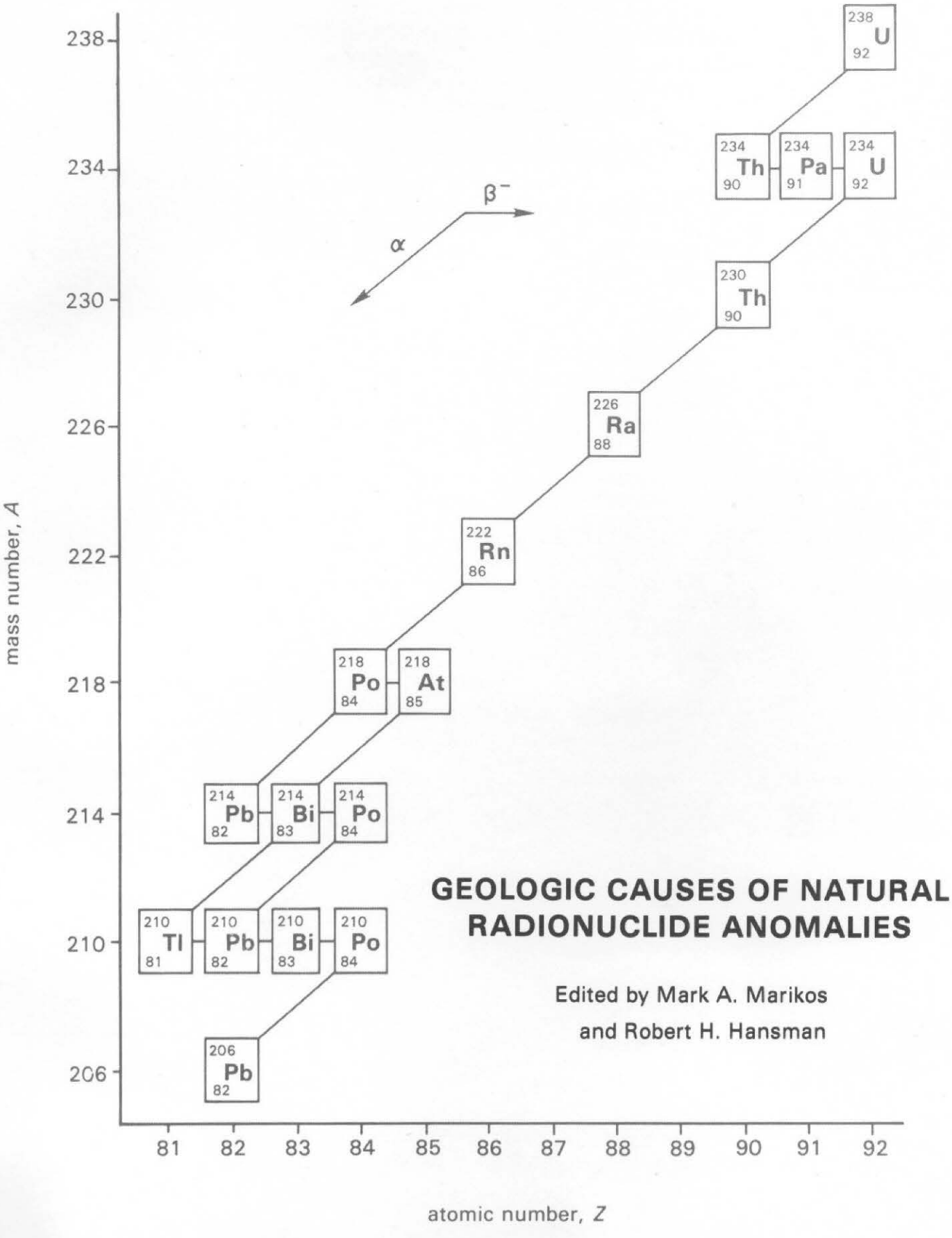
Special Publication #4



GEOLOGIC CAUSES OF NATURAL RADIONUCLIDE ANOMALIES

Edited by Mark A. Marikos
and Robert H. Hansman

MISSOURI DEPARTMENT OF NATURAL RESOURCES
Division of Geology and Land Survey

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GEOLOGIC CAUSES OF NATURAL RADIONUCLIDE ANOMALIES

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Edited by
Mark A. Marikos
and
Robert H. Hansman

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FOREWORD

The geologic causes of naturally occuring radionuclide anomalies are important to two, sometimes conflicting, disciplines. Exploration geologists require such information to fine-tune their exploration models and discover economic deposits for exploitation. Environmental geologists need the same information to anticipate such deposits and protect the public from exposure to attendant toxic and radioactive hazards.

In the past, mining and environmental concerns have often clashed violently; however, as attendees of GEORAD learned, each side has much to contribute to the other. Much, if not most, of what we know about radionuclide distribution in the natural environment comes from mineral exploration. On the other hand, recent research on movement of radionuclides in the environment may lead to better exploration models. Both concerns benefit from basic geological and geochemical research that may be hard to justify to fiscal managers and public officials.

Good research, no matter what the original justification, always pays dividends far beyond the imaginations of those conducting it. Many theories and basic principles that underpin the reports in this volume were developed by people who lived before the discovery of radioactivity. Their work, however, answered basic questions, which in their time may have been only of academic interest, but it is the foundation upon which we build. In the same way, some work described in this volume will find use beyond the authors' imaginings. Some ideas may lie dormant for decades before finding application, but that should not limit their value.

GEORAD was conceived as a vehicle to facilitate dissemination of current work on geologic causes of naturally occurring radionuclide anomalies. Dissemmination of data and ideas is crucial to the advancement of science. I count GEORAD a success. The papers cover a spectrum of topics and approaches. The real success of the conference was measured by the new questions it stimulated and the lively discussions that followed.

I thank all who participated in any way for making it a success. I also thank the many researchers who have preceded us; we have only built upon the foundation they have so masterfully laid.

Mark Alan Marikos
Missouri Department of
Natural Resources
Conference Coordinator

TABLE OF CONTENTS

	Page
FOREWORD	iii
SOME FACTORS INFLUENCING THE DISTRIBUTION OF RADIONUCLIDES IN NATURE — AN INTRODUCTION *Mark Alan Marikos*	1
RADIOACTIVE HHP (HIGH HEAT PRODUCTION) GRANITES IN THE PRECAMBRIAN TERRANE OF SOUTHEASTERN MISSOURI *Eva B. Kisvarsanyi*	5
GEOLOGICAL VARIATION OF RADON SOURCES AND INDOOR RADON ALONG THE SOUTHWESTERN EDGE OF THE CANADIAN SHIELD *Daniel J. Steck*	17
RADIONUCLIDES IN PENNSYLVANIAN BLACK SHALES OF THE MIDWESTERN UNITED STATES *Raymond M. Coveney et al.*	25
THE GEOLOGIC SETTING OF A SURFICIAL URANIUM DEPOSIT, NORTHEASTERN WASHINGTON *R.A. Zielinski et al.*	43
GEOLOGY AND URANIUM DISTRIBUTION IN THE FISH LAKE SURFICIAL URANIUM DEPOSIT, NEVADA *David L. Macke et al.*	53
RADIONUCLIDE DISTRIBUTIONS IN THE NATURAL ENVIRONMENT IN KANSAS — A REVIEW OF EXISTING DATA *Pieter Berendsen et al.*	65
DISTRIBUTION OF RADIONUCLIDES IN MISSOURI GEOLOGIC TERRANES: A SUMMARY OF AVAILABLE DATA AND THE NEED FOR MORE DATA *Laurence M. Nuelle*	75
CORRELATION BETWEEN GEOLOGY, RADON IN SOIL GAS, AND INDOOR RADON IN THE READING PRONG *L.C.S. Gundersen et al.*	91
ANOMALOUS MISSISSIPPI VALLEY LEADS: ANOTHER SUGGESTION *Timothy M. Millen et al.*	103
GEOMORPHIC AND GEOCHEMICAL ENHANCEMENT OF RADON EMISSION IN MIDDLE TENNESSEE *A.L. Reesman*	119
PROGRESS IN MEASUREMENTS OF SORPTION OF RADON ON POROUS MATERIALS AND IMPLICATIONS FOR THE RELEASE OF RADON AT THE EARTH'S SURFACE *Stephen D. Schery and Stewart Whittlestone*	131
MEASUREMENT OF RADON AVAILABILITY FROM SOIL *Allan B. Tanner*	139

Page

GROUNDWATER GEOCHEMISTRY AND RADON-222 DISTRIBUTION IN TWO SITES ON THE READING PRONG, EASTERN PENNSYLVANIAN 147
Richard B. Wanty and Linda C.S. Gundersen

REGIONAL AERIAL GAMMA-RAY MAPS FOR ILLINOIS AND PARTS OF WISCONSIN, IOWA, MICHIGAN, INDIANA, MISSOURI, AND KENTUCKY 157
Joseph S. Duval and William J. Jones

GEOLOGIC ASSESSMENTS OF RADON HAZARDS: A COLORADO CASE HISTORY 167
James K. Otton et al.

HYDROCARBON DISTRIBUTION PATTERNS OVER URANIUM DEPOSITS — IMPLICATIONS FOR SURFACE-PETROLEUM GEOCHEMICAL PROSPECTING TECHNIQUES 169
James L. Fisher

RADIONUCLIDE ANOMALIES IN GEOLOGIC EXPLORATION 171
William L. Mansker

AN INITIAL IDENTIFICATION OF AREAS WITH A POTENTIAL FOR HIGH INDOOR RADON LEVELS 173
R. Thomas Peake and Susan M. Rush

A CHALLENGE FOR GEOSCIENTISTS: CAN WE LEARN TO MAKE THE ELEPHANT MOVE 175
Lorraine H. Filipek

SOME FACTORS INFLUENCING THE DISTRIBUTION OF RADIONUCLIDES IN NATURE

AN INTRODUCTION

Radionuclide distributions in nature are determined by the often complex interplay of chemical transformations and nuclear transmutations. Chemical transformations occur at rates controlled by kinetic factors; equilibrium considerations serve as a feedback mechanism controlling the extent to which a reaction approaches completion. Nuclear transmutations are also controlled by kinetics, but the attendant "equilibria" are a result of the kinetic rates, not a control over them. Chemical equilibrium is determined by the chemical and physical environments and the species present; therefore, the chemical kinetics are also controlled by these factors. On the other hand, the kinetics of radioactive decay are, for all practical considerations, independent of chemical or physical environments and depend only on the identity of the decaying nuclide.

At any particular time, a radioactive atom may decay to the next nuclide in its decay chain and thereby drastically change its geochemical behavior. In a perfectly closed system or a well-constrained open system, continual changes in chemical content would be predictable. In nature, however, there are few, if any, closed systems, and not many more that can be adequately constrained by our present knowledge. Because of the differences in behavior (particularly solubility) between the various members of a decay chain, considerable fractionation of the chain may result. As Wanty et al. (this volume) point out, chemical equilibrium forces (thermodynamics) therefore often oppose the establishment of secular equilibrium in the open systems of nature.

Equilibrium activities of daughter nuclides are only reached after several half-lives of the parent nuclide. In some cases, nuclide half-lives may be geologically significant periods, whereas chemical reactions generally occur in geologically insignificant time spans. In other cases, a nuclide may be extremely short-lived compared to the time required to establish chemical equilibrium with its environment; therefore, the relative differences between chemical and radioactive decay rates will determine whether a particular nuclide's geochemical behavior controls its movement in an open system. If a soluble nuclide decays slowly, it may be transported a considerable distance before decaying to an insoluble daughter nuclide. If it is insoluble in its environment (slow rate of hydration or complex formation) it may not move any significant distance before it decays. In the meantime, the more mobile daughter nuclides may be flushed from the system in aqueous or gaseous phases, only to precipitate elsewhere when they transmute to the next immobile nuclide or enter different geochemical environments.

Because of such processes as burial, erosion, uplift, weathering, mass transport, volcanism, basin dewatering, or metamorphism, geologically long-lived nuclides may change geochemical environments during decay without leaving their original matrix. Changes in the geochemical environment may mobilize the parent nuclide and leave some of the accumulated daughters behind, or conversely, the daughters could be mobilized leaving the parent nuclide behind. Such processes may create complex effects if more than one of the chain members is affected by changes in environment. An intermediate member of the chain could be isolated without supporting parents or progeny, or a particular member of the chain may not be present in quantities anticipated from both parent and progeny nuclide activities. Obviously, timing of the environmental changes would be controlling factors in such unusual activity distributions.

An example of such a case would be tectonic uplift of a uranium deposit into the vadose zone in a humid climate. Frequent flushing of the deposit by fresh, oxidizing groundwater would strip uranium from the deposit but not affect accumulated radium; however, if the aquifer is open or open fractures cut the deposit, radon emanating from the deposit may escape to the surface before decaying and leave a deposit containing radium and any insoluble progeny that were present before the change in environment. Activity ratios from such a deposit could be very difficult to interpret.

In other words, superposition of the chemical kinetics and the radioactive decay kinetics may prove difficult to model without a detailed geological history of a deposit. As both types of kinetics are based on statistical rates, it is impossible to predict the state of

any particular atom at any time, with respect to its chemical or nuclear condition. We may therefore refer only to average or statistical behavior for a large number of atoms. With this limitation in mind, we may make some general statements about kinetic controls on migration. Except for possible exceptions discussed below, the two kinetic rates are independent of each other; therefore, there is no direct competition, per se, between them. Instead, each may be considered to interfere with the other's approach to equilibrium. If the chemical kinetics controlling the solubility of a particular nuclide are slower than its decay rate, chemical equilibrium may never be established before the atoms transmute to a chemically distinct nuclide; therefore, that nuclide may never exert any statistically significant influence on migration of the atoms. If the chemical kinetics controlling the solubility of a particular nuclide are significantly faster than its decay rate, chemical equilibrium will determine the migration behavior of the atoms of that nuclide. Both rates will also be overprinted by the rate of change of the geochemical or hydrodynamic environment.

Other kinetic factors that further complicate the picture are the hydrodynamic and/or gas-dynamic effects of flow and diffusion. No matter what the solubility of a nuclide is, if there is no flow or diffusion through an aquifer, the nuclide will not move. In the case of high flow rates, however, even short-lived mobility may result in considerable separation between parent and daughter nuclides, a process well shown by radon-222. Despite its relatively short half-life of 3.86 days, radon-222 may migrate meters from its radium source before attenuation to insignificant levels. Such a short half-life would normally render it insignificant in normal groundwater dynamics, but in aquifers where flow is controlled by channels and open fractures, flow rates may result in significant transport of even short-lived nuclides. An excellent example is given by Gundersen et al. (this volume) in their description of the now-famous Reading Prong.

Geologic events may greatly alter the hydrodynamics or geochemistry of a deposit's environment. A normally sluggish groundwater system may be greatly accelerated by changed head relationships following a tectonic disturbance. Plutonic intrusion may drastically change flow patterns in an aquifer. Kisvarsanyi (this volume), in her description of high heat production (HHP) granites, alludes to some geologically long-lived thermal systems that may profoundly affect the groundwater dynamics of a region, not to mention their input of radionuclides and stable species into the system. Glaciation (Zielinski et al., this volume), tectonically induced geomorphological changes, climatic variations (Macke et al., this volume), or weathering (Reesman, this volume) may also change the fluid dynamic and chemical environments in ways that effect separation of members in a decay chain. Zielinski et al. even implicate such benign agents as beavers in rearranging the chemical and physical parameters of a system to effect separation of nuclides. Their conclusions bring into question the effects that man, currently the greatest agent of geological change, may have on such processes.

The above statement that chemical and radioactive kinetics are independent is probably not totally correct. Energetics of the radioactive decay process can influence the course and kinetics of chemical reactions. Ionizing gamma radiation may change chemical kinetics by promoting faster production of a necessary intermediate ion or radical. Sufficiently energetic alpha and beta particles may likewise change chemical reaction rates. Alpha-recoil, the "equal and opposite reaction" to the ejection of an alpha particle from a nucleus, may promote an atom to a higher energy level where the atom may be able to escape bonds that had held it immobile, or it may enter into reactions that were kinetically hindered in its ground state. The atom may be ejected from an entombing crystal lattice, or implanted below the active surface of a growing crystal. In some cases these perturbations act to enhance solubility of an atom, and in others, to remove it from the aqueous or gaseous phase.

The energetics of the decay process may also change the matrix components of an aquifer system in ways that affect their ability to adsorb or release radionuclides. Radioactive heating of a rock mass, such as in HHP granites, may change the solubility of radionuclides (thermal-chemical effect), may increase groundwater flow rates (thermal-hydrodynamic effect), and may fracture the host rock (thermal-mechanical effect). Radiation damage of crystal lattices may allow water (solvent) molecules easier access to contained radionuclides (Millen et al., this volume), or may change the surface characteristics of grains in ways that influence their adsorption capacity for radionuclides. Radiation damage of dissolved or precipitated organic (and certain inorganic) molecules may result in polymerization to larger mole-

cules that more effectively chelate radionuclides, or may split such molecules and allow release of chelated radionuclides.

A nagging question is whether these perturbations are self-canceling, or are there cases where certain effects dominate. If so, it is possible that the decay process itself can either promote or retard migration of radionuclides. The effect may also be different for different members of a chain, and it may further unbalance the conditions toward, or away from, secular equilibrium.

It is obvious that more basic data is needed before many of the above questions and problems can be fully resolved. More data are needed on distribution of radionuclides in various geological materials and terranes (Steck, this volume; Coveney et al., this volume; Berendsen et al., this volume; Nuelle, this volume; Duval, this volume) and on the processes that control migration of the various nuclides (Schery and Whittlestone, this volume; Tanner, this volume). Basic radionuclide and geochemical inventory studies may be hard to justify financially, yet they are almost indispensable at this time. Perhaps even harder to justify are such esoteric studies as the effect of grain surface characteristics on adsorption and migration of nuclides, yet such studies provide the basic data needed to model movement of radon through rock, soils, and building materials. As geoscientists (and related scientists) we must present a unified front to the authorities from whom we get our research dollars. We must also learn to communicate effectively with them and demonstrate the need for basic research.

The natural radionuclide issue is not going to disappear in the forseeable future; its appearance was a product of increased knowledge of our surroundings, not a fundamental change in those surroundings. We must continue to learn more about our planet if we hope to solve these and other problems. While we have some distance to go, many advances we have made in environmental sciences over the last two decades happened because of increased public awareness and concerted effort towards a defined goal. The earth science community can serve as a catalyst to focus the attention of decision makers and the general public on basic research needs. If we do, we will all reap benefits beyond our wildest imaginations. To echo Lori Filipek's comments (this volume), it will only happen when we learn how to coordinate the various disciplines that comprise the "Geoscience Elephant," and make the elephant move. The hosts of GEORAD hope that this conference has indeed been a suitably "pointed stick" to goad the cumbersome behemoth into coordinated movement toward a positive goal.

I again thank all who had a part in making GEORAD a success: Keith Wedge for administrative assistance; Myrna Reiff and Barbara Miller for logistical assistance and registration; Phillip Streamer for graphics and videotaping; James H. Williams and Jerry Vineyard for their encouragement, opening and closing statements, and liaison with the U.S. Geological Survey; Harry Tourtelot and Lori Filipek for their banquet comments and enthusiatic support; and Dallas Peck, Director of the U.S. Geological Survey, for his support. The U.S. Geological Survey has underwritten a portion of the cost of the proceedings volume; for that I am grateful. Without speakers the conference would have been quite dull, so again I thank the speakers and authors for the excellent papers. It would have been no fun for the speakers and organizers had there been no one to listen and discuss. I especially thank Pieter Berendsen, Tom Peake, Jim Otton, Art Reesman, Gary McNutt, and Bill Mansker for their participation in the panel discussion.

Mark Alan Marikos

RADIOACTIVE HHP (HIGH HEAT PRODUCTION) GRANITES IN THE PRECAMBRIAN TERRANE OF SOUTHEASTERN MISSOURI

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ABSTRACT

Granites and rhyolites of the Middle Proterozoic St. Francois terrane are among the most uraniferous igneous rocks in the United States. They are only partly exposed, as tips of icebergs in a "sea" of sedimentary rock, in a 3500 mi² area in the St. Francois Mountains of southeastern Missouri, but underlie thousands of square miles in the midcontinent. The terrane formed in an anorogenic tectonic environment through subcontinental-scale melting of older crustal rocks. The anatectic melts were enriched in LIL (large-ion lithophile) and radioactive elements, rose to high crustal levels, and were emplaced through explosive volcanism as ash-flow sheets and associated subvolcanic granitoid ring complexes.

The granitoids were intruded in three stages: concordant subvolcanic massifs, arcuate ring intrusions, and discordant plug-like central plutons in resurgent cauldrons. The central plutons, fourteen of which have been identified from drillholes and outcrops in southeastern Missouri, are late-stage differentiation products of highly evolved magma and are abnormally radioactive. They are typically two-mica, S-type granites containing quartz, twinned microcline, accessory garnet, topaz, allanite, monazite, zircon, apatite and fluorite, and little magnetite. They contain as much as 34 ppm uranium and 54 ppm thorium, and are classic tin granites with tin, tungsten, niobium, yttrium, and beryllium enrichments. They are distinctive HHP granites that generate heat through radioactive decay of potassium, uranium, thorium, and their daughter products, and are capable of producing thermal anomalies and convective circulation of hydrothermal fluids in their crustal regime for geologically significant time.

Although no uranium minerals were positively identified in the granites, petrographic studies suggest that some of the opaque inclusions with pleochroic haloes in biotite are uraninite. Fission track data (Nash, 1977) indicate that most of the uranium in the granites is associated with iron oxide, including both primary opaque phases and secondary red iron oxides mobilized along grain boundaries and in feldspars. This uranium is readily leached, mobilized, and redistributed by supergene or hydrothermal solutions. The implications of this process are twofold: secondary enrichment of uranium may have produced sedimentary deposits in Paleozoic strata onlapping the Precambrian, and natural radionuclide anomalies in streams and soils around the Precambrian outcrops may give rise to environmental concern.

INTRODUCTION

In 1968 the Missouri Geological Survey, now part of the Department of Natural Resources, started Operation Basement, a continuing in-depth study of exposed and buried Precambrian rocks in Missouri. Early in the project the Survey sponsored a mapping program in the St. Francois Mountains (Berry, 1970) in the course of which 27 granite and 45 rhyolite samples were analyzed by gamma-ray spectrograph at the Grand Junction, Colorado laboratories of the U.S. Atomic Energy Commission, now Department of Energy. The results first called attention to the fact that one of the exposed granites, the Graniteville Granite, contains as much as 19 ppm uranium and 43 ppm thorium, and is among the most uraniferous igneous rocks in the United States (Malan, 1972).

Subsequent investigations by the U.S. Geological Survey focused on the evaluation of uranium resource potential and on the determination of radioelement distributions in the exposed granites (Nash, 1977). Joint studies by the Missouri Geological Survey and the Department of Geology and Geophysics, University of Missouri at Rolla, identified other radioactive granite plutons from drill cores (Missouri Geological Survey, unpublished data, 1973). Petrographic and geochemical study of hundreds of drill cores led to the identification of 14 granite plutons similar to the Graniteville, in the buried Precambrian terrane of southeastern Missouri (Kisvarsanyi, 1981).

