydraulic analyses would be a very useful approach to ground water studies.

5. TRITIUM ANALYSIS: A MODIFICATION OF THE BENZENE SYNTHESIS METHOD

Introduction

Tritium is produced naturally in the upper atmosphere by interaction of cosmic ray produced thermal neutrons with nitrogen and oxygen. It is formed artificially in nuclear fusion reactions, and since 1954, when the first major thermonuclear device was detonated in the Pacific, thermonuclear test explosions have produced worldwide pulses of tritium. These rapid increases in the abundance of the sole radioactive isotope of hydrogen that occur in nature, coupled with the fact that tritium is an actual part of the water molecule, make tritium an important hydrologic tracer.

The method herein described was initially developed by Tamers et al (1961). Tamers and Bibron (1963) and Tamers (1964) developed the technique somewhat further. The method is closely related to a popular means of radiocarbon analysis described by Noakes et al (1965). The modification of the benzene synthesis method for tritium analysis described in this paper simplifies the procedure further and has been shown to produce results that agree very satisfactorily with data from other laboratories. The method should prove valuable to the hydrologist who wishes to perform his own tritium analyses, and is particularly suitable for a limited production volume.

Theory

The water sample containing tritium as a contaminant is converted into acetylene by hydrolysis of calcium carbide. The tritiated acetylene is then trimerized to benzene using an extremely efficient vanadium catalyst (Noakes et al, 1965). A constant isotope effect lowers the tritium activity per gram hydrogen of the benzene to about 80% of that in the water sample. Hence a constant portion of the tritium, originally in the water sample, now satisfies the carbon bonds of the benzene molecules in the synthetic benzene. The benzene is of high purity and is an excellent counting liquid when mixed with the primary fluor PPO. The tritium beta radiation is then counted in a liquid scintillation counter. Pertinent chemical equations in the procedure are:

$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2 \qquad (1)$$

$$3C_2H_2 \xrightarrow[\text{vanadium catalyst at 25 in. vacuum}]{} C_6H_6 \qquad (2)$$

Operational Procedure

A schematic diagram of the benzene synthesis apparatus is shown in Figure 11. On the left is the acetylene generator G and a 50 ml burette that permits the drop-by-drop addition of the water sample to the calcium carbide contained in a 3 l flask. The entire system was evacuated, flushed with argon, then evacuated again to 30 inches vacuum. The 3 l flask is partially immersed in an ice water slush to remove heat from the flask during the exothermic hydrolysis and to condense any steam that may form. In addition, the slush maintains a constant temperature, which stabilizes the reaction chemically and isotopically. Spattering is avoided by introducing the water below the level of the carbide, and excessive absorption of water by the residue is prevented by using a large excess of CaC_2 and slowly adding the water. In this procedure, 120 grams of carbide is reacted with 50 ml of sample water, which is the volume that empirically produces 17 l of C_2H_2 (STP). The use of an auxiliary tank storage volume of 17 l is not arbitrary but reflects the volume of acetylene necessary to yield 17 ml of benzene with a conversion efficiency of 75%. Typical efficiencies are usually in excess of 90%, however.

Adjacent to the acetylene generator, two purification columns (P_1 and P_2) are connected in series. The first contains powdered calcium carbide and is water cooled. This column is used to convert any water vapor evolved in the generator to C_2H_2. The next column contains, in the upper position, reagent grade $PbCl_2$, which extracts sulfides, and in the lower position, P_2O_5, which removes traces of water and ammonia. The acetylene is passed through trap A, which is cooled by a dry ice alcohol slush bath to remove gases that are condensible above -78°C. The purified acetylene is finally collected in a liquid nitrogen cooled trap (trap B).

The acetylene to benzene conversion is a one-step catalytic reaction. The frozen acetylene is permitted to sublime at room temperature from the cold trap (B) through the storage tanks (S) onto the evacuated catalyst column(CC). The column contains 375 grams of vanadium activated silica alumina catalyst (available through John E. Noakes, Oak Ridge Institute for Nuclear Studies, Oak Ridge, Tennessee). The catalyst has been baked under vacuum at 380°C for 3 hours to remove associated water, which inhibits the reaction. The catalyst is allowed to cool before mounting on the system and is cooled with ice water during the conversion reaction. Cooling is of paramount importance for high yields because it prevents both vapor blocks and surface area contamination of the catalyst pellets. In addition, cooling prevents appreciable pyrolysis of acetylene and benzene into more polymerized hydrocarbons. Upon completion of the reaction (45 minutes to 1 hour),