Recent studies of abnormally radioactive granite plutons, the Conway Granite of New Hampshire (Fehn et al., 1978), and in the United Kingdom (Durrance et al., 1982; Lee et al., 1987), indicate that such plutons sustain intensive and vigorous thermal activity for geologically significant time, and are classed as high heat production (HHP) granites. They may have generated hydrothermal ore deposits in the surrounding permeable country rocks, raised geothermal gradients, and increased heat flow in their respective crustal regimes. The Graniteville and other similar plutons constitute a distinct HHP granite province in the Precambrian basement of Missouri. The purpose of this paper is to describe the mineralogy, geochemistry, and geologic occurrence of these granite plutons and thus provide a geologic background for future environmental studies.

PRECAMBRIAN GEOLOGY OF SOUTHEASTERN MISSOURI

The St. Francois Mountains of southeastern Missouri expose a small portion of an extensive Middle Proterozoic igneous terrane, which is mostly covered by younger sedimentary rocks in the midcontinent. The relationship between the Precambrian and Phanerozoic rocks is one of erosional unconformity: the sediments were deposited on an ancient erosion surface. The Precambrian rocks are exposed in a 3500 mi^2 area at the crest of the Ozark dome, where the older terrane has become partially uncovered by regional uplift and erosion. The Precambrian geology of this region has been studied by combining outcrop data with subsurface information from approximately 500 drillholes, most of them core drilled, and with data from aeromagnetic maps. The following account of the regional geology is based on previous studies by Berry (1970), Bickford and Mose (1975), Kisvarsanyi (1972, 1975, 1979, 1981), Cordell (1979), Cordell and Knepper (1987), and Sides et al. (1981).

The St. Francois terrane comprises an unmetamorphosed assemblage of anorogenic granite and rhyolite, and lesser volumes of trachyte and basalt. These rocks formed through explosive volcanism and comagmatic, epizonal plutonism from anatectic melts in an extensional tectonic environment. The terrane is mostly 1.45 to 1.48 Ga (Ga: billion years) old but includes younger rocks of 1.35 Ga (Bickford et al., 1981; Thomas et al., 1984). It consists of more than a dozen overlapping granitoid ring complexes, calderas, cauldron subsidence structures with ring intrusions, and resurgent cauldrons with central plutons (fig. 1). The granitoids were intruded in three stages: concordant subvolcanic massifs (biotite granite, table 1), arcuate ring intrusions (amphibole granite, table 1), and discordant, plug-like central plutons in resurgent cauldrons (two-mica tin granite, table 1). The most radioactive HHP granites are the central plutons, which are late-stage differentiation products of highly evolved LILE-enriched magma.

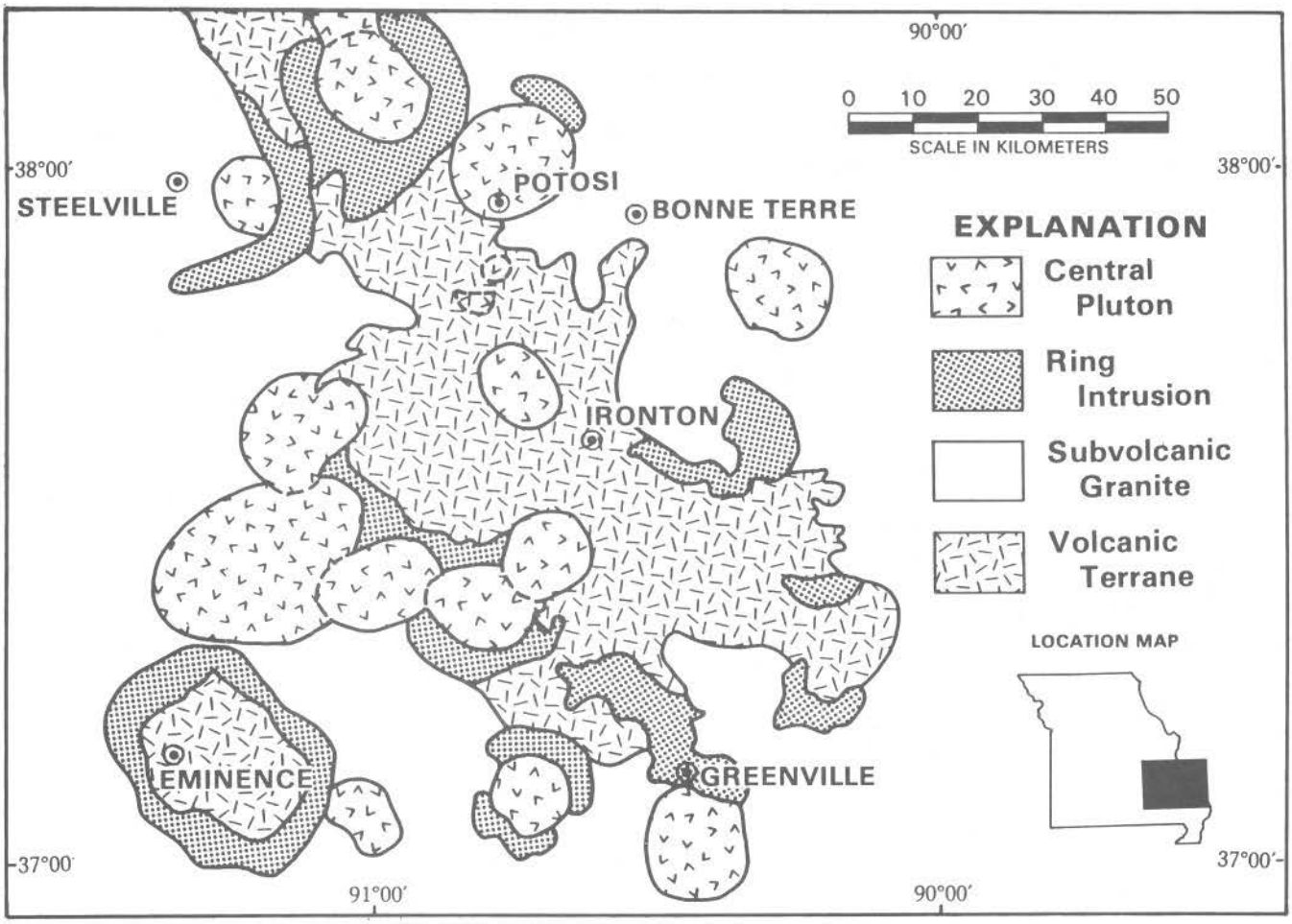


Figure 1 — Geologic map of the St. Francois terrane, southeastern Missouri, interpreted from outcrop, drillhole, and aeromagnetic data (adapted from Kisvarsanyi, 1981).

GRANITEVILLE GRANITE

The Graniteville Granite is the only partly exposed central pluton in the St. Francois Mountains. It forms giant, picturesque residual boulders resembling a herd of sitting elephants in Elephant Rocks State Park (SE¼ SE¼ NE¼ sec. 15, T. 34 N., R. 3 E.), Iron County. The site is a classic granite tor and was designated a State of Missouri Geologic Natural Area in 1978 (fig. 2). Graniteville Granite outcrops are restricted to three small areas on the eastern and southeastern sides of a sediment-filled depression, the Belleview Valley. Morphologically the valley is square, bounded by straight topographic escarpments, and is a prominent feature on satellite imagery of the region. Drillholes indicate that Graniteville Granite underlies a 300- to 600-ft-thick section of sedimentary rocks in Belleview Valley. Aeromagnetic maps show the pluton as an oval magnetic low, an outstanding example of magnetic signature zonation of a granite pluton (Cordell, 1979), coincident with Belleview Valley.

The Graniteville Granite is a medium- to coarse-grained muscovite-biotite (two mica) alkali granite averaging 55 percent alkali feldspar, 40 percent quartz, and less than 5 percent mafic minerals. In this rock, the common alkali feldspar is typically microcline-microperthite, but albite and orthoclase-microperthite are also present. Both primary and secondary muscovite (sericite) occur. The rock con-

TABLE 1
Petrographic characteristics of the principal granite types, St. Francois Terrane

	Biotite granite	Amphibole granite	Two-mica (tin) granite
Essential minerals (by volume %)	quartz 25-45% orthoclase-microperthite 40-60% biotite 3-8% plagioclase 0-10%	quartz 15-30% orthoclase-microperthite 35-50% plagioclase 10-40% amphibole 5-10% biotite 3-8%	quartz 30-35% microcline-microperthite 25-50% albite 18-20% biotite 5-10% muscovite 5-10%
Accessory minerals	magnetite, zircon, apatite, (fluorite)	magnetite, zircon, apatite, sphene, (fluorite, pyrite)	fluorite, topaz, spinel, apatite, allanite, cassiterite, molybdenite, (zircon, magnetite)
Common textures	fine-, medium- and coarse-grained; granophyric; rapakivi	medium- to fine-grained; porphyritic	medium- to coarse-grained; pegmatoid
Common colors	red	light to dark gray, brown	pink, white (red)
Vein mineralization	none	hydrothermal-pneumatolytic	pegmatite
Petrologic classification*	alkali-feldspar granites (alaskites)	granites, quartz syenites, quartz monzonites	alkali-feldspar granites, leucogranites
Correlation†	Butler Hill and Breadtray Granites	Silvermine, Slabtown, and Stono Granites, granite porphyries	Graniteville Granite

*After Streckeisen (1967)
†Exposed Precambrian granites named by Tolman and Robertson (1969)

tains a varied suite of accessory minerals, including abundant fluorite and zircon; cassiterite and molybdenite are rare. Complex pegmatites with topaz, beryl, muscovite, fluorite, rutile, cassiterite, and sulfide minerals have been reported (Tolman and Goldich, 1935). In table 2, a chemical analysis of Graniteville Granite is compared with Nockolds' (1954) average of 17 muscovite-biotite alkali granites. Anomalously high concentrations of tin, beryllium, yttrium, niobium, fluorine, and uranium in Graniteville Granite led to its identification as a tin-granite pluton (Kisvarsanyi, 1981).

HHP GRANITE PLUTONS IN THE BURIED PRECAMBRIAN TERRANE

Granite cores showing many of the mineralogical and geochemical characteristics of Graniteville Granite were recovered from the buried Precambrian terrane around the St. Francois Mountains outcrops. Without exception, all are coincident with distinctive circular or oval low magnetic anomalies reminiscent of that associated with the Graniteville pluton (Gay, 1976; Kisvarsanyi, 1980, 1981; Cordell and Knepper, 1987). On the basis of the mineralogical, geochemical, and geophysical analogies, these core samples are inferred to represent buried central plutons whose size and shape are expressed on aeromagnetic maps by their associated negative magnetic anomalies. The subsurface distribution of these plutons can be mapped with reasonable confidence from the aeromagnetic maps (fig. 1). Ring-shaped and arcuate high magnetic anomalies around the plutons reflect amphibole granite or trachyte porphyry ring intrusions, and volcanic-rock remnants. A detailed account of the theoretical considerations on the emplacement of central plutons in general, and descriptions of the central plutons inferred in the St. Francois terrane are given in Kisvarsanyi (1981, p. 34-44).

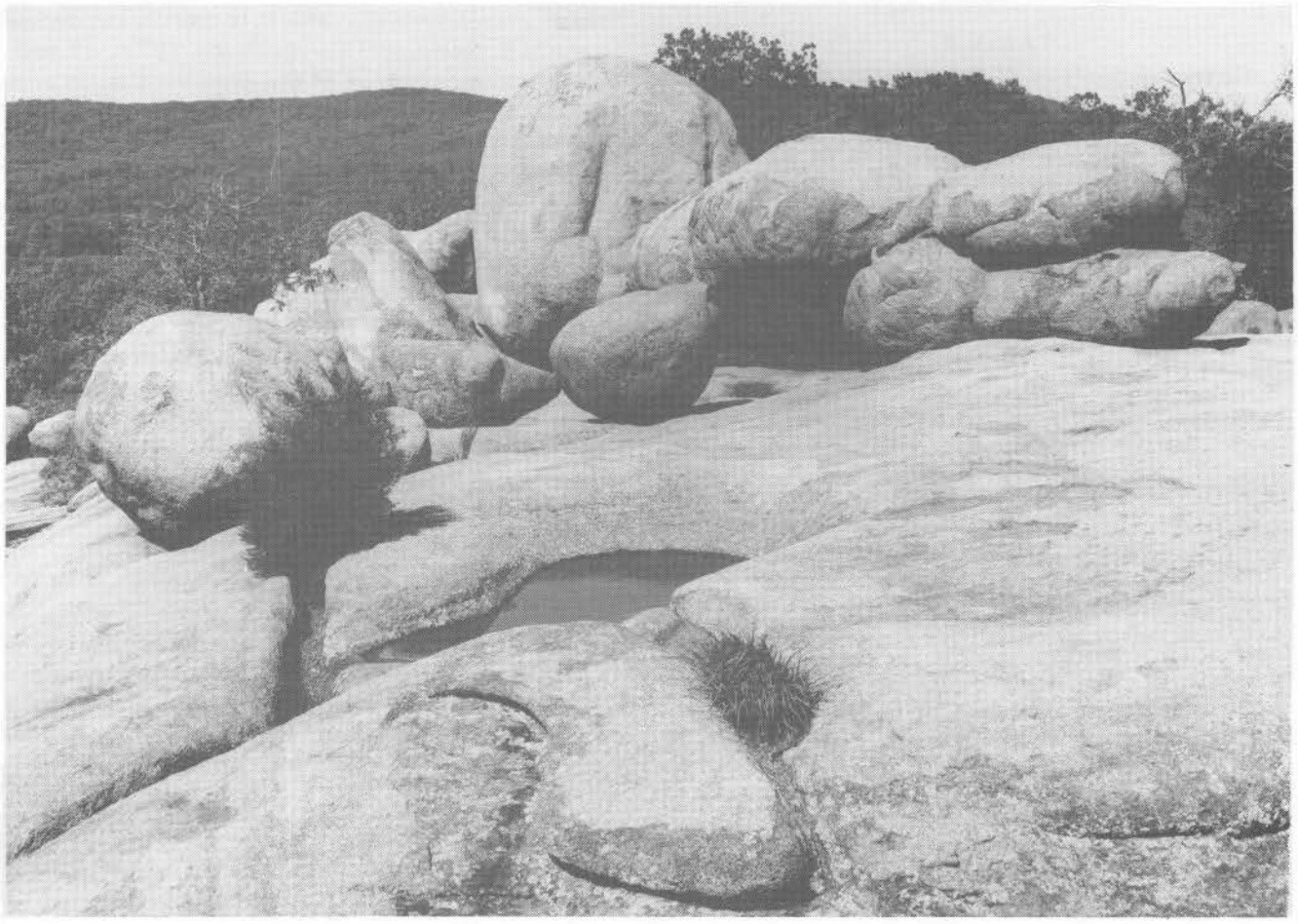


Figure 2 — "Elephant Rocks": spheroidally weathered giant boulders of Graniteville Granite in Elephant Rocks State Park. In this view to the northeast, the largest "elephant" atop the granite bald is 25 ft (7.5 m) high. Photo by Art Hebrank.

The central granite plutons in southeastern Missouri are shown as named features 1 through 14 in figure 3. As shown by Operation Basement core samples, petrographic thin sections, and trace element data, these plutons are typically two-mica, S-type granites containing quartz, twinned microcline, albite, and accessory garnet, topaz, allanite, monazite, zircon, apatite, and fluorite. They are classic tin granites characterized by enrichments of tin, tungsten, niobium, yttrium, and beryllium; they are also classed as HHP granites with high uranium and thorium contents. Although no uranium minerals were positively identified in the core samples, petrographic study suggests that some opaque inclusions with pleochroic haloes in radiation-damaged biotite are uraninite (fig. 4).

RADIOELEMENT DATA

Malan (1972) first called attention to the abnormally high levels of uranium and thorium in the Precambrian granites of the St. Francois Mountains. The uranium, thorium, and potassium contents obtained by gamma-ray spectrographic analysis were found to be uniquely high in the Graniteville Granite. High values for these elements were found in the Butler Hill and Breadtray Granites as well, which form extensive, subvolcanic massifs in the St. Francois terrane. Among the granitoids, the lowest radioelement values were obtained from the ring intrusions, the Slabtown, Silvermine, and Knoblick Granites, and the granite porphyries (table 3).

TABLE 2
Chemical analysis of Graniteville Granite

	Graniteville Granite*	Average muscovite-biotite alkali granite**
SiO_2	76.44	74.63
Al_2O_3	12.48	13.86
Fe_2O_3	0.44	0.52
FeO	0.45	0.89
MgO	0.05	0.33
CaO	0.95	0.57
Na_2O	3.67	3.05
K_2O	4.84	5.16
H_2O^+	0.13	0.63
H_2O^-	0.05	—
TiO_2	0.07	0.14
P_2O_5	0.00	0.18
MnO	0.00	0.04
F	0.41	—
S	0.02	—
BaO	0.01	—
Total	**100.01**	**100.00**

* Analysis no. 57 *in* Kisvarsanyi, 1972
**From Nockolds, 1954

In an assessment of uranium resources conducted by the U.S. Geological Survey (Nash, 1977), 42 additional outcrop samples of the granitoids were analyzed by delayed neutron activation. The results confirm Malan's (1972) data and show that the Graniteville Granite, particularly in the eastern part of its outcrop near the intrusive contact with a granite porphyry ring intrusion, is the most radioactive and has four times the uranium values of granitic rocks in general. The maximum obtained values were 34.4 ppm uranium and 54.7 ppm thorium, and the mean values for 10 samples were 16.9 ppm uranium and 42.6 ppm thorium (Nash, 1977). Field gamma-spectrometric measurements at 86 outcrop sites, made with a broad-band gamma-scintillator and 4-channel Geometrics 400A gamma-spectrometer, indicate that the regional radioactivity is uniformly high over the granite outcrops (Nash, 1977).

Core samples from three buried plutons, the Buick, Graniteville, and Bunker (nos. 6, 7, and 8 in fig. 3), were selected for gamma-ray spectrographic analysis to test the theory that the coarse-grained two-mica Graniteville Granite-type granites of the terrane have similar high radioelement contents. This investiga-

1. Pea Ridge pluton(s)
2. Steelville pluton
3. Potosi pluton
4. Dent Branch-Furnace Creek pluton(s)
5. Hawn Park pluton
6. Buick pluton
7. Graniteville pluton
8. Bunker pluton
9. Corridon pluton
10. Redford pluton
11. Sabula pluton
12. Van Buren pluton
13. Piedmont pluton
14. Greenville pluton
15. Cherryville ring intrusion
16. Floyd Tower-Indian Creek intrusion
17. Lesterville intrusion
18. Silvermine ring intrusion
19. Redford-Annapolis ring intrusion
20. Eminence ring intrusion
21. Marquand-Buckhorn ring intrusion
22. Eminence cauldron subsidence structure

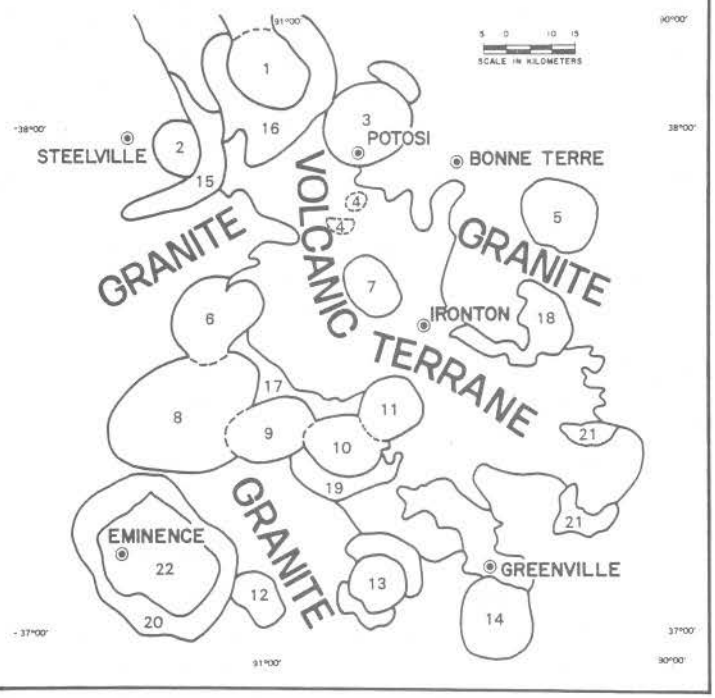


Figure 3 — Regional map of the ring complexes in the St. Francois terrane. Named features 1 through 14 are inferred central plutons; 15 through 21 are inferred ring intrusions; features 20 and 22 constitute the Eminence cauldron subsidence structure (Kisvarsanyi, 1981).

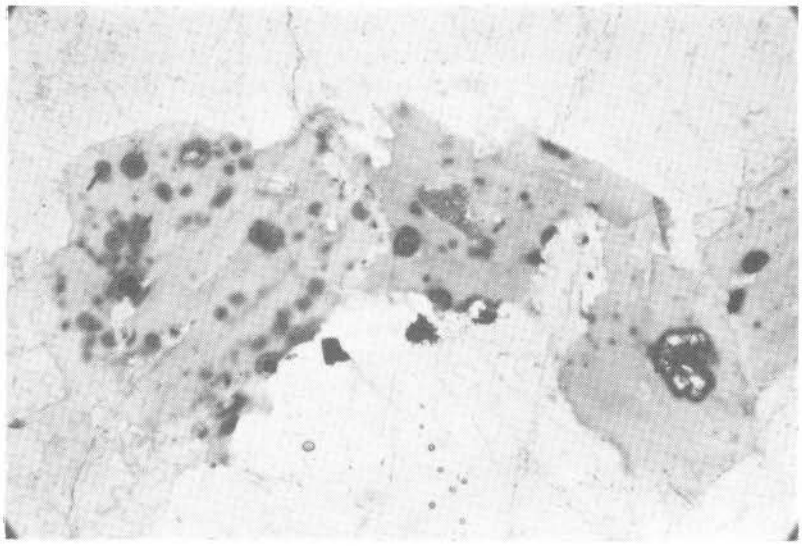


Figure 4 — Photomicrograph showing zircon (lower right) and uraninite (?) inclusions with pleochroic haloes in radiation-damaged biotite from the Bunker pluton (no. 8 in fig. 3). Length of bar scale is 1 mm.

tion was part of a joint study with Dr. Geza Kisvarsanyi of the University of Missouri at Rolla, and the U.S. Atomic Energy Commission, in 1972 and 1973, but the data have not been discussed previously. The results show generally lower radioelement values in the core than in the outcrop samples (table 4). Only one sample from the Buick pluton (I-66-1800) is comparable to the uranium and thorium contents in quarry samples of Graniteville Granite; however, the results also show that within individual plutons there are considerable lateral and vertical variations in radioelement values. For example, the core sample of Graniteville Granite (I-28-393) is from the southwestern, most deeply buried part of the pluton, and its radioelement values are relatively low compared to outcrop samples of this rock.

Data from the Bunker pluton are particularly interesting, because they imply considerable vertical variations in the radioelement distributions within individual plutons. A core hole, Sh-13, in the western part of the pluton intersects 3671 ft of granite and is the deepest probe into the Precambrian basement in the midcontinent. The six samples

TABLE 3
Distributions of thorium, uranium, and potassium in the granitoids of the St. Francois Mountains

Rock Type*	Classification**	No. Samples	Mean ppm Th	Mean ppm U	Mean %K	Th/U
Graniteville Granite	Central pluton	4	41.7	13.7	4.3	3.0
Butler Hill Granite	Subvolcanic massif	3	24.0	7.4	4.4	3.2
Breadtray Granite	" "	3	22.5	6.4	5.0	3.5
Carver Granite Porphyry	Ring intrusion	4	15.4	4.2	4.7	3.7
Munger Granite Porphyry	" "	4	10.1	5.1	4.8	2.0
Slabtown Granite	" "	3	8.1	3.6	3.4	2.3
Silvermine Granite	" "	3	6.8	2.5	3.8	2.7
Knoblick Granite	" "	3	7.1	2.5	3.0	2.8
	Totals	**27**				
	Wt. average		**17.6**	**5.9**	**4.2**	**3.0**

Source of gamma-ray spectrographic data: Malan, 1972
* Formal names from Tolman and Robertson, 1969
**Adapted from Kisvarsanyi, 1980

analyzed show a distinct increase of radioelement values with depth: the three deeper samples contain significantly more thorium and uranium than the three shallower samples (table 4), a surprising discovery in view of the fact that the granite in this core is very uniform and the six samples selected for analysis are megascopically similar to each other. The low thorium/uranium ratios in the deeper samples are uncommon for such silicic rocks in general, but seem to be characteristic of the granitoids of the St. Francois terrane (Malan, 1972). Although the deeper samples contain abnormally high radioelement levels, they are considerably less radioactive than outcrop samples of Graniteville Granite.

Granite samples were obtained from the shaft in the Milliken Mine, the southernmost of the lead-zinc mines in the Viburnum Trend district. They are from the southeastern part of the Bunker pluton and are labeled Re-55 in table 4. The thorium and uranium values in the mine samples are much lower than in core hole Sh-13 and approach those in the granite porphyry ring intrusions (compare tables 3 and 4).

TABLE 4
Distributions of thorium, uranium, and potassium in core samples from southeastern Missouri

Named Pluton	Sample no.*	ppm Th	ppm U	%K
Buick	I-66-1800	43.1	17.5	4.05
"	Dn-3-1900	29.7	9.4	4.18
Graniteville	I-28-393	28.8	6.9	4.08
Bunker	Sh-13-2290	15.2	2.5	3.84
"	Sh-13-2820	15.6	2.6	3.81
"	Sh-13-3298	16.1	3.2	3.99
"	Sh-13-3822	23.8	8.1	3.47
"	Sh-13-4308	25.4	11.9	3.60
"	Sh-13-4972	26.2	9.0	3.50
"	Re-55-1240	12.7	9.0	2.58
"	Re-55-1350	13.0	5.5	3.61
"	Re-55-1400	11.9	4.0	3.69
"	Re-55-1450	11.6	4.8	3.97

*Operation Basement core numbers from Kisvarsanyi, 1975. Last digits show depth of sample in feet.

(Analyses were made by gamma-ray spectroscopy. Grand Junction, Colorado, 1973)

DISCUSSION AND RECOMMENDATIONS

The high radioactivity in the granitoids of the St. Francois Mountains is a geological "fait accompli," the result of natural processes that operated in Precambrian time. Until recently, when environmental concern about radionuclide pollution became a factor, the natural radioactivity of these rocks was considered to be of interest only because of the possibility of associated ore deposits. Nash (1977) reported fission-track data showing that most of the uranium in the granites is associated with iron oxide and is readily leached, mobilized, and redistributed by supergene or hydrothermal solutions. Of four possible types of uranium deposits, porphyry uranium, intragranitic veins, unconformity type, and sedimentary, the occurrence of syngenetic or epigenetic deposits in Paleozoic sedimentary rocks onlapping the Precambrian was considered to be the most probable.

Radioelement enrichment of several granite plutons in the St. Francois terrane is believed to be a significant feature in the metallogenic evolution of the region (Kisvarsanyi, 1981). As shown by Fehn et al. (1978), Durrance et al. (1982), and Lee et al. (1987), highly radioactive HHP granites can generate hydrothermal systems of considerable magnitude through radioactive decay. These systems may be active for geologically significant periods after emplacement of the plutons. Not only could the radioactive plutons have generated hydrothermal uranium and other metallic and nonmetallic deposits but, perhaps more significantly, they could have sustained considerable thermal anomalies within their crustal regime. Ore deposits in both the Precambrian and Paleozoic rocks in southeastern Missouri have a close spatial relationship to the inferred HHP plutons (fig. 5). The high heat flows generated by these plutons can be expected to have created favorable ore-concentrating environments not only in the Precambrian rocks but also in the overlying younger sedimentary rocks. The HHP plutons could, therefore, have profoundly influenced the metallogenesis of the entire region; however, until quantitative measurements are obtained on heat distribution and convective flow patterns around the plutons, this metallogenic concept remains hypothetical.

Of immediate concern at this time are the answers to the following questions. What effect, if any, do the radioactive granites have on the contamination of the environment, particularly streams and soils, in southeastern Missouri? Are structures in the area contaminated with radioactive radon gas, as were

many houses in the Reading Prong, in eastern Pennsylvania, where the environmental hazard of radon gas was first recognized in 1984?

Measurements of radon emanation in Missouri so far have been restricted to the New Madrid seismic zone (Steele et al., 1982), where radon activity was found to be a function of barometric pressure and seismicity. Increased radon concentrations were found along linear zones corresponding to faults, and near peripheral regions of plutons inferred in the subsurface. Existing fractures tend to be favorable sites for radon emanation, outgassing of sediments, and increased fluid circulation.

Fluid circulation in fractures and along faults is considered to be a significant factor in the redistribution of radionuclides from the Precambrian terrane in southeastern Missouri. Easily mobilized uranium from HHP granites at depth may be incorporated in upward moving solutions and enter the groundwater and soil. Future environmental studies should concentrate on sampling and measurements around the plutons, and use existing geologic data as a basis.

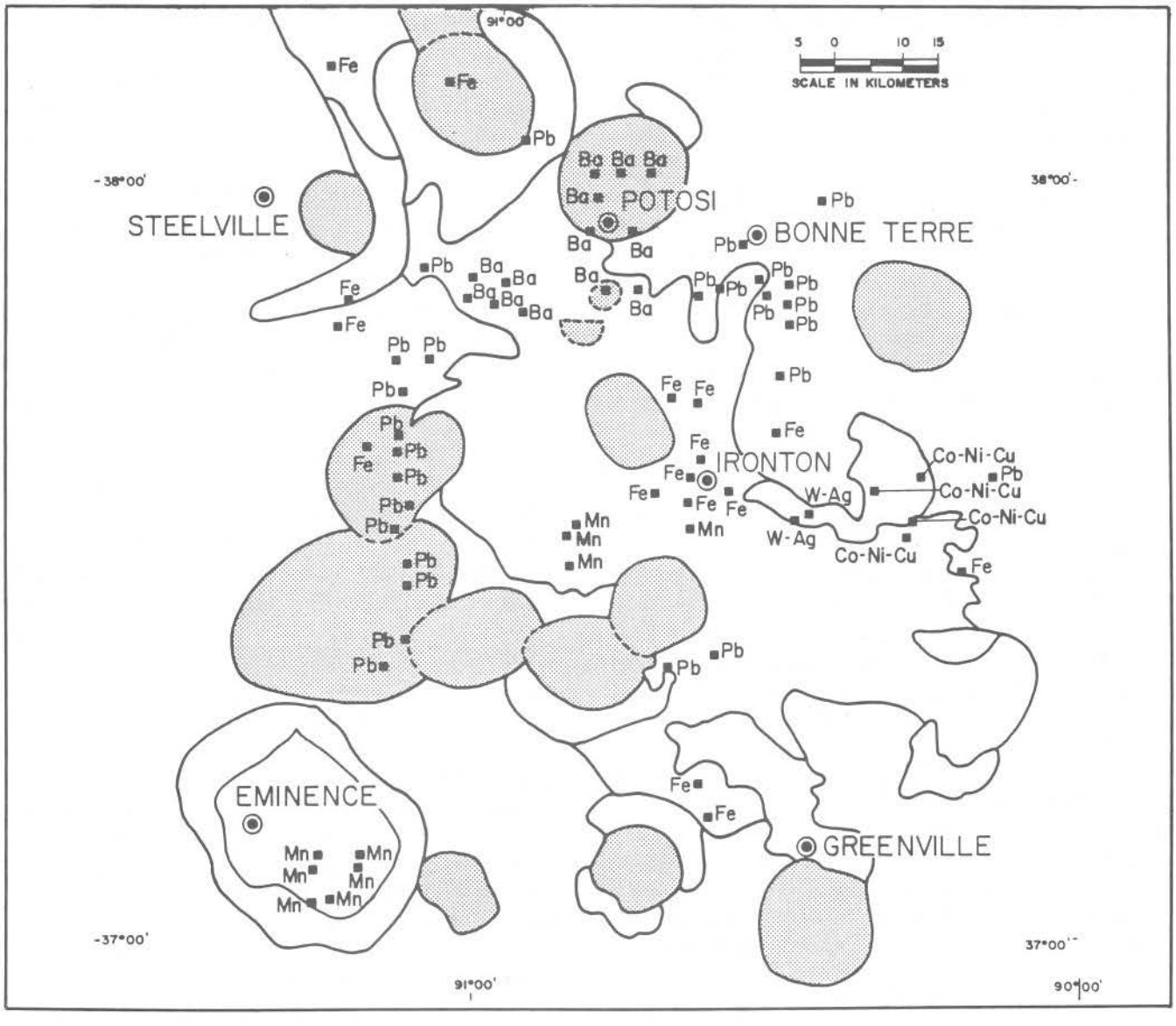


Figure 5 — Spatial relationships of ore deposits to HHP plutons (patterned) in southeastern Missouri (adapted from Kisvarsanyi, 1981).

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GEOLOGICAL VARIATION OF RADON SOURCES AND INDOOR RADON ALONG THE SOUTHWESTERN EDGE OF THE CANADIAN SHIELD

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ABSTRACT

Radon source and indoor radon concentrations were measured in 70 houses and a number of other sites along the southwestern edge of the Canadian shield. Waterborne radon activity ranges from 400 to 3.6 x 10^5 Bq/m^3 [10:10^4 pCi/L], and appears to be log-normally distributed, with an average value of 8600 Bq/m^3 [230 pCi/L]. Soilborne radon was determined by four techniques. In laboratory analysis, samples showed an average available radon emanation of 4 Bq/kg [0.1 pCi/g], and an average radon activity of 34 Bq/kg [0.8 pCi/g]. The in situ surface bismuth-214 activity ranged from 10 to 100 Bq/kg [0.2 to 2 pCi/g] and the soil gas radon activity averaged 5 kBq/m^3 [100 pCi/L]. Indoor airborne radon activity ranged from 20 to 1100 Bq/m^3 [0.5 to 30 pCi/L] and varied with season, year, compartment, and local geology.

INTRODUCTION

Previous research has indicated that indoor radon concentrations are influenced by local geology, hydrology, meteorology, housing characteristics, and lifestyles (Gessell, 1983; Nero, 1983). At present, there are few indoor radon and radon source measurements from such complex geological terrains as our glacially ravaged region punctuated by ancient bedrock outcrops. Given the Precambrian origin of our bedrock, glacial history of our soil, and the trend towards energy-efficient housing, the southwestern edge of the Canadian Shield is a region where a wide variety of radon sources affect houses. The distribution of indoor airborne radon concentrations may add to the understanding of the relationships between radon source concentrations, indoor airborne radon concentrations, and geology.

To represent a variety of surface geologies and housing stock, over 70 houses in a 3 x 105-km^2 region of Minnesota, northern Wisconsin, and the Upper Peninsula of Michigan were included in the 1983-1986 survey. Radon source materials were collected at these sites and elsewhere in the study area, to characterize both local and regional source concentrations.

EXPERIMENTAL METHODS

Waterborne radon activities were measured using a small-sample, liquid scintillation technique (Prichard and Gessell, 1977). The sensitivity of this method is approximately 20 pCi/L and the reproducibility is approximately 10 percent, which is less than the temporal radon variability of most water sources.

Two laboratory-based techniques and two *in situ* techniques were used to characterize soilborne radon concentrations. Soil samples for laboratory analysis were collected at depths of about 0.5 m, within 1 m of each house. Available radon emanation activities were measured with a modified liquid scintillation technique (6). Soilborne radon (or radium) activities were determined from closed container gamma spectroscopy using either a NaI (7.6 x 7.6 cm) or a HpGe detector. Measurement of the 1.6 to 2.6 MeV gamma flux provided a rapid, overall relative measure of the surface bismuth-214 activities in houses and throughout the study region. These flux measurements were made by a carborne shielded 7.6 x 7.6 cm NaI scintillator. To minimize meteorologically induced variations, the flux was measured during extended periods of stable weather. Radon soil gas activities at a depth of 0.5 m were measured with track registration detectors capped with thoron (radon-220) filters.

Time-averaged indoor air radon concentrations were measured by track registration material (CR39) enclosed in 250 ml or 50 ml containers sealed with a microporous polycarbonate membrane (Alter and Fleischer, 1981; Fleischer et al., 1975). A detector was placed in each of the two lowest compartments of each house, usually at a height of approximately 2 m for a period of 3 months (summer) to 9 months (winter), a method reproducible to within approximately 30 percent at low exposures and better than 10 percent at higher exposures.

RESULTS

Statistical summaries of the average waterborne, soilborne, and indoor air radon activities for data collected between June 1983 and February 1987 are shown in tables 1 and 2. Selected source and indoor air radon distributions are shown in figures 1 through 6.

TABLE 1
Statistical summary of radon sources*

Data Set	Units	Number	Range	Average	Deviation
Waterborne	Bq/m^3	387	400:3.6x10^5 [10:10^4]	15000 [400] (geometric)	
				8600 [230] (arithmetic)	factor of 2.8
Soilborne					
Available radon	Bq/kg	65	0.4:14 [0.01:0.4]	4.2 [0.1]	±1.8
Surface bismuth-214	Bq/kg	10^4 km	10:100 [0.2:2.0]	~30 [0.8]	
Radium/radon	Bq/kg	11	15:50 [0.4:1.4]	34 [0.9]	±12
Soil gas	Bq/m^3	25	750:22000 [20:600]	4000 [100]	±400

*Units of the values enclosed in square brackets are either pCi/L or pCi/g, as appropriate.

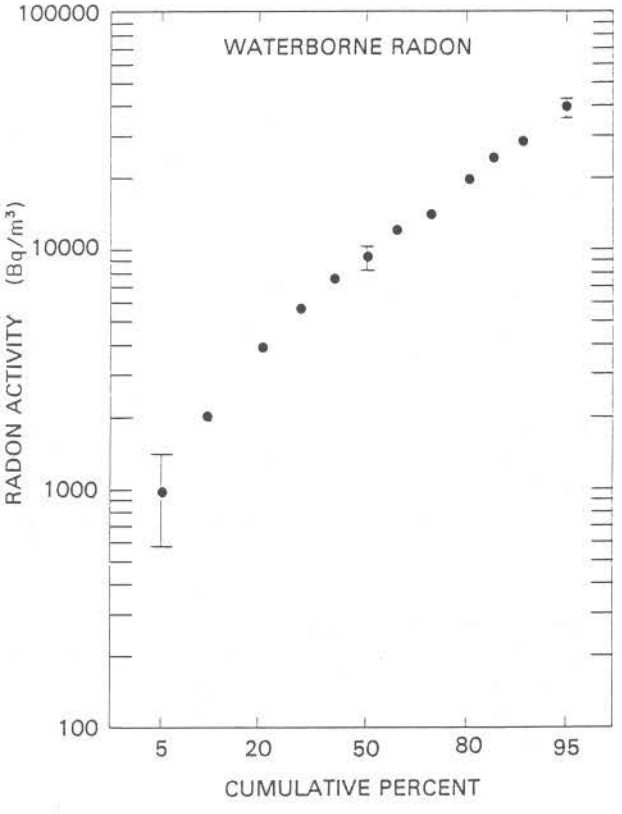


Figure 1 — Waterborne radon distribution.

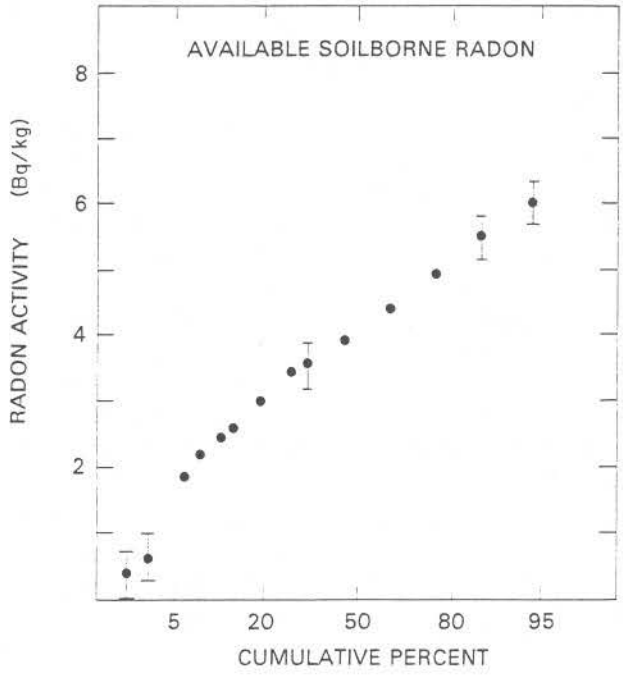


Figure 2 — Available soilborne radon distribution.

TABLE 2
Statistical summary of indoor air radon

Data set	Number	Range	Arithmetic average	Geometric average	Standard deviation
All (to date)	197	20:1100 [0.5:30]	140 [3.8]	100 [2.7]	$\times\div$ 2.0
Winter	128	20:850 [0.5:23]	130 [3.5]	100 [2.7]	2.0
Basement	61	30:850 [0.8:23]	160 [4.3]	125 [3.4]	2.0
First floor	67	20:630 [1:17]	110 [3.0]	90 [2.4]	1.9
Summer	35	40:1100 [1.1:30]	160 [4.3]	90 [2.4]	2.6
Basement	20	40:1100 [1.1:30]	240 [6.5]	130 [3.5]	3.0
First floor	15	40:140 [1.1:4]	70 [1.9]	60 [1.6]	1.6

Units: Bq/m^3; values enclosed in square brackets are pCi/L.

DISCUSSION

Radon source activities appear to be near the U.S. averages (Natural Council on Radiation Protection and Measurements, 1975). A preliminary analysis of the data suggests some significant regional variation in source strength and some relatively strong local radon anomalies. In particular, the highest waterborne radon concentrations correlate with two closely related bedrock terranes that appear to share the same aquifier. The radon available to the atmosphere (as judged from bismuth-214 activity in the upper 10 cm of soil) also varies by a factor of five across the study region. In addition, local variations of a factor of two have been observed (fig. 7). A qualitative review of the data indicates that the bismuth-214 activity, when combined with soil sampling techniques (described below), may be a useful indicator of regionally elevated indoor radon concentrations.

Closed container measurements of soil samples in the laboratory showed less variation in radium content than radon emanation. Clearly, physical soil parameters are playing an important role in determining the *in situ* radon-daughter concentrations. A study is underway to determine if strong correlations exist between radon emanation strengths of soil samples and indoor, below-grade radon activities.

Average indoor air radon activities observed in this study are significantly above the reported U.S. average but fall within previously observed regional extremes (Gessell, 1983; Nero, 1983). The indoor radon activities differ by compartment, season, region, and year. The activities are nearly log-normally distributed with an overall geometric mean of 100 Bq/m^3 [2.7 pCi/L] and the standard deviation is a factor of 2.0 indoor activities. At least one localized "hot" spot appears to correlate with a bedrock fracture zone.

Generally, the indoor radon activity below grade is relatively constant throughout the year. Above grade, the typical house has a radon activity approximately 70 percent of the below-grade value in the winter and approximately 50 percent of the below-grade value in the summer.

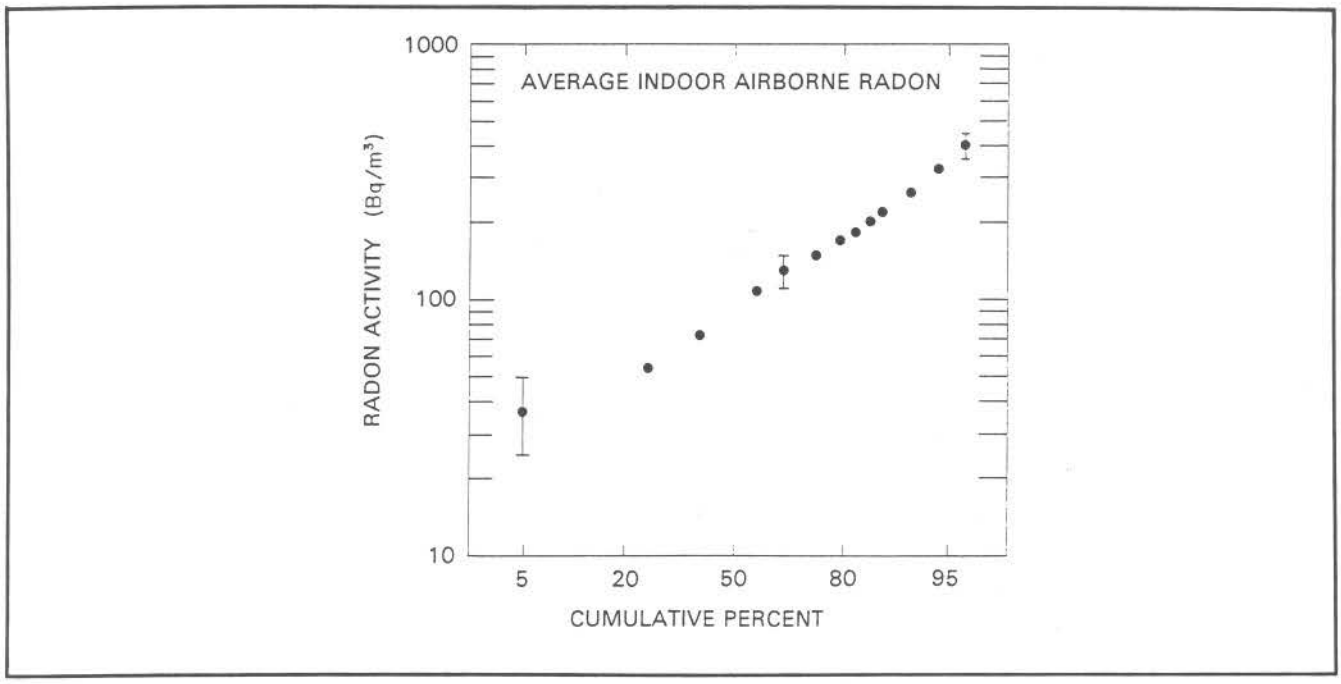


Figure 3 — Indoor airborne radon distribution.