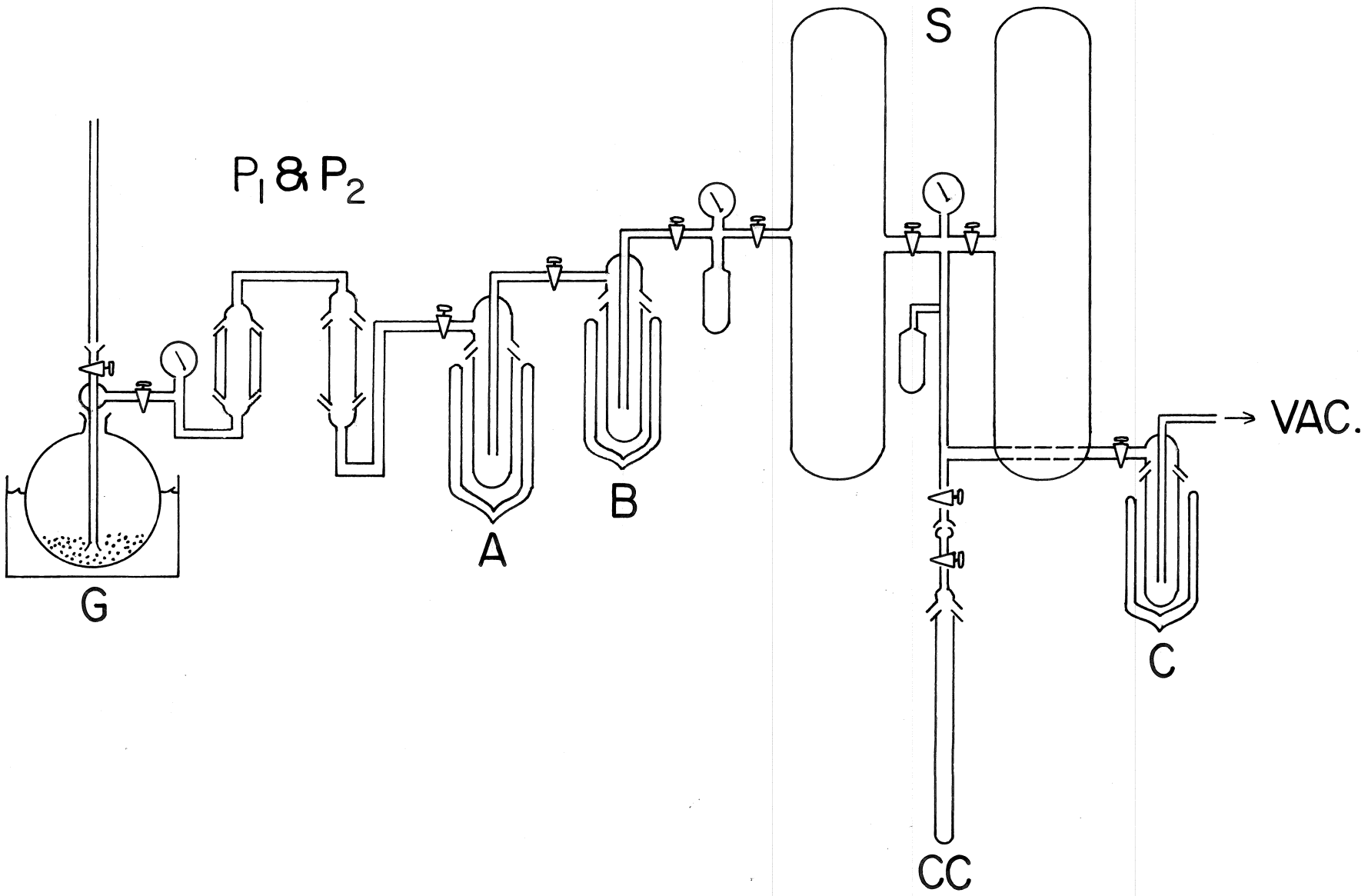


Figure 11. Diagrammatic sketch of benzene synthesis system. G: acetylene generator. P_1,P_2: purification columns. A,B,C: cold traps. S: storage tanks. CC: catalyst column.

a heating jacket is applied to the catalyst column, raising the temperature of the column to 100°C, and the benzene is drawn off under vacuum into a dry ice alcohol slush cooled trap (C).

A 15 ml aliquot of the synthetic benzene is placed in a 20 ml nylon counting vial (obtained from Nuclear Chicago, 333 E. Howard Ave., Des Plaines, Illinois 60018) and 60 mg of the primary fluor, PPO, is added. Sample preparation takes place in a photographic darkroom under red light. This procedure eliminates phosphorescence in the vial and its contents, thereby providing minimal background fluctuation during the counting period. The tritium beta radiation is counted to the desired error, and the sample count is preceded and succeeded by efficiency and background counts. In this way, any possible counter fluctuations are closely monitored. An external standard (^{137}Cs) is employed to check for sample quenching; however, no quenching has been observed to date.

Fractionation Effect

Reproducibility of fractionation effects for hydrogen isotopes is the keystone of the benzene synthesis method of tritium analysis.

Tritiated water analyzed by Ostlund at the Marine Institute of the University of Miami was processed by the benzene synthesis method at full strength, as well as at half and quarter strength dilutions. The mean fractionation effect for tritium equals 19.3% ±0.2%.

Several interlaboratory cross checks were performed with the cooperation of Ostlund at Miami and the U.S. Geological Survey Tritium and Radiocarbon Counting Laboratory in Washington, D.C. Results of the comparison checks are shown in Table 7. Agreement is surprisingly good; the two data sets agree within one sigma error in most cases. The errors associated with our answers are large, mainly because of the high background count rate of our liquid scintillation counter. Additional lead shielding might be helpful. The lower detection limit of the system is about 10 TU (10 tritium atoms per 10^{18} protium atoms) presuming absolute counter stability.