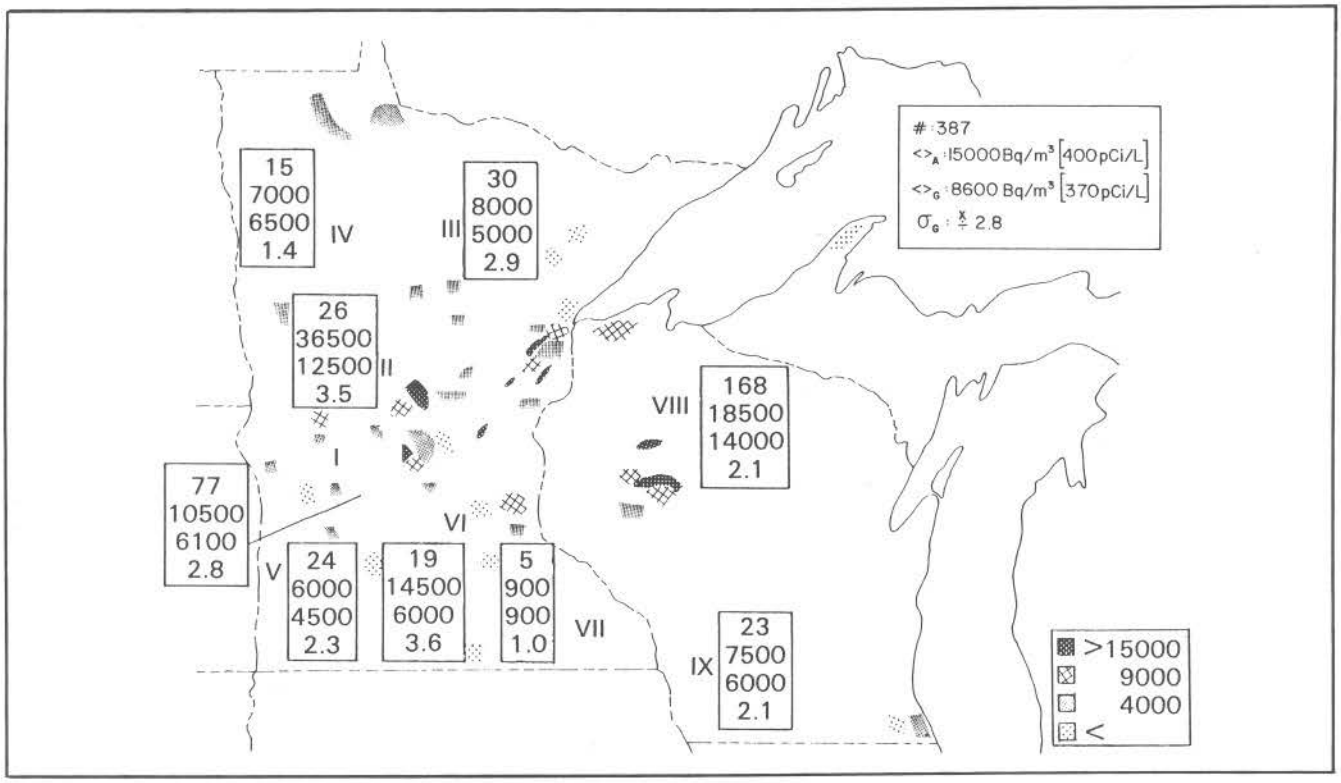


Figure 4 — Geographical distribution of waterborne radon summarized by region (I-IX). Box in upper right corner summarizes complete data set.

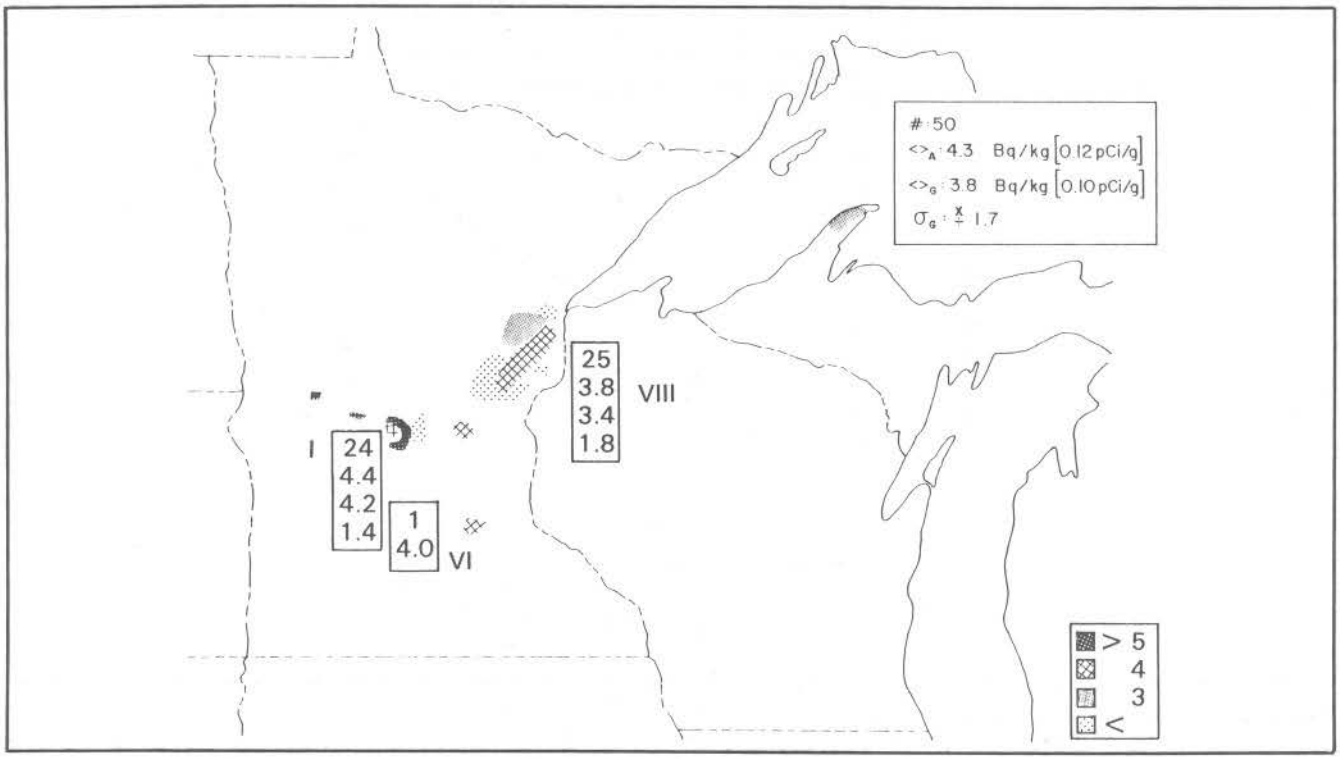


Figure 5 — Geographical distribution of available soilborne radon. Box in upper right corner summarizes complete set.

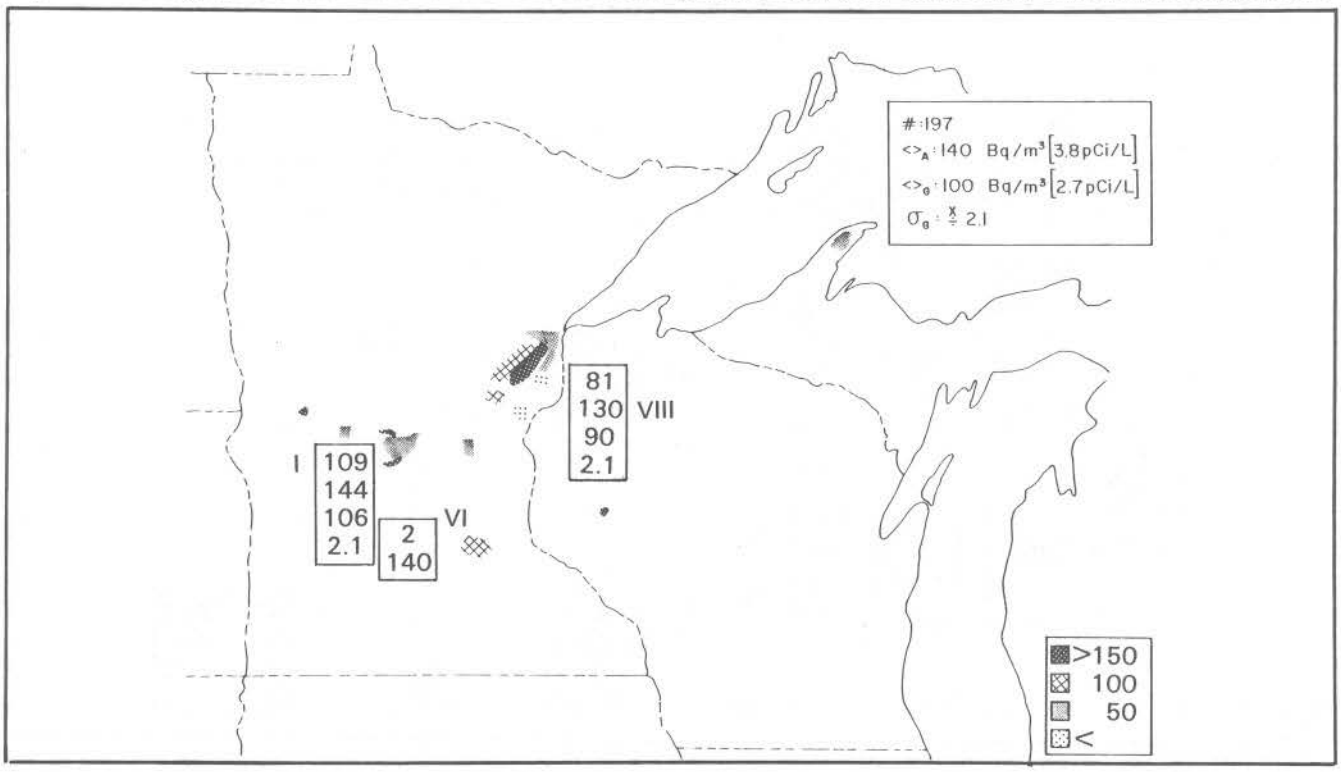


Figure 6 — Geographical distribution of indoor radon. Box in upper right corner summarizes complete data set.

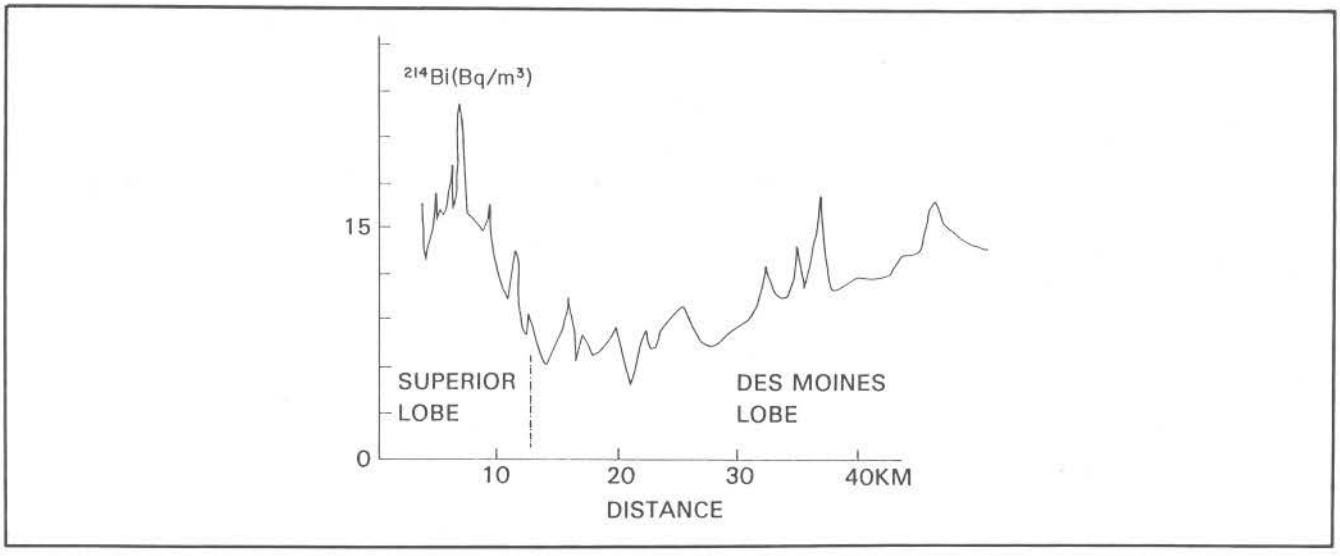


Figure 7 — Sample record of the bismuth-214 gamma flux taken in south-central Minnesota.

CONCLUSIONS

Minnesota and adjacent sections of Wisconsin and Michigan have regionally elevated indoor radon activities. Radon source strengths vary widely. None of them, taken alone, appear to provide an adequate indicator of indoor air radon activity; however, surface bismuth-214 gamma flux combined with subsurface radium activity appears to provide some clues to regional average indoor radon activities.

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RADIONUCLIDES IN PENNSYLVANIAN BLACK SHALES OF THE MIDWESTERN UNITED STATES

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ABSTRACT

Underlying hundreds of thousands of square kilometers of the Midwest are dozens of thin black Pennsylvanian shales containing abundant uranium. Such shales are typically less than 0.5-1.0 m thick, but they occur repetitiously every 15 to 50 m in stratigraphic sections (e.g., Howe, 1956, 1961; Martin, 1982). Hence, it is not uncommon to find several such beds exposed on a single hillside. In most cases, uranium contents of Pennsylvanian black shales range from about 20 to 200 ppm (0.002 to 0.02 wt. percent), but values as high as 700 ppm have been recorded, greatly exceeding normal crustal values (1.8 ppm). In contrast, thorium abundances are close to the crustal average of 7.8 ppm.

In the same region, uranium is also concentrated in parts of the Devonian Chattanooga Shale, the Cretaceous Pierre Shale, and in some Precambrian granites. Uraniferous rocks of the Midwest may have importance with respect to resource estimates, and radon emissions from them may be significant to human health.

INTRODUCTION

This article concerns certain widespread (fig. 1) Pennsylvanian black shales in the Midwest, that contain 20-700 ppm uranium (0.002-0.07 wt. percent). Such enriched uranium contents are considerably greater than those for average crustal rocks and are sufficient to arouse concern about the effects of radon and other radionuclides on the local environment. There are dozens of shales of this type in the Midwest (fig. 2); hence, such concerns are likely to be of more than local interest.

Many buildings have been erected on or in stratigraphic sequences containing Pennsylvanian black shales, particularly in urban areas such as Kansas City (Coveney and Parizek, 1977; Parizek, 1982; Rudy, 1982; Rudy and Coveney, 1985). Because of their jointed and relatively permeable nature, the black shales also serve as aquifers for domestic water in rural areas (e.g., O'Connor, 1971). Clearly such practices may unwittingly expose users to needless risk.

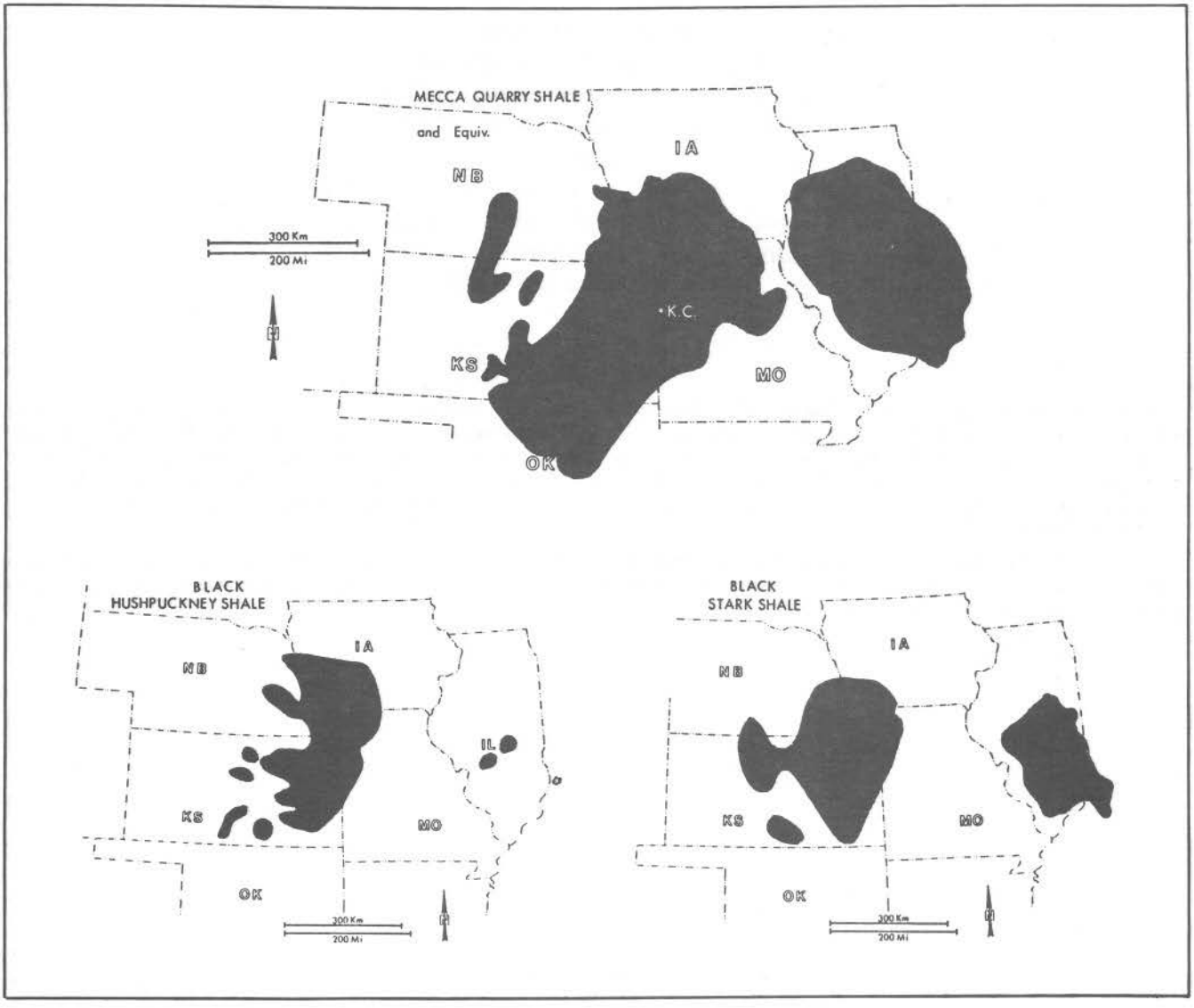


Figure 1 — Regional distributions of black shale in Hushpuckney, Stark, and Mecca Quarry Shale Members and stratigraphically equivalent beds (after Wanless and Wright, 1978).

PREVIOUS STUDIES OF URANIUM IN BLACK SHALES

For many years it has been recognized that black shales are commonly enriched in uranium and other heavy metals (Beers, 1945; Russell, 1944, 1945; Vine et al., 1958; Tourtelot, 1956). Tourtelot (1970) summarizes much of the early literature on the subject. Important uranium reserves hosted by Cambrian shales are known in the Scandinavian countries (Bell, 1978) where some shale-hosted deposits have even been mined for uranium (Armands, 1972; Tourtelot, 1979), although the prospects of future mining of such uranium resources are in doubt (Nash et al., 1981). No mining of black shales for uranium has occurred in the United States, but uranium contents of sufficient quantity to stir past economic interest are known from numerous Paleozoic and Mesozoic stratigraphic horizons. For example, uranium levels averaging about 50 ppm uranium have been reported from the Devonian Chattanooga Shale of Tennessee and adjacent states (Bates and Strahl, 1957) and correlative shales of the central United States (e.g., Ohio, Indiana, Kentucky, Missouri, Kansas, and Michigan). Similarly, organic-rich beds of the Sharon Springs Member of the Pierre Shale of the Dakotas, Colorado, Nebraska, and Kansas (Tourtelot, 1956; Kepferle, 1959) contain up to 200 ppm uranium. Numerous thin black Pennsylvanian shales are also known to contain significant amounts of uranium (Russell, 1944, 1945; Runnels et al., 1953; Ostrom et al., 1955; Swanson, 1960, 1961; Hyden and Danilchik, 1962; Woodland, 1963; James, 1970; Vine, 1964, 1966; Vine and Tourtelot, 1970; Cubitt, 1975, 1979; Martin, 1982; Coveney and Martin, 1983; Allen, 1986).

METHODS

All analyses of stratigraphic units reported in this paper were performed on channel samples: continuous, uninterrupted samples chipped from grooves perpendicular to bedding planes in outcrops, or sawed directly from diamond drill cores. Values reported here, therefore, represent average compositions of the indicated stratigraphic intervals.

Previous studies of uranium contents were chiefly by x-ray fluorescence spectrography (e.g., Coveney and Martin, 1983), but this paper concentrates on results from instrumental neutron activation analysis (INAA), a far more reliable technique. Some check assays for uranium used fluorimetric techniques and delayed neutron analysis. Assays for thorium, potassium, and rubidium mainly used INAA; a few samples were analyzed by inductively coupled plasma spectrometry. Investigative techniques used for typing organic matter and determining mineralogy are reported elsewhere (Coveney et al., 1987; Leventhal, 1981; Coveney and Martin, 1983).

GENERAL GEOLOGY AND DISTRIBUTION OF THE PENNSYLVANIAN SHALES

Middle and Upper Pennsylvanian hard black marine shales are spread throughout hundreds of thousands of square kilometers of the Midwest (figs. 1 and 2), covering wide sections of the states of Kansas, Iowa, Missouri, Illinois, and Indiana, and smaller parts of adjoining states. Fifteen such shales underlie areas exceeding 20,000 km^2 of the central United States (fig. 2); several exceed 100,000 km^2 [Wanless and Wright (1978)]. About a dozen other less widespread Pennsylvanian black shales are present in the region. Most noteworthy of the additional shales are the Logan Quarry and Holland shales of Parke and Vermillion Counties in Indiana, which are in cyclothems below that containing the Mecca Quarry shale, the most widespread of the black shale units. Swanson (1961) estimates there are about 40 uranium-rich organic Pennsylvanian black shales in the Midwest. Other uraniferous Pennsylvanian shales are known from the periphery of the Midwest [e.g., the Minnelusa Formation of the Southern Black Hills in South Dakota and Wyoming (Vine, 1966; Coveney, 1985)].

Few Pennsylvanian black shales are thick enough to be accorded formational status, because their thicknesses are usually under a meter. Nevertheless, because such black shales are widespread (fig. 1) and because they occur repetitively in cyclic stratigraphic sections (cyclothems), it is not uncommon for several black shales to crop out on (and underlie) a single hillside in the Midwest. Middle Pennsylvanian black marine shales commonly overlie coal (fig. 3). Similar beds included among Heckel's (1977) core shales are known from the Upper Pennsylvanian, where they overlie gray shales or limestones (fig. 4).

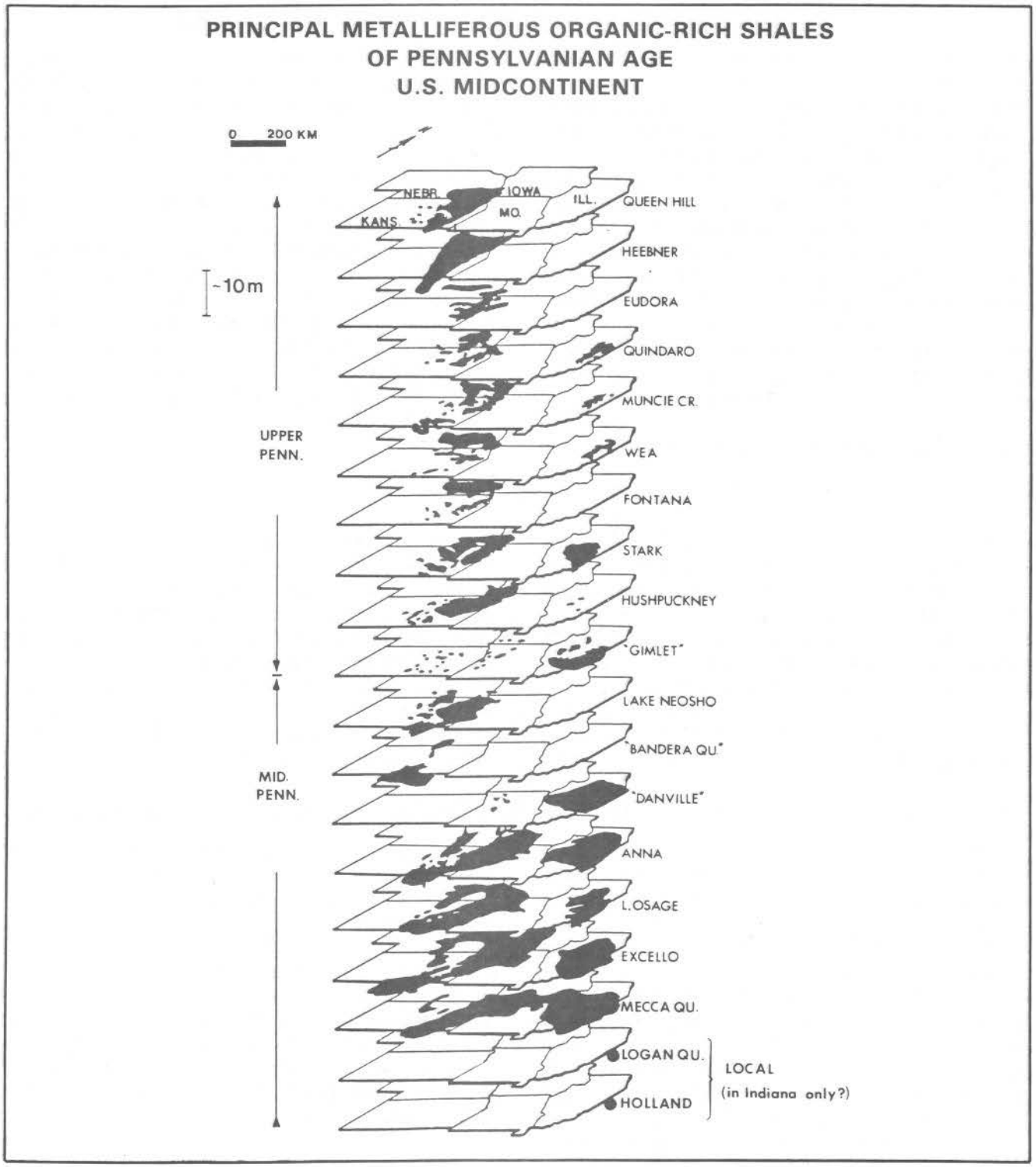


Figure 2 — Regional distributions of black shale facies in Pennsylvanian shales. The Holland and Logan Quarry Shale Members occur only locally in Indiana, but 15 of the units shown have areas exceeding 20,000 km². The distribution of the beds are modified after Wanless and Wright (1978).

CHARACTERISTICS OF THE PENNSYLVANIAN BLACK SHALES

Black Pennsylvanian shales containing abundant uranium are usually well-indurated and enriched in organic matter. The hardness results in a resistance to weathering unusual for shale. Locally, outcrops in stream beds commonly form riffles or low falls. Middle Pennsylvanian black shales are characteristically platy and segmented into blocks by vertical joints spaced about 0.5-1.5 m apart (Zangerl and Richardson, 1963). Joints in shale beds are not confined to Middle Pennsylvanian shales but occur in those of the Upper Pennsylvanian, well-exemplified by the Hushpuckney (fig. 5a), Stark (fig. 5b), Quivira, Muncie Creek, and Eudora Shale Members in the Kansas City Area.

The organic-rich shales can easily be split into thin hard sheets and are often described as "slates" by drillers and quarry workers. In most cases, Midwestern black shale beds have never been subjected to temperatures sufficiently high to metamorphose them. Strictly speaking, therefore, the term "slate" is petrographically inappropriate; nevertheless, the slaty appearance of the rock is a pervasive property that is helpful in distinguishing beds likely to be enriched in uranium, from other dark shales.

Minerals in the black shales include (in general order of abundance) quartz, illite-montmorillonite (mixed layer) clays, kaolinite, chlorite, pyrite, and

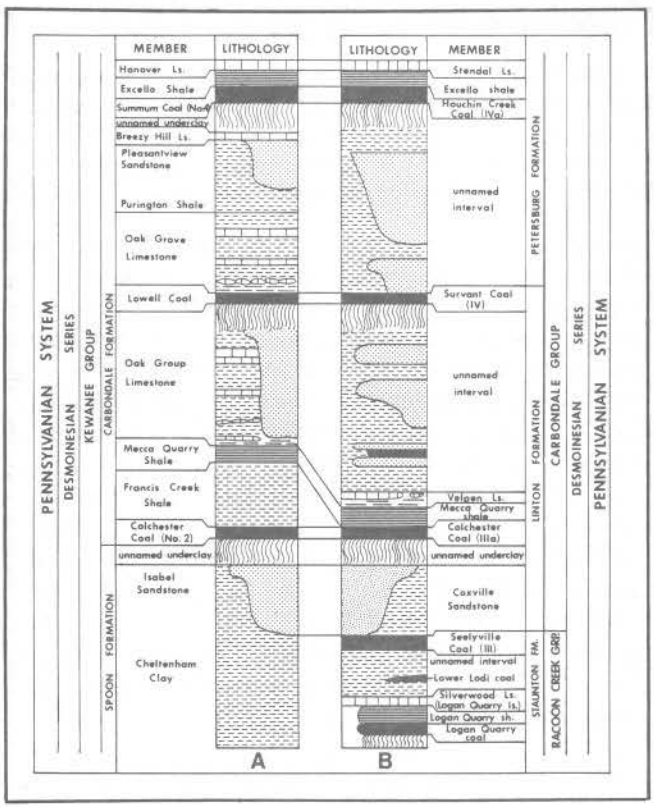


Figure 3 — Local stratigraphic setting of selected Middle Pennsylvanian uraniferous shales of Illinois and Indiana (from Martin, 1982, by permission). Note that stratigraphic members containing platy black shales, such as the Mecca Quarry Shale Member, constitute only about 6 percent of the total thickness of the stratigraphic section (and only about half of each shale consists of uranium-rich black horizons).

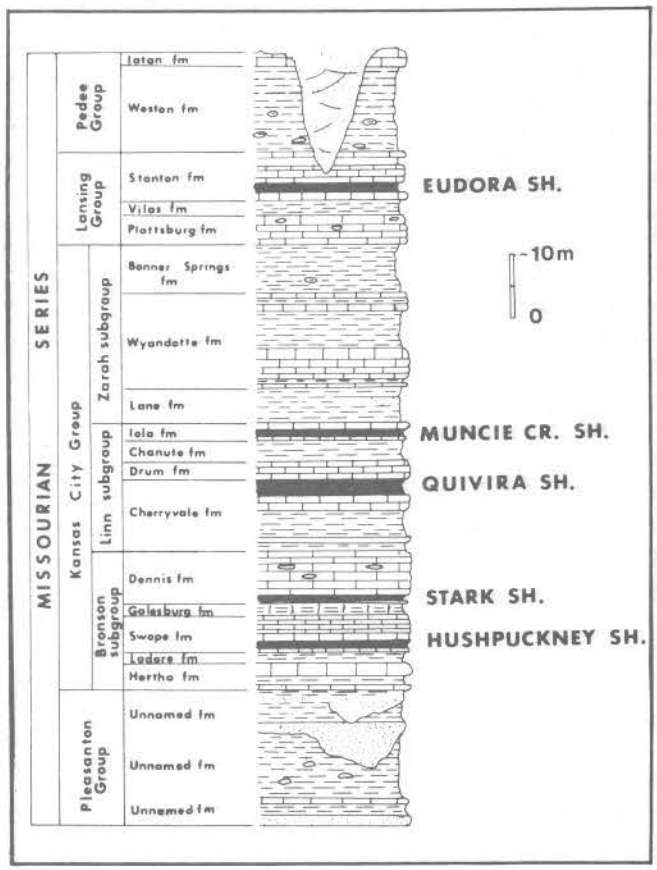


Figure 4 — Local stratigraphic setting of the five Upper Pennsylvanian uranium-bearing shales (after Parizek, 1982 with data from Howe, 1961). Note that shale members containing black shale constitute only 7 percent of the thickness of the stratigraphic section (and only about half of each shale consists of uranium-rich black horizons).

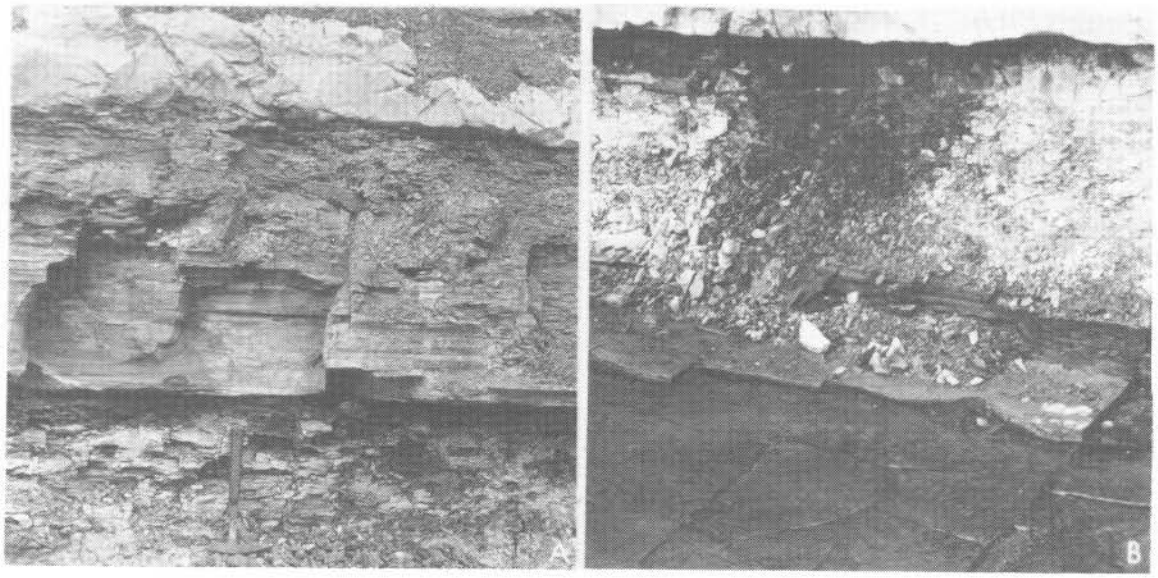


Figure 5 — Kansas City-area roadcuts containing (A) the Stark Shale Member and (B) the Hushpuckney Shale Member. Note that each shale member consists of a ~0.5-mm-thick black uraniferous bed overlain by a gray shale bed of similar thickness. Also the platy, uranium-rich horizon of each shale is segmented into blocks by vertical joints. In the subsurface these open joints permit the shales to act as moderately effective aquifers. Figure 5A is from a roadcut on Highway 150 in Unity Village, Missouri; figure 5B is from Interstate Highway 435 and 63rd Street, on the east side of Kansas City, Missouri.

sphalerite, with traces of chalcopyrite, covellite, and clausthalite (Tourtelot, 1963; Coveney, 1979, 1984, 1985; Coveney and Martin, 1983). Apatite occurs in nodules and in phosphatic fossils, especially fish and conodonts. Phosphate nodules are particularly prevalent in shales of the western part of the study area and in the middle of the Illinois Basin, where they are so concentrated along certain beds as to cause whole-rock phosphate contents to be several percent. Minor amounts of calcite and dolomite are present in some cases (Coveney, 1979), but their presence is largely restricted to the phosphatic nodules that are concentrated in selected layers.

No primary uranium minerals per se have been identified in the shales, although it seems likely that submicroscopic uraninite is present in some cases, as Vassiliou (1980) has found to be the case for many uraniferous shales. Where phosphate nodules are common, uranium substitutes for calcium in apatite (Runnels et al., 1953; Ostrom et al., 1955; Hyden and Danilchik, 1962). For example, the Hushpuckney shale contains nodules, micronodules, and phosphate layers where autoradiographs disclose abundant uranium (fig. 6). It should be noted, however, that some particularly uraniferous beds in Indiana and South Dakota contain only small amounts of phosphate (<0.2 percent). In such shales the uranium appears to be dispersed in organic matter, which constitutes 10 to about 60 percent by weight of the beds and is particularly abundant in near-shore areas, where it is predominantly of terrestrial origin (James and Baker, 1972; Coveney et al., 1987). The association of uranium with beds enriched in terrestrial-type organic matter may have genetic significance, because Szalay (1957, 1964), Szilagyi (1967; 1971), Swanson (1960; 1961), Vine et al. (1958), Disnar (1981), Johnson et al. (1987), and others have noted the ability of organic matter to retain uranium and other elements. Even beds that are rich in phosphate may have originally accumulated uranium by organic fixation.

In some cases the shales directly overlie coals. For example, in Indiana the Mecca Shale Member of the Linton Formation overlies the Colchester coal, a circumstance that may explain why the Mecca is so rich in terrestrial organic matter. Commonly beds enriched in terrestrial organic matter are particularly rich in uranium (Coveney et al., 1987). Such shales were referred to as Mecca-type shales by Coveney (1984). The Mecca Quarry and Logan Quarry shales of Indiana (Zangerl and Richardson, 1963) are typical examples.

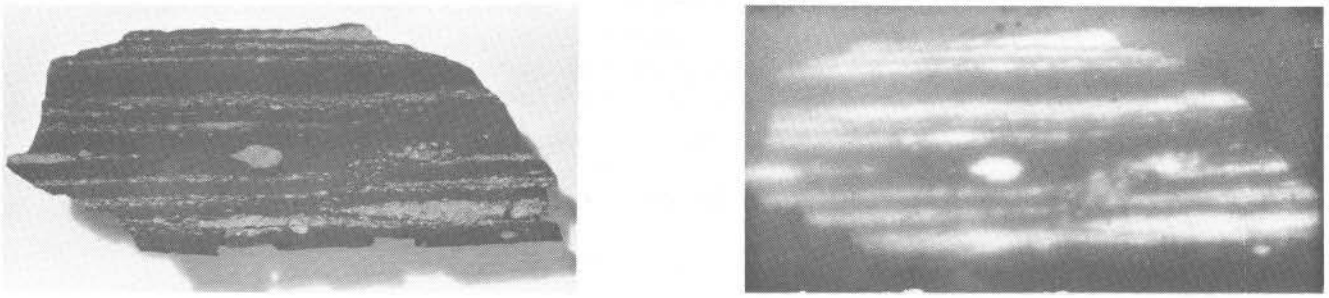


Figure 6 — Autoradiograph of Hushpuckney Shale. Note that the radiation from this shale is largely confined to nodules and laminae of phosphate that are abundant in the Hushpuckney of Kansas and Missouri. In shales where phosphate is less common, such as the Mecca Shale Member of Indiana, uranium occurs dispersed in organic-rich layers. Sample from Parkville, Missouri; exposure 1 month in direct contact with Kodak (no-screen) medical x-ray film.

Other types of Pennsylvanian black shales overlying gray shales or limestones are enriched in phosphates. Most typically, Upper Pennsylvanian black shales are of this type. The Hushpuckney and Stark Shale Members, in the Upper Pennsylvanian Kansas City Group, are in this category, referred to as Heebner-type shales by Coveney (1984). This type of shale overlaps Heckel's (1977) core (or off-shore) shales, although, strictly speaking, Heckel's off-shore shales include some gray beds. Some Middle Pennsylvanian shales in the western part of the study area are considered to be Heebner-type shales, because they are phosphatic and contain only about 10-20 percent organic matter. For example, the Middle Pennsylvanian Little Osage Shale Member and the Excello Shale (in Missouri and Kansas) are Heebner-type shales. Moreover, even the Kansas stratigraphic equivalent of the Mecca Shale (an unnamed bed above a gray shale in the Middle Pennsylvanian Cabannis Formation in Kansas) is a Heebner-type shale containing more phosphate, lesser amounts of total organic matter, and proportionately more organic matter of marine origin than the Mecca Shale Member of Indiana.

GEOCHEMISTRY

The thin black Pennsylvanian shales have long been known to contain significant amounts of uranium (Russell, 1944, 1945; Runnels et al., 1953; Ostrom et al., 1955; Swanson, 1960, 1961; Hyden and Danilchik, 1962; James, 1970; Vine, 1966; Vine and Tourtelot, 1970; Cubitt, 1975, 1979; Martin, 1982; Coveney and Martin, 1983; Allen, 1986). The shales also are enriched in other elements besides uranium, most notably molybdenum, vanadium, selenium [all of which are common in the Colorado Plateau-type and Wyoming roll-front-type uranium deposits of the western United States (e.g. Nash et al., 1981)] and zinc (Cubitt, 1979; Coveney 1979, 1984, 1985; Coveney and Martin, 1983; Coveney et al., 1987).

The abundances of several radionuclides have been investigated in the Pennsylvanian black shales. Typical INAA analyses are shown in table 1. Of all the radionuclides occurring at or above the parts per million level, uranium is most enriched in the shales. Average values for uranium consistently occur at one to two orders of magnitude above accepted averages for the earth's crust. For example, in Middle Pennsylvanian black shale members, uranium contents range from about 20 to 700 ppm, and average 81 ppm, as compared with a crustal average of 1.8 ppm (Mason and Moore, 1982) and typical values for ordinary rocks of 0.001-3.7 ppm [cited by Turekian and Wedepohl (1961)]. In Middle Pennsylvanian shales, the highest uranium contents occur in the eastern part of the Midwest (e.g., Mecca Shale in Indiana averages 89 ppm uranium, whereas its equivalent in Oklahoma averages 28 ppm uranium). Upper Pennsylvanian black shales average about 70 ppm uranium, which may be more uniform over a broad geographic scale [e.g., see Hushpuckney and Stark shales (figs. 7 and 8)] than the uranium in the Mecca-type shales. Radioactivity is such a persistent

TABLE 1
Contents of uranium, thorium, potassium, and rubidium in Pennsylvanian black shales of the central United States
(INAA results)

County	Quad	Bed	Thickness (cm)	ppm U	ppm Th	ppm Rb	wt.% K
MECCA QUARRY SHALE AND ITS STRATIGRAPHIC EQUIVALENTS							
INDIANA (Mecca Shale Member)							
Parke	Mecca	Hesler Farm A	8.9	148.9 [1]	7.99	104	1.97
"	"	Hesler Farm B	17.0	143.4 [2]	7.44	100	1.92
"	"	Hesler Farm C	8.8	85.0 [3]	10.95	145	2.84
"	"	Hesler Farm D	4.2	62.4 [4]	8.32	95	1.71
"	"	Barren Creek A	20.3	65.1	11.36	136	2.50
"	"	Barren Creek B	27.9	63.8	10.11	131	2.57
"	"	Barren Creek C	12.7	73.8	11.59	143	2.82
"	"	Barren Creek D	3.8	70.9	7.88	88	1.71
"	"	Mine Creek A	25.4	79.9	11.15	138	2.32
"	"	Mine Creek B	20.3	110.3	8.36	112	2.26
"	"	Mine Creek C	7.6	33.7	9.40	175	3.40
"	"	Mine Creek D	2.5	84.7	9.10	101	1.79
Warrick	Holland	B (Top)	8.9	166.3	6.71	80	0.02
Pike	Velpen	A	14.0	43.5 [5]	11.99	123	2.36
"	"	B	15.2	123.6 [6]	7.25	93	1.64
"	"	C	22.9	112.1 [7]	10.27	142	2.51
"	"	D	2.5	48.6 [8]	7.83	74	1.23
KENTUCKY (Mecca Quarry Shale Member)							
Daviess	Curdsville	D	2.4	150.1	7.29	95	1.73
Union	Dekoven	A	5.7	80.9	11.42	83	2.66
"	"	B	15.2	111.4	9.97	181	2.61
"	"	C	7.0	65.5	12.38	154	2.83
"	"	D	3.2	258.4	6.57	149	1.75
ILLINOIS (Mecca Quarry Shale Member)							
LaSalle	Lowell	A	17.5	71.8	7.55	89	1.76
"	"	B	19.2	104.6	4.91	64	1.49
"	"	C	9.5	102.0	8.03	100	2.38
"	"	D	6.2	76.1	6.51	81	1.99
Knox	Knoxville	A	32.4	54.1	6.45	86	1.91
"	"	B	9.9	99.0	7.25	95	1.95
"	"	C	5.8	56.0	11.79	156	3.00
"	"	D	6.3	75.1	7.54	83	1.93
IOWA (Oakley Shale Member)							
Polk	Grimes	CP 47.4-5	17.8	49.3	8.16	95	2.02
"	"	CP 47.3	6.4	45.4	6.93	84	2.03
"	"	CP 47.1-2	25.4	134.1	5.60	71	1.47
Wapello	Ottumwa S.	CP 7.5	2.5	21.9	10.07	121	2.34
"	"	CP 7.4	15.2	21.2	8.24	115	2.55
"	"	CP 7.3	6.4	61.8	7.34	95	2.01
"	"	CP 7.1-2	25.4	120.9	4.88	63	1.42

TABLE 1 (cont.)