Discussion

Overall, several factors have proved important in the determination of tritium by this method:

Table 7

INTERLABORATORY CHECKS

No.	Description	Known TU	Measured TU
1	groundwater*	70.5 ± 3.9	71.2 ± 5.5
2	groundwater*	13.2 ± .08	15.4 ± 11.
3	rainwater	31. ± 1.2	27.7 ± 8.4
4	rainwater	40.9 ± 2.0	43.9 ± 8.5
5	rainwater	31.6 ± 1.4	30.9 ± 6.7
6	rainwater	54.3 ± 2.6	51.1 ± 10.

* Collected and analyzed by the U.S. Geological Survey, Tritium and Radiocarbon Counting Laboratory, Washington, D.C.
Collected and analyzed by Ostlund at the University of Miami.

1. The stability of counter background and counting efficiency is of prime concern since counting times are long when the sample is of low specific activity, i.e., 48 hours. Most of the modern liquid scintillation counters that employ ambient temperature photomultiplier tubes meet this requirement within acceptable limits.

2. The choice of a calcium carbide that is low in sulfides is imperative since excess sulfides quench the catalyst and benzene counting liquid and contribute heavily to the loss of sample hydrogen as H_2S. Carbide of low sulfide content may be purchased from Research Inorganic Chemical Company of Sun Valley, California. This carbide is 'dead' with respect to ^{14}C. Spillover of radiocarbon beta activity into the tritium counting channel would result in variable count rates that are difficult to correct because of the low specific activities involved.

3. Successful use of the catalyst is dependent upon complete removal of associated water. The catalyst will maintain its own vacuum during the conversion. Generally, the lower the pressure, the higher the benzene yield.

Conclusion

The distinct advantages of this modification to the benzene synthesis method for tritium analysis are three.

1. Samples may be prepared easily by the isotope hydrologist and/or his technician.

2. In its present form, without enrichment, the system is suitable for groundwater studies where large volume sample processing is not required.

3. Results compare favorably with those from other laboratories.

6. TRITIUM HYDROLOGY OF THE TALLAHASSEE, FLORIDA AREA

Field Methods and Procedures

Samples of ground and surface waters in Leon, northern Wakulla, and eastern Gadsden counties were taken over a two year period. Sampling sites consisted of wells, both table and artesian, Wakulla Spring, the St. Marks River, and Lakes Iamonia and Jackson. The sample sites were chosen to represent, broadly, the local geohydrologic environment. Determination of sample tritium concentration was done in part at Miami Institute of Marine Sciences, in part, by Isotopes, Inc., Westwood, New Jersey and, in part, at the Florida State University using the newly developed benzene synthesis-liquid scintillation counting method described in the previous section.

Sample Locations and Analytical Results

A sample location map is shown in Figure 12. The specific location and description of each sample point is presented in Table 8. Many of the groundwater samples were drawn from the Floridan aquifer. The Floridan aquifer is composed of marine limestones and dolomites which range from Eocene through Miocene in age. The formations function as a unit because their porosity and permeability are similarly developed. The formations which make up the Floridan aquifer in the Tallahassee area are the Upper Eocene Crystal River formation, the Oligocene Suwannee limestone, and the lower Miocene St. Marks formation (Hendry and Sproul, 1966). The Floridan aquifer is overlain by surficial sands, silts, and clays of the Miocene Hawthorn formation. The overlying veneer of sediments is of highly variable thickness. Additional information on the hydrology and the geology of the study area may be obtained from Sellards (1917), Moore (1955), Gremillion (1965), Hendry and Sproul (1966), Stringfield (1966), and Sever (1966).

In conducting a study where natural rainout tritium is to be used as a tag for water, which is the case with the present problem, several questions must be answered:

1. What are the input activities of tritium from precipitation and what have they been in the past?

2. What are the tritium activities at present in the ground waters of the study area?

3. What were the natural groundwater tritium activities?

(Stewart and Farnsworth, 1968)

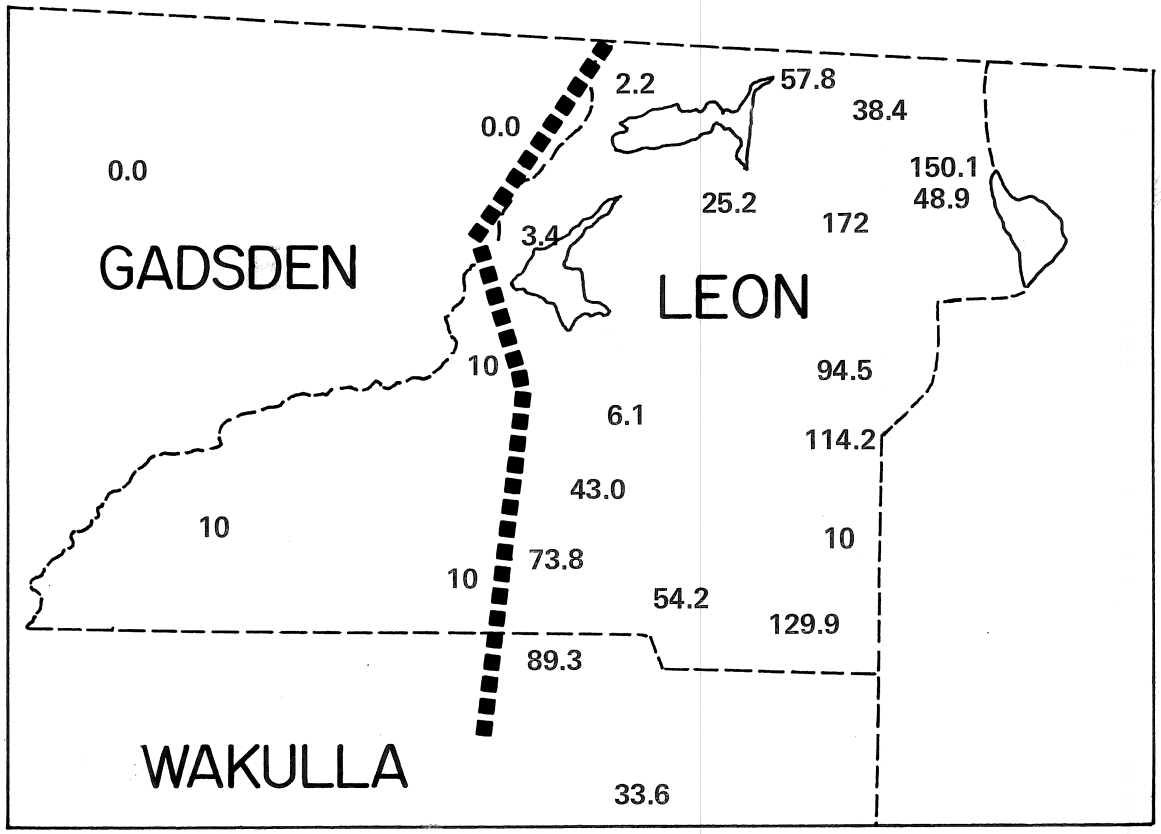


Figure 12. Map of Tallahassee and surrounding area showing tritium content of Floridan aquifer well water. Dashed line separates slow (left) and fast (right) recharge regimes.

Table 8

TRITIUM CONCENTRATION OF SELECTED WATERS
WITH PERTINENT SAMPLING INFORMATION

Sample Number	Date of Collection	Sampling Location and Details	T.U.	Date of Analysis
LG-01	1-27-67	#6 Municipal Well at Lafayette Park, Tallahassee, Fla., Wln. IN-IE, 30cc, depth 413 ft., cased to 170 ft. open only to Suwannee L.S. at 170 ft.	6.1 ± 00.5*	9-20-67
LG-02	10-15-67	Lake Jackson nr. Capital Circle Trk. Rt., Wln. 1N-1W-566 Depth 194 ft. cased to 140 ft., open only to Suwannee L.S., 140 ft.	13.9 ± 01.0*	1-03-68
LG-03	10-22-67	N.W. Lk. Iamonia Shore, Leon Co., Wln. 3N-1E-Zod, depth 268 ft., cased to 260 ft., open only to Suwannee L.S. at 260 ft.	2.2 ± 00.3*	1-03-68
LG-04	10-20-67	Jctn. U.S. 319 & S-261 at Big Bend Trk., Rt. Wln. 1S-1E-19C, depth 100 ft., cased to 70 ft., open only to St. Marks	43.0 ± 31.0*	1-03-68
LG-05	10-20-67	Wdvlle. Mncpl. Well, Wln. 2S-1E-8dd, depth 183 ft., cased to 32 ft., open to St. Marks & Suwannee L.S. at 15 ft. and 110 ft. respectively	54.2 ± 03.7*	1-03-68
LG-06	11-16-68	Well at Chaires Gen. Str., No well info. available	114.2 ± 09.2***	1-23-69

Table 8 - Continued

Sample Number	Date of Collection	Sampling Location and Details	T.U.	Date of Analysis
LG-007	11-15-68	Well at Sunny Hill Farm, Wln., 3N-2E 14-d, depth 148 ft., cased to 103 ft., open only to Suwannee at 103 ft.	38.5 ± 08.4***	1-28-69
LG-008	11-15-68	Well S. of Iamonia, Wln., 3N-ZE-nc, depth 33 ft., Shallow well	57.8 ± 05.8***	1-31-69
LG-009	11-15-68	Well on the N.W. Shore Lk. Micc., Shallow well, no info. available	151.0 ± 08.8***	2-03-69
LG-010	11-15-68	Well at Gen. Str. Town of Micc., Wln., 2N-3E-8bb, depth 235 ft., open to Hawthorn at 65, St. Marks at 105, Suwannee 185 ft.	48.9 ± 08.4***	2-06-69
LG-011	11-15-68	Well at Felkel 2N-2E-3cb, depth 179 ft., 50 ft. to Hawthorn, 80 ft. to St. Marks, 110 ft. to Suwannee	17.2 ± 13.4***	2-09-69
LG-012	11-15-68	Well near Gardner 1N-2E-15 ca, depth 220 ft., cased to 177 ft., open to Suwannee L.S. at 185 ft.	94.0 ± 13.8***	2-13-69
LG-013	11-16-68	1.75 mi. E. Corey on 261A Wln., IS-ZE-29cb, depth? 70 ft. to St. Marks, 75 ft. to Suwannee L.S.	$\leq$10 ***	2-16-69
LG-014	10-25-68	Well Lk. McBride Elem. School, 3 mi. E. of U.S. 319 Rd., connecting Brdfdvlle and Cntrvlle, no info. available	26.2 ± 11.2***	2-20-69