County	Quad	Bed	Thickness (cm)	ppm U	ppm Th	ppm Rb	wt.% K
MISSOURI (unnamed black shale member over Croweburg Coal Member in Verdigris Limestone)							
Randolph	Jacksonville	ORC 19.5-6 (Top)	34.3	33.0	8.71	116	2.59
"	"	ORC 19.3-4	22.9	58.4	6.95	75	1.74
"	"	ORC 19.2	19.1	37.0	8.72	113	2.15
"	"	ORC 19.1 (Base)	15.2	13.8	6.42	82	1.59
"	"	BM 2.5-6 (Top)	17.8	24.6	8.62	117	2.72
"	"	BM 2.3-4	27.9	70.7	6.80	88	2.05
"	"	BM 2.2	7.6	60.6	9.15	120	2.40
"	"	BM 2.1 (Base)	3.8	11.2	2.06	39	0.72
KANSAS (unnamed black shale over Croweburg Coal Member in Cabannis Formation)							
Bourbon	Ft. Scott	A9,10	25.4	14.6	8.92	126	2.50
"	"	A8	7.6	24.7[9]	8.39	108	2.26
"	"	A7	10.2	53.7[10]	8.11	92	1.87
"	"	A6	7.6	39.2[11]	10.10	113	2.17
"	"	A3-5	25.4	36.9	9.42	106	2.36
"	"	A1	7.6	17.5[12]	8.36	100	2.10
OKLAHOMA (unnamed black shale below Verdigris Limestone and above Broken Arrow Coal Member, Rogers Mine)							
Nowata	New Alluwe	Top	12.7	40.2	12.91	146	2.56
"	"	A1-2	10.2	17.5	11.32	171	3.01
"	"	A3-5	16.5	34.7	8.64	124	2.01
"	"	A6-7	11.4	24.2	12.28	148	2.79
"	"	A8-9	11.4	22.7	10.99	146	2.68
OTHER DESMOINESIAN (MIDDLE PENNSYLVANIAN) SHALES							
INDIANA (Excello Shale)							
Pike	Bethel		~6.0	107.0	7.41	111	1.98
INDIANA (Logan Quarry Shale)							
Parke	Montezuma	Logan Farm #F	12.0	54.2	10.02	126	2.47
Parke	Midway	Kb	8.9	36.7	5.11	47	0.88
"	"	Eh	33.0	125.0	6.16	83	1.58
INDIANA (Mecca, Barren Creek)							
Parke	Holland	5	7.6	704.2	10.04	78	1.57
"	"	4	33.0	161.7	8.88	105	1.99
MISSOURIAN (UPPER PENNSYLVANIAN) SHALES							
KANSAS (Heebner Shale)							
Douglas	Lawrence W		99	35.1	8.72	118	2.22
KANSAS (Muncie Creek Shale) middle portion of bed							
Wyandotte	Kansas City		44	49.5	0.69	4	2.25
MISSOURI (Stark Shale) lower part, fig. 5a							
Jackson	Lee's Summit		41	80.4	7.63	97	2.16
MISSOURI (Hushpuckney Shale) lower part, fig. 5a							
Jackson	Kansas City		45	49.6	8.94	111	2.25
"	Lee's Summit		36	64.4	8.70	115	2.14

Values by the delayed neutron counting method (Coveney et al., 1987)

1. 162 ppm
2. 158 ppm
3. 66.2 ppm
4. 74.4 ppm
5. 78.2 ppm
6. 120 ppm
7. 70.0 ppm
8. 70.0 ppm
9. 30.8 ppm
10. 41.5 ppm
11. 33.7 ppm
12. 26.5 ppm

characteristic of the widespread Upper Pennsylvanian beds that well loggers are able to use the beds as stratigraphic markers on gamma logs. When channel samples are split into thin laminae (such as the 5-cm intervals used in figure 9) it becomes clear that

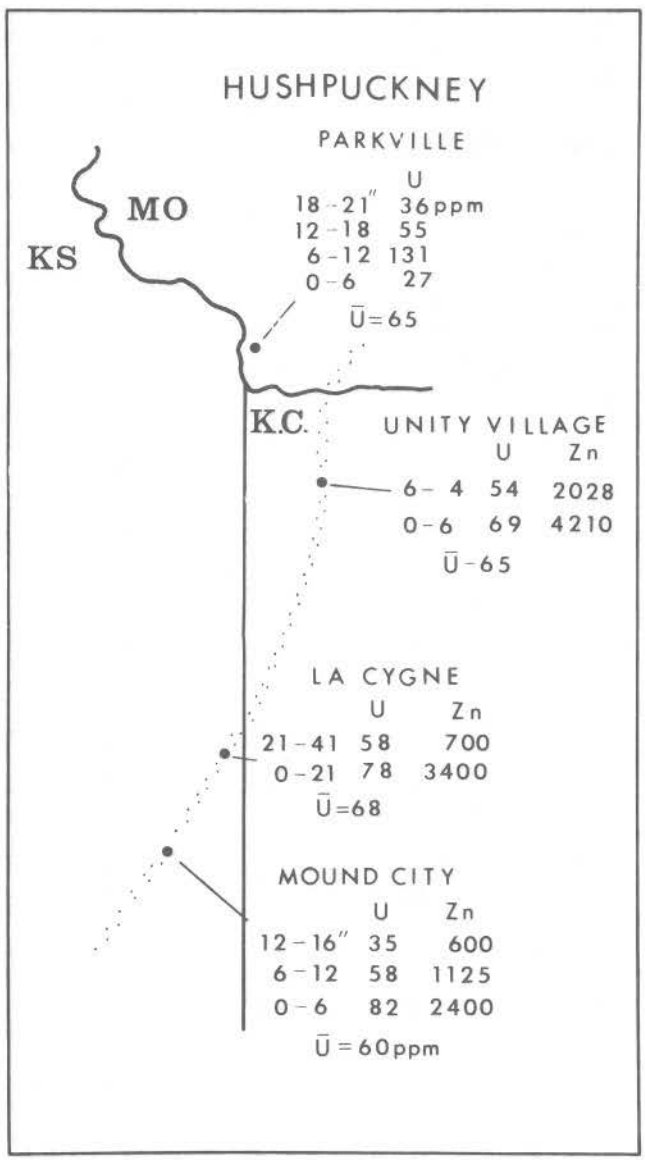


Figure 7 — Analyses for uranium and zinc in the Hushpuckney Shale Member. Note the relative uniform consistency for uranium in the bed in western Missouri and eastern Kansas (K.C. = Kansas City). The outcrop belt shown in the figure is very generalized and should not be used to assess risk levels. The bed is inclined gently westward (a dip less than 1°) and so is present in the shallow subsurface, in a belt about 20 mi wide. Bed thicknesses are in inches (").

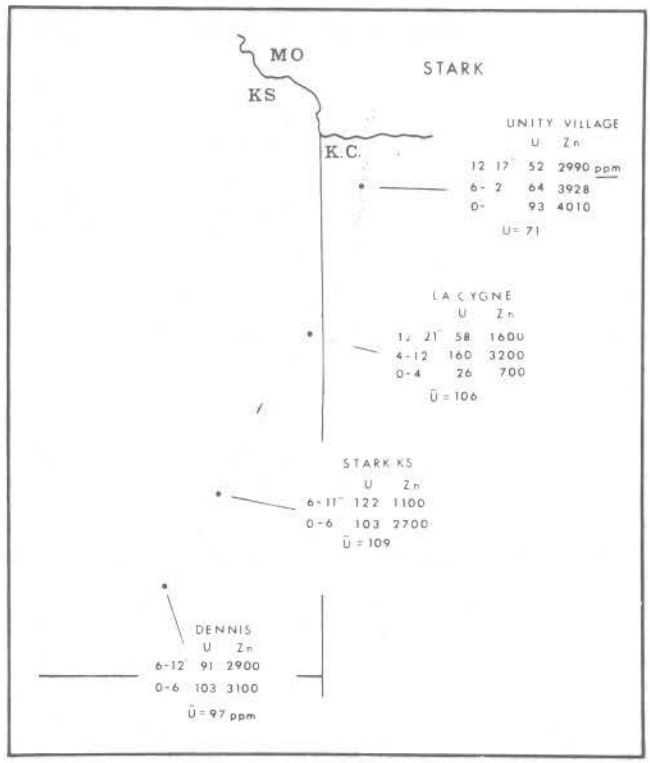


Figure 8 — Analyses for uranium and zinc in the Stark Shale Member. Note the relative uniform consistency for uranium in the bed in western Missouri and eastern Kansas (K.C. = Kansas City). The illustrated outcrop belt for this westward-dipping bed is very generalized and should not be used to assess risk levels.

uranium contents are not uniformly distributed vertically through the shales. Generally high uranium contents correlate with enrichments of organic carbon; however, presumably because of reshuffling of elements during diagenesis, the uranium is preferentially concentrated in the phosphate nodule layers in Heebner-type, phosphate-rich shales such as the Hushpuckney (fig. 6). In Mecca-type shales, which are less phosphatic, most uranium is dispersed in organic matter, perhaps as finely divided uraninite Nevertheless, even in Mecca-type shales, which are not generally phosphatic, analyses of fish fossils have shown that elevated levels of uranium are present in the fish bones.

Except for uranium (and presumably its daughter products) other radionuclides in the shales are probably not enriched markedly above crustal averages. For example (table 1), thorium contents range from about 4.9-12.9 ppm, compared to an average for the earth's crust near 7.8 ppm. Radon-220 (thoron) is

emitted as an intermediate daughter product of the natural decay of thorium, but in view of relatively low concentrations, it is inferred not to be a significant contributor to the radon emitted from the shales. The shales contain up to 3 percent potassium, 420 ppm strontium, and 181 ppm rubidium (table 1). A fraction (Brownlow, 1979) of each of these elements (.01 percent potassium, 7 percent strontium, and 27 percent rubidium) in the shales consists of radioisotopes that decay by emitting alpha or beta particles. These radionuclides contribute to the total radioactivity emitted by the shales, but none of these radionuclides decays to form radon gas.

Uranium is the only parent radionuclide occurring in Pennsylvanian black shales at levels significantly above average crustal abundances. No systematic surveys have been completed assessing radon emissions from such shales. Preliminary surveys indicate that some buildings in Kansas City and other parts of the Midwest contain air with radon levels higher than the average 1-1.5 pCi/L for indoor air [U.S. Environmental Protection Agency (EPA), 1986a; Nero et al., 1986]. For example, in early 1987, a Kansas City-area television news team measured the homes of about 20 employees and found radon concentrations in the range of 2-16 pCi/L [25 percent of the homes tested exceeded the EPA action level (EPA, 1986a) of 4 pCi/L]. Black shales may be the ultimate source of this radon contamination, but this has not been demonstrated.

HUSHPUCKNEY SH. (PARKVILLE)

INTERVAL	TOM	U	
80-85 CM	2.75 %	0 ppm	
75-80	5.78	0	
70-75	3.18	26	
65-70	2.50	0	
60-65	6.85	26	
55-60	6.80	26	GRAY
50-55	11.60	26	BLACK, FISSILE
45-50	18.90	46	
40-45	15.30	26	
35-40	18.70	54	
30-35	22.70	84	
25-30	24.60	163	
20-25	20.00	160	
15-20	17.90	70	
10-15	15.00	54	
5-10	11.50	26	
0-5	6.85	0	
$\bar{x}$ =	16.60	65	(FOR BLACK)

r = .812

Figure 9 — Uranium and organic-matter contents of channel samples of Hushpuckney Shale Member, Swope Formation, eastern Kansas-western Missouri. A linear least squares correlation coefficient, r, of 0.812 exists between uranium values and total organic matter as determined by weight loss accompanying oxidation of samples with H_2O_2. The detection limit for these x-ray fluorescence analyses was 26 ppm uranium.

ORIGINS OF URANIUM DEPOSITS IN THE SHALES

Space precludes a thorough discussion of the modes of emplacement of uranium and other metals, but a brief summary can be given. Previous workers, including Swanson (1960; 1961), Zangerl and Richardson (1963), Vine (1964), Vine and Tourtelot (1970), Tourtelot (1979), Heckel (1977), Cubitt (1979), and others, attributed the origins of metal contents to a combination of factors that may have affected the shales from the time of deposition to the present day. The Pennsylvanian Period has been radiometrically dated between 250 to 300 million years ago; hence, there has been a large interval of time for mineralization.

Coveney and Martin (1983) inferred that metals were emplaced in the shales during and shortly after initial deposition of the muds that formed the shales. They visualized mineralization as resulting largely from fixation of uranium and other metals by organic matter drifting and soaking in the shallow midcontinental Pennsylvanian seas (fig. 10). Most of the organic matter was speculated to be chiefly of terrestrial origin. Recently, Coveney et al. (1987) confirmed that the organic matter in the shales is of terrestrial origin and of a type that earlier workers (e.g., Szalay, 1957) inferred capable of extracting uranium from circulating solutions. A plausible source of this

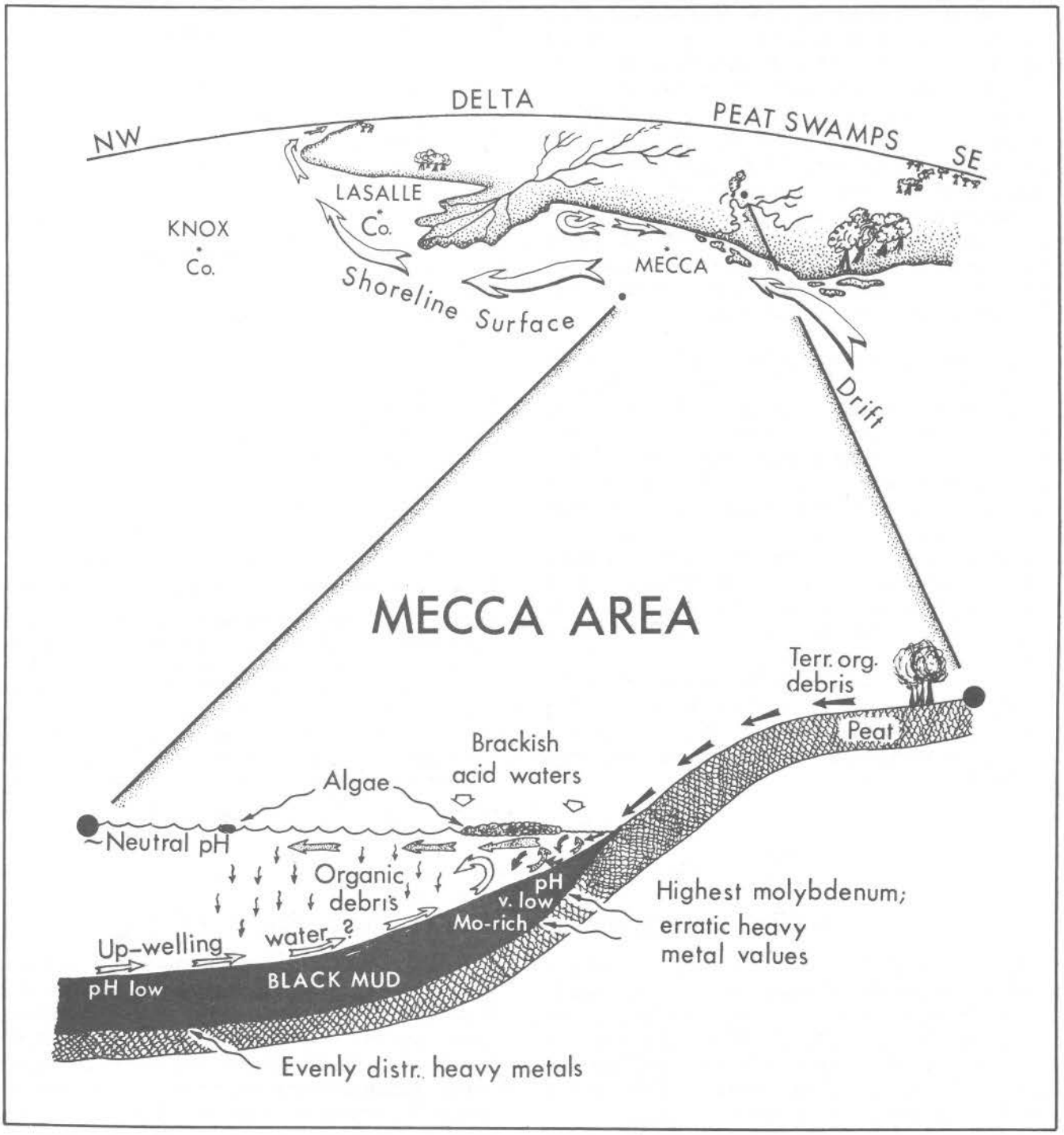


Figure 10 — Coveney and Martin's model for metal enrichment in Mecca Quarry Shale. The model provides for accumulation of metals, including uranium, by the shales during sedimentation (syngenetically) by adsorption on dead organic matter. Coveney et al. (1987) have inferred that further accumulation of metals may have occurred during circulation of formational brines through cyclothems containing the shales, and currently may be taking place from groundwater. There is little doubt, however, that, as shown in the model above, appreciable metals were added to the shales during sedimentation. Figure from Coveney and Martin (1983), Economic Geology, by permission.

organic matter would be the extensive peat swamps that fringed the Pennsylvanian seas and that are represented by the widespread coals in the continental interior.

Coveney et al. (1987) subsequently suggested that a significant proportion of the metals in the Mecca Quarry Shale Member of Indiana *may* have been added long after sedimentation, an inference based largely on the discovery that the shales are still capable of picking up metal ions, such as molybdenum and silver, from aqueous solutions (Coveney et al., 1987). Uranium enrichment may therefore even extend to the current weathering cycle, with metals now being added by groundwater currently in contact with the shales, a working hypothesis close to those suggested years ago by Swanson (1960; 1961) and by Vine and Tourtelot (1970), who inferred that before, during, and after sedimentation, organic matter may play a "never-ending role" in fixing metals from solutions that come in contact with it.

Coveney et al. (1987) also suggested that there might be a temporal problem in deriving significant amounts of uranium from sea water during the short sedimentation interval, particularly if Zangerl and Richardson (1963) were correct in inferring that Mecca-type shales were deposited during only a few years. However, the recent discovery by Johnson et al. (1987) that a high-grade uranium deposit can be formed in peat during less than 7000 years argues against (or at least alleviates) potential difficulties associated with a short sedimentation interval.

ENVIRONMENTAL IMPLICATIONS

As mentioned above, a recent reconnaissance survey by an investigative reporter for a television station in the Kansas City metropolitan area showed several houses had radon levels above the 4 pCi/L action level established by the EPA. The excess radon source has not been established, nor is it clear whether or not higher values may eventually be recorded. Outcropping bedrock in the region consists entirely of cyclic Pennsylvanian sedimentary rocks of the Kansas City Group, including five shales containing 50-100 ppm uranium (Hushpuckney, Stark, Quivira, Muncie Creek, and Eudora Shale Members). Tests are underway to determine whether some or all of these shales may act as environmentally significant sources of radon.

The extreme thinness of these and other Pennsylvanian black shales presents difficulties in making radon risk maps. Where present in the Midwest, shales constitute only a small fraction of the stratigraphy. For example, the five black shales at or near the surface in Kansas City, constitute less than 7 percent of the section (fig. 4), and black shales in the Middle Pennsylvanian Series of Indiana and Illinois form less than 6 percent of the section (fig. 3). As a rule, Pennsylvanian black shales are too thin for scale representation on maps of large areas. Most are therefore mapped as stratigraphic members rather than as formations; nevertheless, it seems prudent to assume that the black shales are an appreciable environmental risk to people in the Midwest and that they may be a critical health factor for individuals who reside or work in structures with basements in direct contact with such shales.

An insidious feature of black shales is their tendency to swell when exposed to air and moisture in the shallow subsurface, even beneath foundations and footings. Coveney and Parizek (1977), for example, discussed the behavior of black shales in extensive underground space warehouses of Kansas City, where Hushpuckney Shale Member underlying concrete or asphalt floors tends to swell and cause maintenance problems. Two to 4 years after construction, large cracks (as well as general distortion) almost invariably appear in the floors. These cracks were attributed by Coveney and Parizek (1977) to oxidation of sulfides in the shales. Other possibilities include release fractures caused by unloading of floors and swelling of clays by moisture. It is important to note that regardless of which process predominates, deterioration of shale is involved and migration of radon through the resultant fractures is likely.

Understandably, shale deterioration is not confined to underground space sites; it occurs at an accelerated rate on outcrops and in the shallow subsurface. Such effects are readily evident in buildings and houses on surface sites (Rudy,

1982; Parizek, 1982; Rudy and Coveney, 1985). In both surface structures and underground settings, cracks in foundations may transmit radon from shales to structures occupied by people. Direct contact between shales and structures is not necessary for genesis of radon problems. Other possibilities include emanations from natural springs and fracture zones that may form a connection between black shales in the subsurface and surface structures.

Typical ores contain about 1000+ ppm uranium; the crustal average is near 1.8 ppm. Thus, the average contents for uranium in the Pennsylvanian shales lie between those for the earth's crust and uranium ores. One would guess, therefore, that the risk to people, from radon emissions from black shales in contact with a house or business would lie somewhere between that experienced by miners in roll-front uranium deposits and that of individuals under average ambient conditions. As a rough approximation, one would expect that rocks, like the Pennsylvanian shales, containing 50-100 times as much uranium as average rocks would produce 50-100 times as much radon as that contained in average interior air. As mentioned above, average interior air contains about 1-1.5 pCi/L (EPA, 1986a; Nero et al., 1986). Conceivably indoor air levels above 50-100 pCi/L (1 pCi/L x 50-100) could be attributed to uraniferous beds, such as the midwestern shales.

In Pennsylvania, Smith et al. (1987) investigated the uranium and other radionuclide contents of soil and bedrock associated with a house that is massively contaminated with radon. Initial measurements at this house (called by them the "Index House") showed radon concentrations up to 2500 pCi/L for sustained periods. The underlying bedrock contains approximately 30-50 ppm uranium and 30-60 ppm thorium. The uranium contents are therefore comparable to those of black shales in the Midwest.

It should be mentioned that radiation hazards from Pennsylvanian shales may not be restricted to radon emission. Individuals involved in excavating such rocks in mines, quarries, and construction sites may find it advisable to take special precautions against inhalation (and possibly even ingestion) of the dust from such rocks. Aside from the normal concerns about particulate levels, dust from these shales may be an unsuspected source of radiation-induced diseases.

Absence of Pennsylvanian shales should not give a false sense of security regarding radon problems. As noted elsewhere, there are other Paleozoic and Mesozoic uraniferous shales in the Midwest, such as the Chattanooga and its age equivalents (Nuelle, 1987). Even in nonsedimentary terrane, crystalline rocks such as certain Precambrian granites in the St. Francois Mountains are appreciably enriched in radionuclides (Kisvarsanyi, 1987).

DIAGNOSIS AND REMEDIES

Careful, detailed geologic mapping may aid in assessing radon risks from Pennsylvanian shales in the Midwest. Such mapping is likely to be most useful in urbanized areas where the shales occur. For example, studies of radon concentrations associated with black shales are underway in Kansas City.