Table 8 - Continued

Sample Number	Date of Collection	Sampling Location and Details	T.U.	Date of Analysis
LG-015	11-17-68	Well at Confdrt. Inn Spr. Blb Ochlockonee, Wln., 1N-2W-23 da., depth 254 ft., cased to 84 ft., open to St. Marks at 40 ft.	≤10.00 ***	2-22-69
LG-016	11-17-68	Well 1 mi. N.W. Int. 261 with 151 Wln., 1N-1E-16d., depth? No info. available	≤10.00 ***	2-26-69
LG-017	11-16-68	Well at Nat. Bridge nr. Wdvl. Wln., 2S-2E-29 da., depth 175 ft., cased to 163 ft., 5 ft. to St. Marks. 36 ft. to Suwannee L.S.	129.0 ± 09.3***	3-01-69
LG-018	11-16-68	Well nr. Bradford Brook on Rt. 61 S., Wln. 1S, 1W-26cb, depth 220 ft., cased to 140 ft., open to Suwannee L.S. at 140 ft.	73.8 ± 10.8***	3-04-69
LG-019	11-17-68	Well at WFSU transmitter Sta. in Apalachiocola Nat'l. Forest, Wln., 1S-4W-35aa, depth 230 ft., cased to 132 ft., open to Jcsn. Blf. at 50 ft. and Hawthn. at 61 ft.	≤10.00 ***	3-07-69
LS-001	10-10-67	Surface sample of Lk. Jsckn. wtr.	115.0 ± 08.0*	1-03-68
LS-002	10-10-67	Surface sample of Lk. Iamonia wtr.	113.0 ± 08.0*	1-03-68
LS-003	8-19-68	Sample of St. Marks Rvr. wtr. at Natrl. Bridge, near Woodville	21.2 ± 03.8***	11-19-68
LP-01	8-06-68	Rainwater collected on FSU Campus during afternoon thunderstorm	13.4 ± 06.3***	8-13-68

Table 8 - Continued

Sample Number	Date of Collection	Sampling Location and Details	T.U.	Date of Analysis
WG-01	10-20-67	Wakulla Co., 4 mi. N. of Wakulla Spring on Rt. 61, depth 43.5 ft., open entirely to St. Marks	89.3 ± 06.3*	1-03-68
WS-01	1-27-67	Wakulla Spring surface wtr., sample taken from pier	36.5 ± 01.5*	9-20-67
WS-02	10-10-67	Wakulla Spring surface wtr., taken over cave	31.3 ± 02.1*	1-03-68
WS-03	10-10-67	Wakulla Spring as above at 50 ft. depth using Van Dorn Bottle	32.8 ± 02.2*	1-03-68
WS-04	10-10-67	As above, but at 85 ft. depth	33.7 ± 02.3*	1-03-68
GG-01	2-15-68	Havana Municpl. Well, located at T3N-R2W-SEC26, Gadsden Co., depth 692 ft., cased to 418 ft.	00.0 ± 00.18**	3-22-68
GG-02	2-15-68	Sprnfld. Elem. Schl., nr. Quincy, Gadsden Co., located at T2N-R4W-SEC5ab, depth 467 ft., cased to 318 ft.	00.0 ± 00.18**	3-22-68

* Analysis performed by Isotopes, Inc.
** Analysis performed by H. G. Ostlund at Miami Marine Institute
*** Analysis by E. I. Wallick using benzene method

To document tritium input to surface and ground waters, the United States Geological Survey established a network in 1958 for collecting and testing rainwater samples for tritium activity. One such station, operated by the Survey is at Ocala, Florida, approximately 170 miles southeast of Tallahassee. Although the Ocala station is the closest to the study area, the following argument must be understood if the significance of these data are to be evaluated.

It has been observed that rain sampling stations near the oceans which receive their precipitation from oceanic air masses have rain which is low in tritium due to great oceanic dilution effects. In contrast, precipitation at continental stations is rather high in tritium. The maximum tritium rainout occurred in the summer of 1963 after a series of nuclear tests that winter. The tritium rainout has declined each subsequent year as an exponential function. Data for the Ocala station alone was obtained from the U.S.G.S. office there and graphed. The months of greatest tritium rainout are June and July. This is so because the greatest amount of precipitation falls at Ocala when meteorological conditions favor greatest tritium concentration in precipitation.

The third requirement for tritium study is a knowledge of the tritium background against which tritium levels may be compared. In the Tallahassee area, we may safely assume that there is negligible tritium background for several reasons:

1. Tritium levels before 1952 ranged from 2 to 10 T.U. and, because Tallahassee receives most of its precipitation from maritime air masses, these levels would have been fairly low initially.

2. In addition, the effects of time and dilution would have reduced tritium levels even further.

3. Although waters in the eastern portion of the study area are generously tagged with tritium, those in the west are virtually background.

Figure 12 is a map which indicates the areal distribution of tritium concentration in the waters of the Tallahassee area. The ± errors associated with the tritium determinations are to be found in Table 8, and are based on the 0.95 confidence level i.e., 2 significance level. The 0.95 error cited is dependent only on counting statistics and does not consider any systematic error.

These data show that waters in western Leon and eastern Leon and northern Wakulla counties have a relatively high tritium content. The tritium concentration of surface and shallow ground waters lying above the Hawthorn formation

aquiclude was much higher than that of the deeper artesian waters of the Floridan aquifer. The range of tritium concentrations is from 0.0± .18 T.U. to 151.0± 8.8 T.U.

Discussion of Results

Several important factors which influence the tritium concentration of groundwater at an observation point are:

1. Tritium input levels are affected by the time, intensity and tritium concentration of precipitation and the distance this precipitation must travel to reach the recharge area;

2. Evapotranspiration of precipitation;

3. Rates of diffusion and hydrodynamic dispersion.

(Stewart and Farnsworth, 1968)

With reference to 1. above, it is important to realize that heavy precipitation resulting in high total tritium rainout, rather than high concentration alone, is of more significance hydrologically.

Evaporation and transpiration may cause the tritium input to differ from the input expected when only the tritium concentration of precipitation from the principal recharge area is considered. In the Tallahassee area, evapotranspiration rates are high owing to the large areal extent of several lake basins, dense foliage, warm climate and good ventilation.

The third factor, mentioned above, is associated with mixing and dispersion. Should permeabilities be anisotropic, and flow patterns complex, then tritium concentrations in groundwater may not closely resemble tritium rainout.

Keeping these factors in mind, we shall draw some conclusions about the geohydrology of the Tallahassee area in light of the tritium in precipitation from Ocala, and tritium determinations in local ground and surface waters.

The most prominent observation of the study is the apparent absence of tritium in groundwaters sampled in western Leon and Gadsden Counties. Evidently, no local recharge occurs here as suggested by the very low tritium levels. Also, because fairly high and very low activity waters are juxtaposed, no significant lateral communication takes place in an east-west direction. High tritium concentrations in groundwaters of eastern Leon and Wakulla counties indicate rapid recharge.

Tritium concentrations fall below about 151 T.U. in waters of the eastern sector, and the observed range is equivalent to that found in recent rainfall. A tentative age for waters in the shallow aquifer is between zero and two years old based on the fact that tritium levels in rain began to fall within the observed range only as early as August, 1967. Tritium concentration of rainwater preceding this date are much higher due to the nuclear tests of winter, 1963.

Generally then, waters of the western sector of the study area are devoid of tritium suggesting an origin as rain prior to 1952, year of the first fusion bomb test. Tritium levels in the shallow groundwaters of eastern Leon and northern Wakulla Counties are very young waters with an origin as rain within the last two years.

Some observations have been made on a more intensive level. In northern Leon County, there is an increase of tritium activity toward the east, suggesting that recharge increases in the direction of Lake Miccosukee.

Water leaving the Floridan aquifer at Wakulla Spring, the principal discharge point for the study area, had a tritium content of 33.6 T.U. when sampled during the "dry season" during January, 1968. A tritium content 89.3 T.U. was observed in a shallow water well some four miles up-gradient from the spring. Tritium in rainout at Ocala during this time ranged from 20-30 T.U. Tritium content of water of the No. 6 municipal well in Tallahassee, sampled in January, 1967, was 6.1 $\pm$0.5 T.U. Tritium levels in rain at this time, were 50-70 T.U. The relative stability of the tritium content of Wakulla Springs water from the "dry season" in 1967, to that of 1968, is certainly worthy of note. It is reasonable that very low tritium concentration is attributed to the deeper waters of the Floridan aquifer which travel south to Wakulla Spring. The 6.1 T.U. Tallahassee water, the 13.9 $\pm$1.0 T.U. Lake Jackson well water, and the 2.2 $\pm$0.3 T.U. Lake Iamonia well water are indicative of low tritium in deep artesian waters. The reader is referred to Table 8 for the depths of these wells and other particulars. The low tritium deep waters apparently mix with the younger tritium rich waters of the shallow aquifer to yield water of an intermediate tritium concentration. This water is discharged at Wakulla Spring, and at numerous other springs and streams.

Given: T.U. Deep Water = 6.1 T.U.
T.U. Shallow H_2O = 84.2 T.U.
T.U. Spring H_2O = 33.6 T.U.