Quite frankly, in view of the difficulties involved in mapping such thin beds, the individual homeowner would probably find it much more convenient to use the more direct technique of measuring radon concentrations with activated charcoal canisters or other commercial techniques. Should problems be ascertained, a step-wise procedure for alleviation of danger has been outlined by the EPA (U.S. EPA, 1986b,c).

There are indications that concentrations of radon above the EPA (4 pCi/L) action level are prevalent in some houses in Kansas City, and probably similar levels exist in other areas of the Midwest where Middle and Upper Pennsylvanian rocks predominate (figs. 1 and 2). These include such major metropolitan areas as Omaha, Des Moines, Peoria, and Springfield (Illinois), in addition to Kansas City. More radiometric information about the region is needed, particularly data that directly compare radon emissions with bedrock types (Nuelle, 1987). In order to evaluate possible hazards from the shales under discussions, data more detailed than those resulting from NURE aerial surveys must be acquired. If measurements

appreciably above the maximum 16 pCi/L currently known are determined in the Kansas City area and elsewhere in the Midwest where black shales occur, legislation requiring tests for radon levels before construction or sale of buildings should be considered (perhaps standards for permissible radon levels should be incorporated into local building codes).

The remediation of the radon problem at the Index House in Pennsylvania should cause optimism. Even in this presumably extreme case, where 2500 pCi of radon were measured per liter of air, it was possible to retrofit the home to achieve radon levels tolerable for human habitation (Smith et al., 1987); hence, comparable problems that may exist in the Pennsylvanian outcrop belt of the Midwest should also be controllable.

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THE GEOLOGIC SETTING OF A SURFICIAL URANIUM DEPOSIT, NORTHEASTERN WASHINGTON

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ABSTRACT

A recently discovered ore-grade uranium enrichment occurs in surficial, organic-rich, low radioactivity sediments of late Pleistocene to Holocene age. It is a geologic model for locating other examples of young, and therefore, daughter-poor, uranium deposits. The uranium is concentrated in valley-fill sediments, as much as 4 m thick, along the upper reaches of the north fork of Flodelle Creek, Stevens County, Washington. These sediments range from peat (50 to 60 weight percent organic matter) to clay, silt, and sand of lesser organic content, and were deposited in shallow ponds formed on postglacial topography or in response to subsequent beaver activity. Uranium contents of the sediments ranges from <0.01 to 0.9 percent of dry weight and are positively correlated with organic matter contents. Local bedrock is a Cretaceous two-mica quartz monzonite that is anomalously uraniferous: 28 outcrop samples average 5.9 ± 4.2 ppm uranium and 13 core samples average 15.8 ± 2.7 ppm uranium. The bedrock is locally fractured and faulted and is mostly covered by as much as 2 m of glacial drift. Transport of uranium from this local source rock to nearby organic-rich sediments is via anomalously uraniferous (17-320 ppb uranium) surface water and groundwater, which include subsurface runoff and springs that issue from till-covered slopes or that well up in valley-bottom sediments. Recent glaciation was critical to the establishment of this mineralizing system, because it simultaneously provided (1) renewed exposure and comminution of a favorable source rock, and (2) renewed formation of environments suitable for ponding, where organic-rich sediments accumulate and trap dissolved uranium.

INTRODUCTION

The concentration of radionuclides at or near the earth's surface is a matter of obvious environmental and health concerns. Uranium deposits in surficial soils and sediments are examples of such concentrations that have only recently been discovered and classified (Toens and Hambleton-Jones, 1984; Otton, 1984; Culbert et al., 1984). The deposits are typically very young (Holocene-Pleistocene) and are formed when uranium is extracted or precipitated from groundwater and surface water onto such suitable substrates as organic matter, carbonates, or gypsum. General characteristics of the organic-rich varieties of these deposits include small size (usually <250 metric tons of uranium), variable grade (100-1500 ppm of dry weight), spatial association with granitic terrain, and radioactive disequilibrium (uranium>> daughters). The latter characteristic is of particular importance because daughter-poor deposits of this type yield very little gamma-ray activity and can be overlooked or underestimated by conventional radiometric measurements (Levinson and Coetzee, 1978; Levinson et al., 1984). Clearly, the successful exploration for these low-radioactivity uranium deposits must rely more heavily on the recognition of favorable geologic settings and on direct measurement of uranium concentrations.

The environmental hazard posed by surficial uranium deposits remains to be fully assessed, but the deficiency of daughter products relative to uranium suggests that the major consequence of deposit disturbance will be uranium contamination of local water supplies. Ingested uranium is possibly a radiation carcinogen as well as a cause of kidney damage (Cothern et al., 1983).

This paper summarizes the geologic environment of an unusually uraniferous, organic-rich, surficial uranium deposit. The low-radioactivity deposit is in northeastern Washington and was inadvertently "discovered" during stream-sediment sampling intended to seek vein-type uranium deposits in local bedrock. Because this occurrence represents a new class of uranium deposit, the U.S. Geological Survey is conducting multidisciplinary studies, so that conditions leading to its formation and preservation can be better understood (Otton and Zielinski, 1985; Zielinski and Otton, 1986a, b; Zielinski and Schumann, 1987; Zielinski et al., 1987; Johnson et al., 1985, 1987). To the extent that this deposit is a type example, the resultant geologic model will be useful in seeking additional deposits in similar geologic settings.

REGIONAL GEOLOGY

Northeastern Washington is underlain principally by variably metamorphosed late Precambrian rocks (fig. 1; Harrison, 1972). These include siltite, argillite, quartzite, and subordinate carbonate rocks of the Belt Supergroup (Middle Proterozoic), and metasedimentary and metavolcanic rocks of the Windermere Group (Middle? and Late Proterozoic). All the Precambian rocks are unconformably overlain by Paleozoic miogeosynclinal rocks, and the sedimentary section is extensively intruded by Jurassic through early Tertiary granitic rocks (Miller and Engels, 1975). Other geologic units of regional interest are domal metamorphic core complexes, probably of pre-Belt age, composed of high-grade metamorphic rocks flanked by zones of mylonitized rocks (fig. 1; Cheney, 1980; Rhodes and Hyndman, 1984).

Major structural features of northeastern Washington include (1) the Kootenay Arc, a northeast-trending fold belt up to 100 km wide that was probably formed during Jurassic to Early Cretaceous time (Hoy, 1977), and (2) the Newport fault, a northward-dipping low-angle fault active during a period of regional crustal extension in the early Tertiary. The fault juxtaposes a lower block containing Precambian gneisses and Mesozoic granitic plutons with an upper block containing weakly metamorphosed Belt Supergroup and Paleozoic rocks and Tertiary sedimentary rocks (fig. 1; Miller, 1971; Harms and Price, 1983).

During the Pleistocene, northeastern Washington was periodically covered by glaciers that left extensive glacial drift, including glaciofluvial and glaciolacustrine deposits. The last of the glaciers left the area about 10,000-15,000 years B.P. (fig. 2; Waitt and Thorson, 1983), after which, erosion and sedimentation further modified the topography.

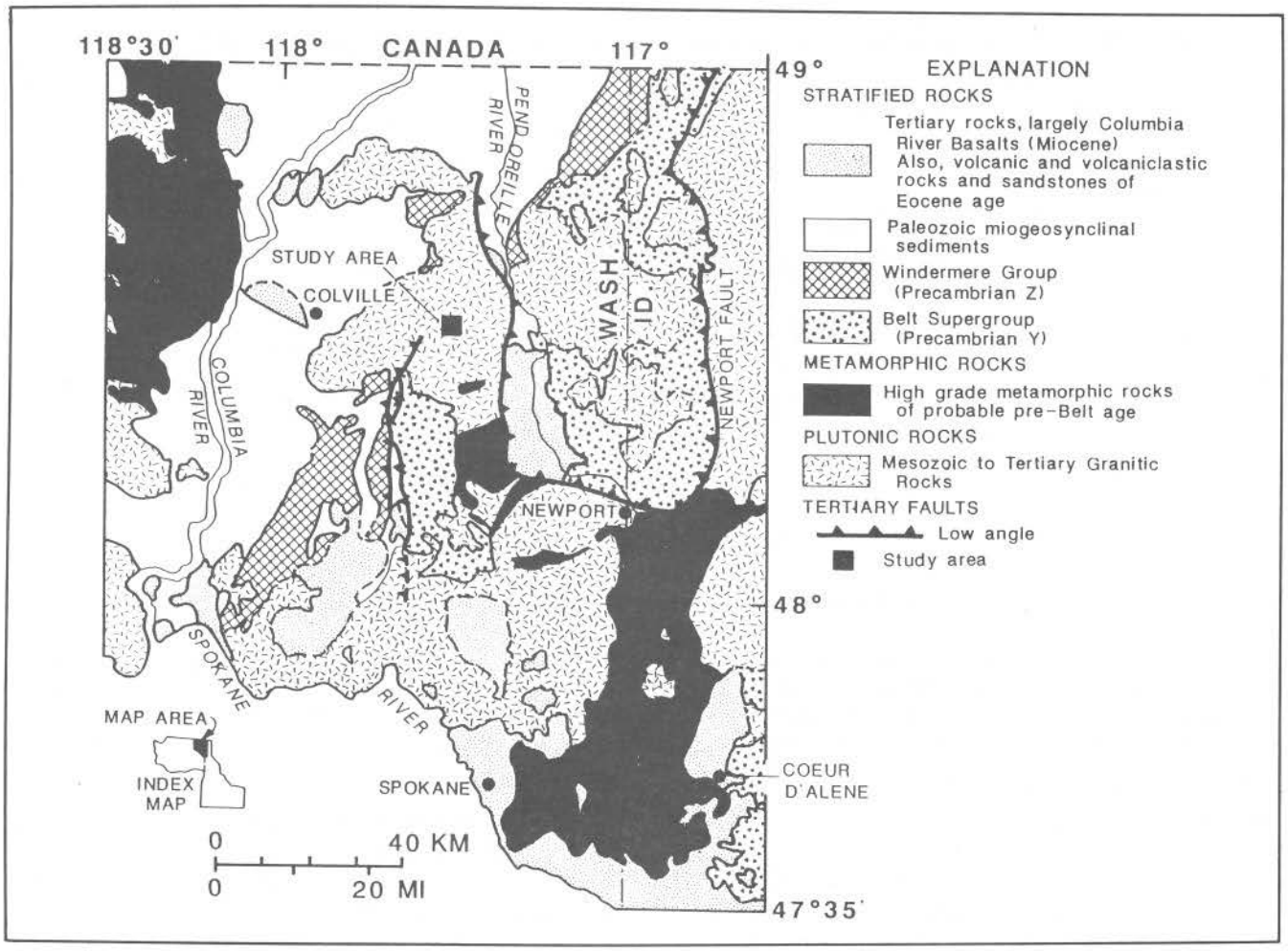


Figure 1 — Generalized geologic map of northeastern Washington and adjacent Idaho. Modified from Cheney, 1980, (fig. 3, eastern part). Note location of the Flodelle Creek drainage near the center of the figure.

SITE DESCRIPTION

The surficial uranium deposit occurs in organic-rich valley-fill sediments of the north fork of Flodelle Creek, Stevens County, Washington (figs. 1 and 2). This first-order stream accepts runoff from a very limited (4.1 km^2) drainage basin entirely underlain by granitic bedrock. Topographic relief in the basin is about 180 m. The stream drops approximately 50 m in elevation along the first 1.6 km of its flow and is confined to a narrow valley flanked by steep (30-65 percent) slopes. It then enters a broad and relatively flat meadow (meadow mine of fig. 2). From the drainage divide to the outlet of the meadow, surficial organic-rich sediments are anomalously uraniferous and constitute the Flodelle Creek deposit.

URANIUM OCCURRENCES

Valley-bottom sediments comprise coarse-grained to granular glaciofluvial sands overlain by as much as 4 m of uraniferous organic-rich sediments, which range from fibrous woody peat of 50-60 weight percent organic matter, to sand, silt, muck, and clay of lesser and highly variable organic content (Johnson et al., 1985, 1987). A volcanic ash-rich unit, 0-60 cm thick, is observed in many measured sections at the meadow mine, and at some upstream localities near the spring pool (fig. 2). The separated ash contains $<$ 2 ppm uranium and, on the basis of shard chemistry and accessory mineralogy (Zielinski and Otton, 1986b), and of bracketing ^{14}C ages (Johnson et al.,

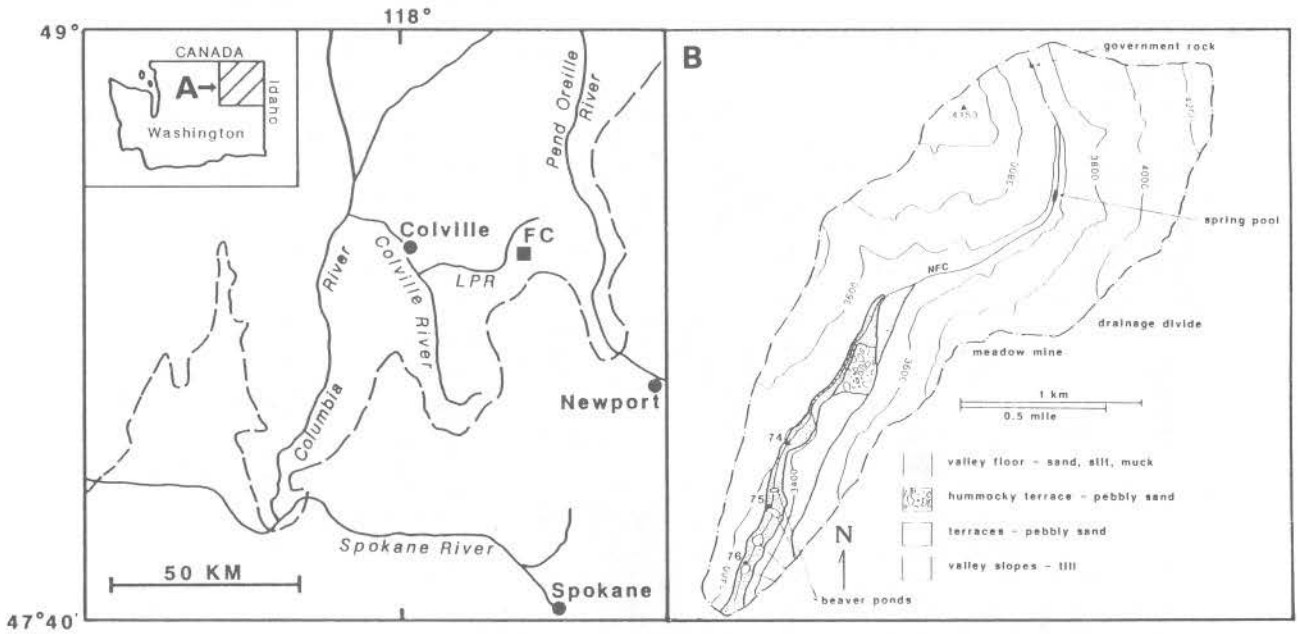


Figure 2 — A) Map showing the location of the study area in the Flodelle Creek drainage (FC), and its position relative to the approximate southern termination of the Cordilleran ice sheet during Fraser glaciation (dashed line). LPR = Little Pend Oreille River. Modified from Johnson et al., 1987. B) Map of surficial deposits of the north fork of Flodelle Creek (NFC) drainage basin. Contour intervals in feet. Modified from Johnson et al., 1987a.

1987), is identified, at 6700-7000 years B.P., as the Mazama ash.

Uranium contents of the organic-rich sediments range from <0.01 to 0.9 weight percent (dry basis) and are positively correlated with organic matter content (Otton and Zielinski, 1985). The calculated correlation coefficient is 0.75 for 76 samples from the meadow mine, and 0.78 for 18 samples collected at the spring pool site (fig. 3; Johnson et al., 1987). The association of uranium with organic matter is verified by fission-track radiography, which indicates preferential uptake of uranium in the structureless finer grained organic matter (humin?) and in charcoal fragments (Otton and Zielinski, 1985). The mechanism of uranium uptake in organic matter is probably via adsorption, ion-exchange, reduction, or a combination thereof (Szalay, 1964; Kerndorf and Schnitzer, 1980; Gamble et al., 1983; Nakashima et al., 1984). No uranium minerals are observed in the sediments; waters in contact with them are calculated to be undersaturated with respect to uranium(VI)-bearing minerals. The water is also calculated to be undersaturated with respect to uranium(IV)-bearing minerals, such as uraninite and coffinite, as long as the ambient Eh of the sediment is greater than 0.1 volt (Zielinski et al., 1987).

BEDROCK

The Flodelle Creek area is underlain by the 100 Ma Phillips Lake Granodiorite, which locally is massive medium-grained muscovite-biotite quartz monzonite and granodiorite, with minor pegmatite (Miller and Clark, 1975; Miller and Engels, 1975). Bulk composition is mildly peraluminous, with corundum appearing in most norms. Accessory minerals include apatite, zircon, allanite, magnetite, and monazite. Preliminary strontium isotope data for the rock unit suggest an origin from pre-Belt continental crustal rocks, possibly with some interaction with Belt Supergroup sediments (R.J. Fleck, U.S. Geological Survey, personal communication, 1987). A sedimentary component in the source region is also suggested by the broad S-type chemistry and mineralogy of this rock.

Outcrops in the drainage basin are sparse and commonly fractured, jointed, and sheared. Core samples of bedrock taken near the spring pool site show petrographic evidence of stress and shear, i.e., strained quartz, bent micas, and numerous microfractures filled with mineral debris. Minor quartz and calcite occur in some fractures. Plagioclase is partially altered to sericite ± minor epidote, and biotite is partially altered to chlorite.

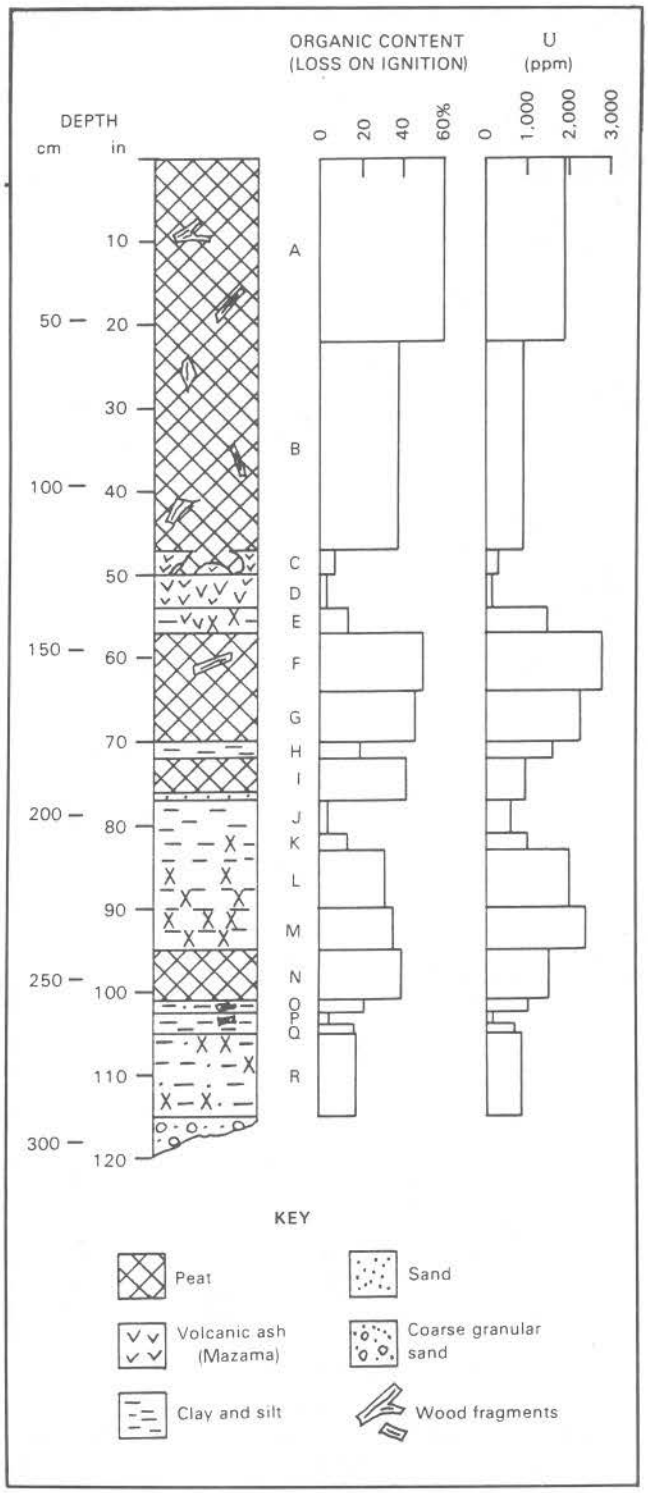


Figure 3 — Generalized lithologic log of a core from the spring pool site, and variation of organic content and uranium content as a function of depth. Modified from Zielinski et al., 1986.

The observations of fracture and shear in core samples and in outcrop are not surprising considering proximity of the drainage to the Newport fault (fig. 1). The drainage also lies in a 10-25-km-wide zone in which postemplacement heating has created discordant potassium-argon ages in biotite-muscovite pairs (Miller and Engels, 1975). The thermal overprint is probably related to a period of regional intrusive activity at 50 Ma. Contours of potassium-argon age discordance suggest a heat source east of the drainage (Miller and Engels, 1975).

The uranium content of 13 core samples of bedrock collected from depths of 31.4-43.9 m averaged 15.8 ± 2.7 ppm. In contrast, 28 outcrop samples from throughout the drainage basin averaged 5.9 ± 4.2 ppm. Comparisons of fission-track radiographs from core and nearby outcrop samples indicate that allanite is particularly susceptible to uranium loss during weathering; some mobilized uranium is redistributed in nearby biotite and microfractures. The reported average regional uranium concentration of the Phillips Lake Granodiorite is 12 ± 6 ppm (Castor et al., 1982), which is anomalously high compared to reported averages of about 4 ppm for granitic rocks (Nash et al., 1981). Likewise, the average thorium concentration in the core samples is 32 ± 4.0 ppm, which is anomalously high compared to typical granitic values of 10-20 ppm (Wedepohl, 1970). Airborne radiometric surveys indicated unusually high radioelement contents of rocks in the drainage basin, and they detected local anomalies of 1.5-4.0 times the normal background for the Phillips Lake Granodiorite (Castor et al., 1982).

No occurrences of uranium minerals are reported in the bedrock of the drainage area, but uraniferous pegmatites and fracture coatings of secondary minerals (autunite, meta-autunite) are reported from several localities in the Phillips Lake Granodiorite. The nearest group of localities, including mines with some uranium production, is along a 15-km-long, north-northwest-trending lineament approximately 8 km east of the drainage (Castor et al., 1982).