Let: x = the fraction of water of tritium content 6.1 T.U.
y = the fraction of water of tritium content 84.2 T.U.

then,
$$x + y = 1$$
$$6.1x + 84.2y = 33.6$$
$$6.1x + 84.2(1-x) = 33.6$$
$$x = .65$$
$$y = .35$$

A rather rough estimate of mixing coefficients for water of Wakulla Spring during the dry season is, then, 65% deep water and 35% shallow groundwaters.

APPENDIX A:

DETAILED METHODS AND ANALYTICAL PROCEDURES FOR URANIUM ANALYSES

Water Samples

1. Water samples of 14-21 liters were collected in duplicate from each source in one-gallon bottles (alternating a bottle of "A", then a bottle of "B", etc.). In collecting, the samples were passed through a 37 micron sieve to remove any coarse particulate matter that might influence results.

Duplication is necessary to guard against the possibility of laboratory contamination (i.e., the "A" and "B" fractions must be in agreement or they both are suspect). The alternation of collection of "A" and "B" fractions is thought to aid in achieving agreement between "A" and "B" fractions in that it reduces the possibility of one fraction being disproportionately influenced by factors such as drawdown in a small well.

2. Prior to water collection, tracer-carrier solutions are prepared in the laboratory so that a predetermined amount of U-232 spike and iron carrier may be equilibrated with each bottle of sample at the time of collection.

The tracer-carrier solution consists of:

A) U-232 spike of known specific activity and in an amount approximately equal to the expected natural uranium activity of the sample. U-232 is a non-naturally occurring nuclide which was provided under a loan agreement by the U.S. Atomic Energy facility at Oak Ridge.

B) Fe^{+++} carrier (13 mg Fe^{+++} per liter of sample in the form of $Fe(NO_3)_3 \cdot 9H_2O$).

C) 25 ml 16 N HNO_3 (sufficient to cause a pH of 1 or less in 3.5 liters of sample).

3. Samples are placed in a water bath and taken to boiling temperature for one hour to aid in removing dissolved gases, especially CO_2, which in subsequent chemical processing could possibly form sufficient $(NH_4)_2CO_3$ to act as a holdback carrier by complexing with U to form highly soluble carbonate-uranyl complexes.

4. While still hot, the sample is stirred; and the U is almost quantitatively coprecipitated with ferric hydroxide formed by the addition of sufficient NH_4OH to attain a pH of 9.

The high temperature of the solution aids in the coagulation of the gelatinous ferric hydroxide precipitate.

5. The precipitate is allowed to settle overnight and is then decanted, centrifuged, dissolved in HCl, evaporated, and redissolved in 8N HCl. It was found that one-gallon disposable plastic bottles, such as milk is sold in, were well suited to heating in the water bath and facilitated decanting by puncturing the bottle well above the precipitate level.

6. The large amount of iron contained in the 8N HCl solution is mostly removed by solvent extraction with an equal volume of isopropyl ether equilibrated for 30 seconds in a separatory funnel.

7. The sample is heated to remove traces of ether and then is evaporated with 5 drops of $HClO_4$ to remove any remaining organics.

8. The sample is redissolved in 10N HCl for ion exchange.

Ion Exchange

1. The resin used is Dowex 1-X8, 100-200 mesh, ionic form Cl^-, an anion exchange resin.

2. The ion exchange columns consist of a resin bed of approximately 1 cm x 14 cm topped by a 50 ml reservoir and constricted and plugged at the bottom with glass wool.

3. The resin is pretreated in the column by washing the resin with acids in the reverse order that the acids are used in the exchange process.

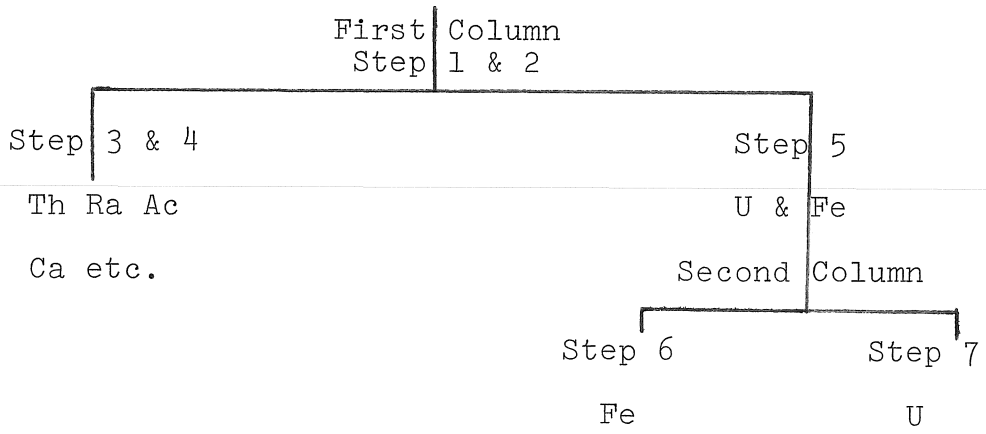
4. Add the sample to the column in 10N HCl; after the sample has passed through the column, the column is washed with 20 ml 10N HCl.

5. Elute uranium from column with 30 ml 0.1N HCl, evaporate with drops $HClO_4$, and redissolve sample in 7N HNO_3.

6. To a pretreated new column, add the sample in 7N HNO_3; after the sample has passed through the column, the column is washed with 20 ml 7N HNO_3.

7. Elute uranium from column with 30 ml 0.1N HCl and evaporate with 5 drops $HClO_4$ for electrodeposition.

FLOW CHART



Electrodeposition

1. The sample is dissolved in 5 ml 2M NH_4Cl (pH 2.5), in a deposition cell consisting of a 1.5 cm chimney and 3 cm stainless steel planchet, and deposited for 30 minutes at 12 volts and 1 amp.

2. While the current is still flowing, a few drops of concentrated NH_4OH are added and the solution discarded.

3. The cell is disassembled and the planchet heated over a burner to volatilize any NH_4Cl, harden the uranium deposit, and provide a thin source for alpha particle spectrometry.

Counting

The planchets are counted in a vacuum chamber with a Technical Measurements Corporation Diffused Passivated Detector, 50 KEv resolution and 300 mm active area. This is coupled to a 100-channel TMC pulse height analyzer with a scale expander which facilitates excellent resolution of the alpha particle spectrum.

Three peaks of greatest interest are U-238 - 4.2 Mev, U-234 - 4.75 Mev, and U-232 - 5.3 Mev. However, peaks such as U-235 - 4.35 Mev, differing in energy by 0.15 Mev from the nearest principal peak, may be resolved.

General Remarks

The average chemical yield of uranium for water samples was 35%, for rocks 38%.

With each series of samples, a duplicate set of blanks were run using the same amount of reagents and tracers from the same batch as used in processing the samples. These blanks are necessary to provide a correction factor for background as well as any contaminants introduced in the chemical processing.

APPENDIX B:

TREATMENT OF URANIUM DATA

Sources of Error

Systematic Errors

Systematic errors arising from malfunctioning of counting equipment are difficult to detect in low-level radioactive determination. The only practical way of ascertaining that the counting equipment is giving a statistically valid response is by periodic counting of calibration standards and by multiple counting of samples and inspection of the data for an unwarranted variation. In this respect, the counting equipment used was found to be very reliable and little rejection of data due to this type of error was necessary.

A second source of systematic error is in calibration of the U-232 spike. To reduce this error to a minimum, the U-232 spike used was calibrated against a uranyl nitrate solution whose activity was calculated from gravimetric and volumetric determinations as well as determined by counting. As an additional check, the U-232 spike was calibrated in a 2π windowless proportional counter against a uranium oxide standard of $\pm 2\%$ accuracy prepared by the National Bureau of Standards.

Random Errors

The possible sources of random errors are:

1. Contaminants introduced in the sampling procedure.

2. Contamination from chemical reagents and glassware used.

3. Failure to achieve equilibration of spike with sample.

4. Variations in counter background.

5. Statistical counting errors.

Analyzing samples in duplicate, along with appropriate blanks, greatly reduces the possibility of the first three types of error going undetected and provides a basis for rejection or correction of the results. Background variations were found to be negligible, and only a slight increase in background with time was noted. Of the various random errors, the only one that can be expressed quantitatively is the

counting error arising from the random nature of the radioactive disintegration process.

Data Handling

1. The recorded spectra, including the three uranium peaks U-238, U-234, U-232, were inspected for inconsistencies and graphically checked for peak energy and linearity.

2. The three peaks of interest were integrated by addition of the counts in a six-channel envelope.

3. Data was spot-checked graphically with the charts given by Jarrett (1946) to see if variations were within the limits expected from statistical variations.

4. Six-channel envelopes corresponding to uranium peak energies were determined for the blank and background spectra.

5. Data were transferred to computer cards for calculation of results.

The equation used to determine the error or a counting rate determination is that given by Jarrett (1946):

$$Y = K\,(N_S/T_S + N_b/T_b)^{1/2}$$

Where N_S = count rate of sample

N_b = count rate of background

T_S = time of sample count

T_b = time of background count

K = 1.96 factor for the 0.05 level of confidence.

The calculated error for each sample is that propagated through multiplication and division, where the fractional error of a product or quotient is equal to the square root of the sum of the squares of the individual fractional error, for $z = xy$:

$$\frac{z}{Z} = \left[\left(\frac{x}{X}\right)^2 + \left(\frac{y}{Y}\right)^2 \right]^{1/2}$$

Fortran IV Computer Program

A Fortran IV computer program was used to treat the raw data. The program performs the stripping of the blank and background contributions from the sample and calculates the desired uranium concentrations, activity ratios and errors. For purposes of calculation, the following errors are assigned: weight or volume ±2%, spike ±2%, 44.6 dph/μg U-238 ±2%. In addition, K is given as 1.96 so that all calculated errors represent the 0.05 level of significance.

APPENDIX C:

REPORTS AND PUBLICATIONS. Research on naturally occurring radioisotopes in the Floridan aquifer supported by Office of Water Resources Research Title I Grants A-005-FLA and A-011-FLA.

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