GLACIAL AND POSTGLACIAL GEOLOGY

During the Fraser (late Wisconsin) glaciation, the Cordilleran ice sheet covered the Flodelle Creek area, and terminated locally several kilometers to the south (fig. 2). As glaciers retreated from the area about 12,000 years B.P. (Johnson et al., 1987), the valley slopes were mantled with as much as 2 m of

massive, poorly sorted glacial till of largely "granitic" parentage (fig. 2). This coarse till is overlain by as much as 40 cm of silt loam and sandy loam and is capped by 2-4 cm of organic litter (Donaldson et al., 1982). The silt loam (loess?) is rich in volcanic ash, probably a reworked equivalent of the Mazama ash observed in valley-fill sediments.

On the east side of the valley floor are discontinous remnants of a 10-30-m-high terrace deposited by early postglacial meltwaters (fig. 2; Johnson et al., 1985, 1987). The variable degree of sorting and stratification and the coarse grain size of most of the terrace sediments suggest deposition by high-energy braided streams of considerably larger discharge than the present creek. Both deposition and incision of this glaciofluvial outwash probably occurred as the retreating ice margin was leaving the drainage and crossing the surrounding drainage divides.

Just south of the meadow mine, on the east side of the valley floor, an area of hummocky terrain, similar in composition and texture to the terrace sediments (fig. 2), is interpreted as a section of collapsed terrace that was initially supported by stagnant ice (Johnson et al., 1985, 1987). The resulting hummocky (kame) terrace is several meters above the valley floor and shows no evidence of stream dissection.

Inspection of the sedimentary record in trenches, and samples from auger and core holes at the meadow mine indicates that shortly after glacial retreat, the relatively wide, flat meadow was the site of continuous deposition from a fluvial system of greatly diminished size and vigor (fig. 4). Stream outflow from the meadow was diverted to the west side of the valley by kames just downstream. This sedimentation pattern persisted at least until deposition of the Mazama ash, 6700-7000 years B.P. About 5000 years B.P. the meadow was occupied by beavers. Buried beaver dams are preserved in an organic-rich layer containing abundant chaotic masses of sticks exhibiting characteristic tooth-marked terminations. Wood fragments from the layer yielded a ^{14}C age of 5100 ± 110 years B.P. (Johnson et al., 1985, 1987). Ponds created by one or more of these beaver dams were sites for accumulation of organic matter in the meadow (fig. 4). Departure of the beavers and gradual filling of the ponds with sediment caused a return to fluvial channel and flood plain deposition. Diatomite layers several cm thick in the downstream area of the meadow suggest that small ponds persisted on parts of the flood plain.

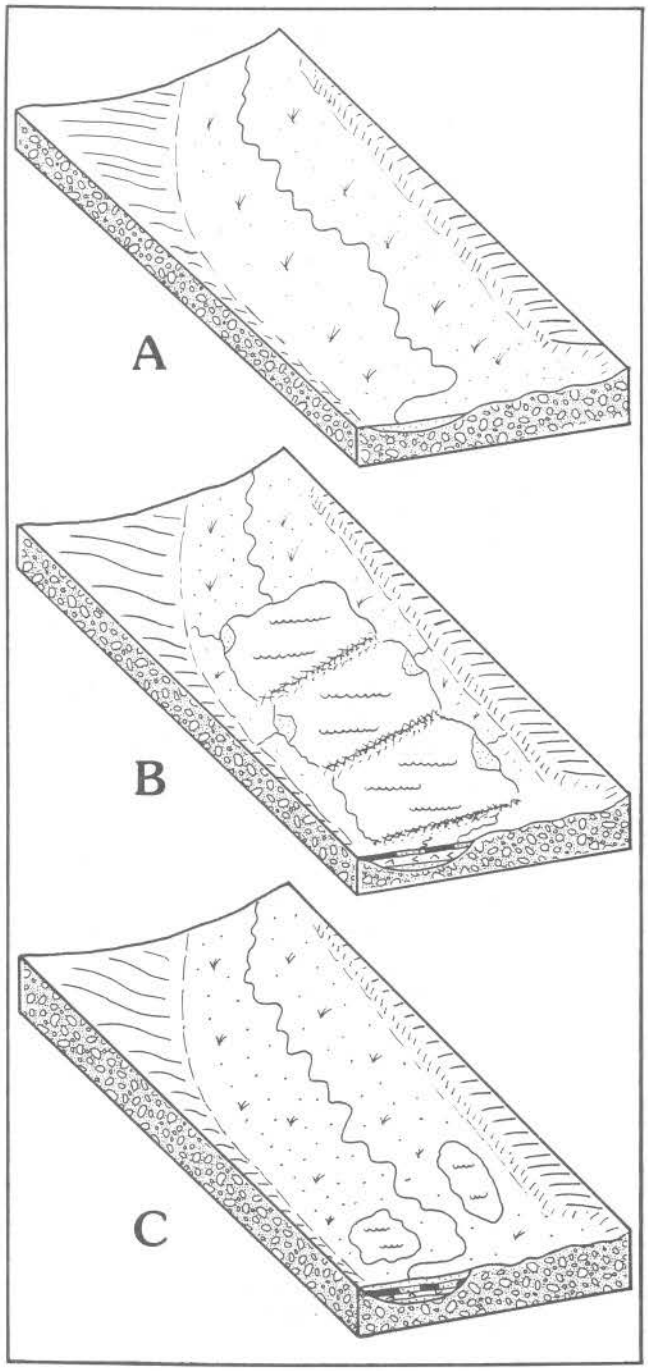


Figure 4 — Postglacial sedimentary history of the meadow mine. A) A small postglacial stream flows through the wide meadow and is partly diverted and restricted by kames at the lower end of the meadow. B) At ~5000 years B.P. beavers built one or more dams in the meadow causing ponding. C) Beaver ponds fill with sediment and fluvial drainage is reestablished. Small flood plain ponds persist. From Johnson et al., 1987.

Inspection of the sedimentary record at the spring pool site (fig. 2) indicates a very different postglacial history. Drainage was impeded shortly after deglaciation, by unconsolidated glacial sediments that slumped from the relatively steep valley walls (fig. 5; Johnson et al., 1985, 1987). Local ponding created an environment suitable for deposition and preservation of organic-rich sediments that extracted uranium from coexisting waters. A nearly continuous postglacial history of uranium emplacement at this site is confirmed by depth-related increase of daughter products, and by uranium-series ages of peat that closely mimic independently estimated depositional ages of the host sediment (Zielinski et al., 1986).

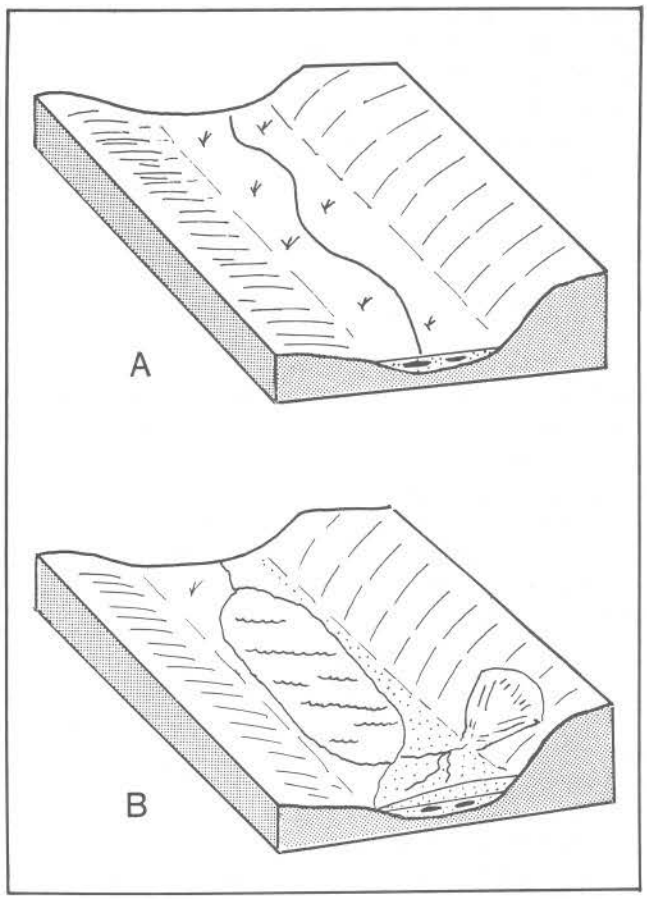


Figure 5 — Postglacial sedimentary history of the spring pool site. A) Small postglacial stream flows through the narrow valley. B) Unconsolidated glacial deposits slump off valley walls and block drainage, creating a small pond. From Johnson et al., 1985.

HYDROLOGY

Local groundwaters and surface waters provide the necessary transport of uranium from uraniferous soils and bedrock to the organic-rich sediments of the valley bottom. Spring, stream, and near-surface waters collected in the drainage are of the calcium-bicarbonate chemical type and are chemically similar to waters draining other granitic terrain, i.e., low conductivity (50 μmho/cm), near-neutral pH (5.85-7.55), saturated with respect to quartz and kaolinite, and undersaturated with respect to calcite. Near-surface waters collected from auger holes in the valley-fill are the more acidic of the sampled waters, a probable function of increased contact with decaying organic matter (Zielinski et al., 1987).

Trace element abundances in the waters are likewise unremarkable, except for uranium. The measured waters contain 17-318 μg/L (ppb) uranium, compared to an average of 2.4 + 1.9 μg/L uranium for springs and streams of the region (R.E. Miller, Joy Mining Company, written communication, 1985). High correlations of dissolved uranium with bicarbonate contents and thermodynamic calculations of uranium speciation indicate that most uranium is transported as inorganic complexes with carbonate or phosphate ions.

Average annual precipitation in the Flodelle Creek area is approximately 60 cm, most of which falls between the first of October and the end of March (Donaldson et al., 1982). During periods of rainfall or snowmelt, runoff is directed along several small intermittent tributaries (fig. 2), or moves downslope as subsurface runoff. The latter is particularly favored because permeable soils cover steep convex slopes underlain by relatively impermeable bedrock (Freeze, 1972). Local variations in subsurface structure or sedimentology can cause subsurface flow to be diverted to the surface and manifest itself as springs that issue from till-covered slopes or that well up in valley-bottom sediments. Upwelling groundwaters produce the 2.5-m-wide pool at the spring pool site and insure the maintenance of water-saturated conditions in the organic-rich sediment column. Upwelling groundwaters are also important transporters of uranium. Water collected at the spring pool and from other springs on the valley walls contains 100-150 μg/L uranium (Zielinski et al., 1987; Zielinski and Schumann, 1987).

MODEL FOR DEPOSIT FORMATION

Unusually high concentrations of uranium in young organic-rich sediments of this drainage indicate that a very efficient mineralizing system has operated since early postglacial time. Sedimentary uranium deposits in the drainage *before* glaciation cannot be ruled out, but the currently proposed model suggests that glaciation was crucial for establishing the present mineralizing system of source-transport-sink.

Radioelement-rich bedrock has existed in the area since Cretaceous time, but glaciation provided several mechanisms for abruptly increasing the leachability of bedrock uranium. First, glacial erosion of previously weathered outcrops exposed relatively fresh uranium-rich rocks to leaching. Second, glacial abrasion created surficial deposits (till) of comminuted bedrock with high surface area and permeability. Third, erosional unroofing and isostatic rebound of previously buried granitic rocks promoted renewed fracturing (Goldich and Mudrey, 1969). The anomalously uraniferous waters of the drainage suggest that local source rocks, recently exposed to leaching, were unusually "prepared," perhaps by earlier shearing and fracturing or by intrusion of uraniferous pegmatites of the type observed nearby.

In addition to source rock modification, glaciation was also crucial to the renewed formation of local environments in which organic-rich sediments could accumulate (figs. 4 and 5). The proximity of these organic-rich uranium traps to sources of labile uranium in bedrock and till, and the funneling of surface waters and groundwaters into these traps made a very efficient mineralizing system. As already mentioned, the spring pool site is perhaps an optimum example of how efficient and long-lived such a system can be. Ponding in the meadow mine was directly related to beaver activity, but indirectly related to glaciation, which provided a suitable wide, low-gradient beaver habitat.

CONCLUSIONS AND SUGGESTIONS FOR FUTURE STUDIES

The low-radioactivity surficial uranium deposit of the north fork of Flodelle Creek, Stevens County, Washington, represents an extreme example of recent uranium enrichment in organic-rich sediments. Deposition was strongly influenced by recent glaciation, which provided increased exposure, comminution, and leachability of local granitic bedrock, and also new sedimentary environments where organic matter could accumulate and begin to extract uranium from local waters. At the spring pool site, ponding occurred shortly after glacial retreat when unstable unconsolidated till slumped from valley walls to the valley floor. At the meadow mine site postglacial drainage was initially restricted by relict glacial topography (kames) on a low-gradient valley floor created by glaciofluvial erosion. Ponding began about 5000 years B.P., when beavers occupied this suitably prepared habitat.

Based on observations and interpretations at the Flodelle Creek locality, future exploration for surficial organic-rich uranium deposits of this type (valley-fill fluviatile) should concentrate on low-order drainages in recently glaciated granitic terrain. Radioelement-rich, previously fractured granites containing allanite and uranium mineralization may be particularly favorable source rocks, but the relative importance of these additional criteria remains to be evaluated. Drainages containing well-developed groundwater flow regimes and/or uraniferous waters should receive special attention. Reconnaissance sampling is done best by chemical or specialized (low-energy gamma) radiometric determinations of uranium in organic-rich sediments (Culbert and Leighton, 1981; Millard and Keaten, 1982).

Silicic *extrusive rocks,* particularly glassy varieties, can also be excellent uranium sources (Zielinski, 1985), and may also host surficial uranium deposits, although this remains to be investigated. More research is also needed to investigate the nature and the strength of uranium-organic bonding, and the physiochemical conditions most likely to produce uranium release from these deposits. Such research will require observations of original and processed (sized, leached) organic matter from various depths and deposit environments, as well as analysis of leachates. Results will contribute to understanding uranium-organic associations in these and in more ancient uranium deposits, and will allow more accurate assessment of health hazards posed by cultural disturbance of surficial uranium deposits.

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GEOLOGY AND URANIUM DISTRIBUTION IN THE FISH LAKE SURFICIAL URANIUM DEPOSIT, NEVADA

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ABSTRACT

Modern surficial uranium deposits contain loosely held, easily remobilized uranium that poses a potential hazard to water supplies. Many deposits of this type may exist but are unidentified due to the low radiation associated with them. More information on surficial uranium deposits is needed for identification of potential hazards.

The Fish Lake Valley, in southern Nevada and California, is host to approximately 675 acres of uranium-enriched lacustrine and marsh sediments in an arid alluvial-fan environment. The deposit was sampled with a 2.5-cm-diameter soil auger to a maximum depth of 6.5 m. Sediment samples were analyzed for uranium and organic matter. Uranium concentrations in the sediments averaged 65.3 ppm (n=257) and reached maximum levels of 800 ppm.

The marsh is fed by spring water flowing from the Silver Peak Range. Samples of the water yielded 2 and 9 ppb uranium. Uranium derived from Tertiary volcanic rocks of the Silver Peak Range enters the base of the deposit via upwelling groundwater and is concentrated in organic-rich layers in the marsh sediments. Accumulation of large deposits of lacustrine and marsh sediment was made possible by a change in the trend of the Silver Peak Range that diverts sediment-laden runoff from the Silver Peak Range away from the marsh.

Disturbance of the marsh environment by man could create hydrologic and geochemical changes that may release uranium to local groundwaters or surface waters.

INTRODUCTION

Surficial uranium deposits may be broadly defined as "uraniferous sediments or soils, usually of Tertiary to Holocene age, that have not been subjected to deep burial and may or may not have been cemented to some degree" (Toens and Hambleton-Jones, 1984, p. 9). Uranium in these deposits is mainly fixed by precipitation or adsorption from groundwaters or surface waters and is loosely held and easily remobilized. Because organic-rich sediments are efficient in trapping uranium, high concentrations in source rocks are not required for surficial uranium deposits to form. Deposits of this type typically have equivalent uranium values of only 5 to 10 percent of chemical uranium (R.R. Culbert, written communication, 1982). The low-energy gamma decay from these deposits is not readily detected by scintillometers and spectrometers, which normally detect the gamma energies associated with late daughters in the uranium decay series (Otton, 1984; Culbert and Leighton, 1981).

Because of the loose binding of the uranium in the sediments and the unconsolidated nature of the host environment, these types of deposits pose a potential environmental hazard, because uranium is a cause of kidney damage (Cothern et al., 1983). These deposits are also of academic interest, because they provide an opportunity to study the formation of uranium deposits in the modern environment.

A surficial uranium deposit in Fish Lake Valley, in Esmeralda County, Nevada (fig. 1), was first identified by Culbert (ca. 1982) during reconnaissance sampling of the Great Basin region (R.R. Culbert, 1982, written communication).

Concentrations of uranium as high as 797 ppm were measured by delayed neutron activation. Concentrations exceeding 1500 ppm were reported by Culbert (1982, written communication; method of analysis unknown). The uranium concentration in 257 samples from the marsh area averaged 65.3 ppm.

PHYSIOGRAPHY AND CLIMATE

Fish Lake Valley occupies approximately 2600 km^2 in an area bounded by the White Mountains to the west, the Candelaria Hills and the Volcanic Hills to the north, the Silver Peak Range to the east, and the Palmetto Mountains, Sylvania Mountains, and the Last Chance Range to the south (fig. 1). The elevation of the valley floor ranges from about 1585 m near the south end of the valley to about 1430 m at the playa in the northeastern portion (Rush and Katzer, 1973). The Volcanic Hills bisect the northern end of the valley. Surface drainages from the northwestern part of the valley skirt the Volcanic Hills and terminate in the playa lake in the northeastern part.

The climate of the region is arid except where rainfall is increased at higher elevations, due to topographic effects. Average precipitation ranges from approximately 100 to 150 mm on the floor and fan apron to approximately 610 mm at elevations above 3570 m in the White Mountains, where it falls principally as snow (Rush and Katzer, 1973).

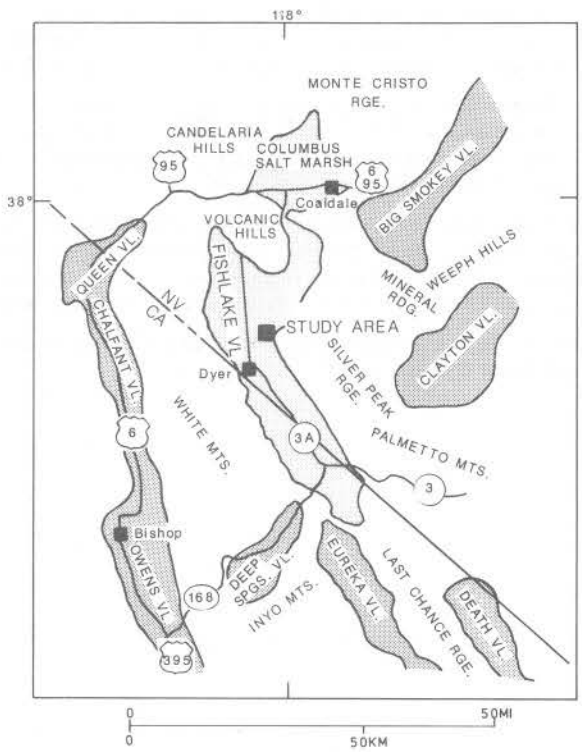


Figure 1 — Location map of Fish Lake Valley, showing adjacent valleys and mountain ranges.

GEOLOGY

The oldest sedimentary rocks in the area are Precambrian to Ordovician and are exposed in the ranges surrounding the valley. Jurassic and Cretaceous intrusions occur at Mineral Ridge and in the White and Palmetto Mountains (Krauskopf, 1971; McKee and Nash, 1967). The White Mountains are primarily rocks of the Inyo batholith, a composite granitic batholith exposed over 1300 km² in east-central California.

Tertiary rock units composed of thick sequences of tuffaceous volcanic sandstones, siltstones, and interbedded air-fall tuffs are exposed in the Silver Peak Range. Late Pleistocene and Holocene deposits include glacial moraines above 2590 m in the White Mountains (Krauskopf, 1971), alluvium (which may be partly glacial outwash), bedded clay and silt, landslide deposits, desert wash, colluvium, playa deposits, and freshwater limestone (Albers and Stewart, 1972). Basalt flows, dikes, and cinders occur in the area of the Volcanic Hills and are locally up to 240 m thick. The basalts correlate with andesite flows and their intrusive equivalents in the White Mountains (Robinson and Crowder, 1973; Crowder et al., 1972).

Alluvial fan deposits, including desert wash, colluvium, and alluvium, together with playa lake deposits, constitute the most abundant Quaternary deposits in the area and may be several hundreds of feet thick. Playa lake and mud flat deposits, generally covered with a thin salt crust (Albers and Stewart, 1972), cover a large area in the northeastern part of the valley.

The Fish Lake surficial uranium deposit is at a bend in the Silver Peak Range, where the fault zone bounding the northwestern part of the range apparently dies out beneath Fish Lake Valley. North of the bend, the bounding fault is downthrown to the west; south of the bend, the west flank of the range dips under the valley, apparently without a bounding fault (Albers and Stewart, 1965). Fault scarps displaying several meters of displacement on alluvial fans on the east and west sides of the valley indicate recent (Quaternary) fault activity along both sides of the valley.

HYDROLOGY

Four of the five major spring complexes in the Fish Lake Valley flow from valley-fill alluvium, the principal source of groundwater in the valley; however, the spring at Fish Lake differs from most springs in the valley in that it flows from carbonate rock (Garside and Schilling, 1979; Robinson et al., 1976; Rush and Katzer, 1973). A line of springs, beginning at Fish Lake and trending northeastward along the flank of Silver Peak Range, follows the fault zone that forms the eastern edge of the valley.

The largest spring in the valley feeds Fish Lake (fig. 2). The estimated discharge from the spring is 0.085 m^3/s, and the total discharge for the spring complex that includes Fish Lake Spring is approximately 0.156 m^3/s (Garside and Schilling, 1979). Water samples from the springs at Fish Lake and at Dyer Cemetery (fig. 2) contained 9 ppb and 2 ppb uranium, respectively.

THE FISH LAKE SURFICIAL URANIUM DEPOSIT

Fish Lake marsh, on the western margin of the valley at Fish Lake spring (figs. 1 and 2), extends approximately 2740 m along the valley axis and is generally less than 800 m wide. On U.S. Bureau of Land Management aerial photographs of 1980, the marsh occupies an area of approximately 2.7 km².

The extent of marsh vegetation is primarily controlled by discharge from Fish Lake spring and Dyer Cemetery spring. Fish Lake spring maintains a permanent pond, which is not that shown on the topographic map (fig. 2). Dyer Cemetery spring provided water to an early homestead site, and had a casing sunk into the ground to concentrate flow. While there is a relatively large area of marshy vegetation associated with this spring, there is no body of standing water comparable to that at Fish Lake. Most of the marsh area north of Dyer Cemetery spring has been drained and is now covered by meadow grasses.

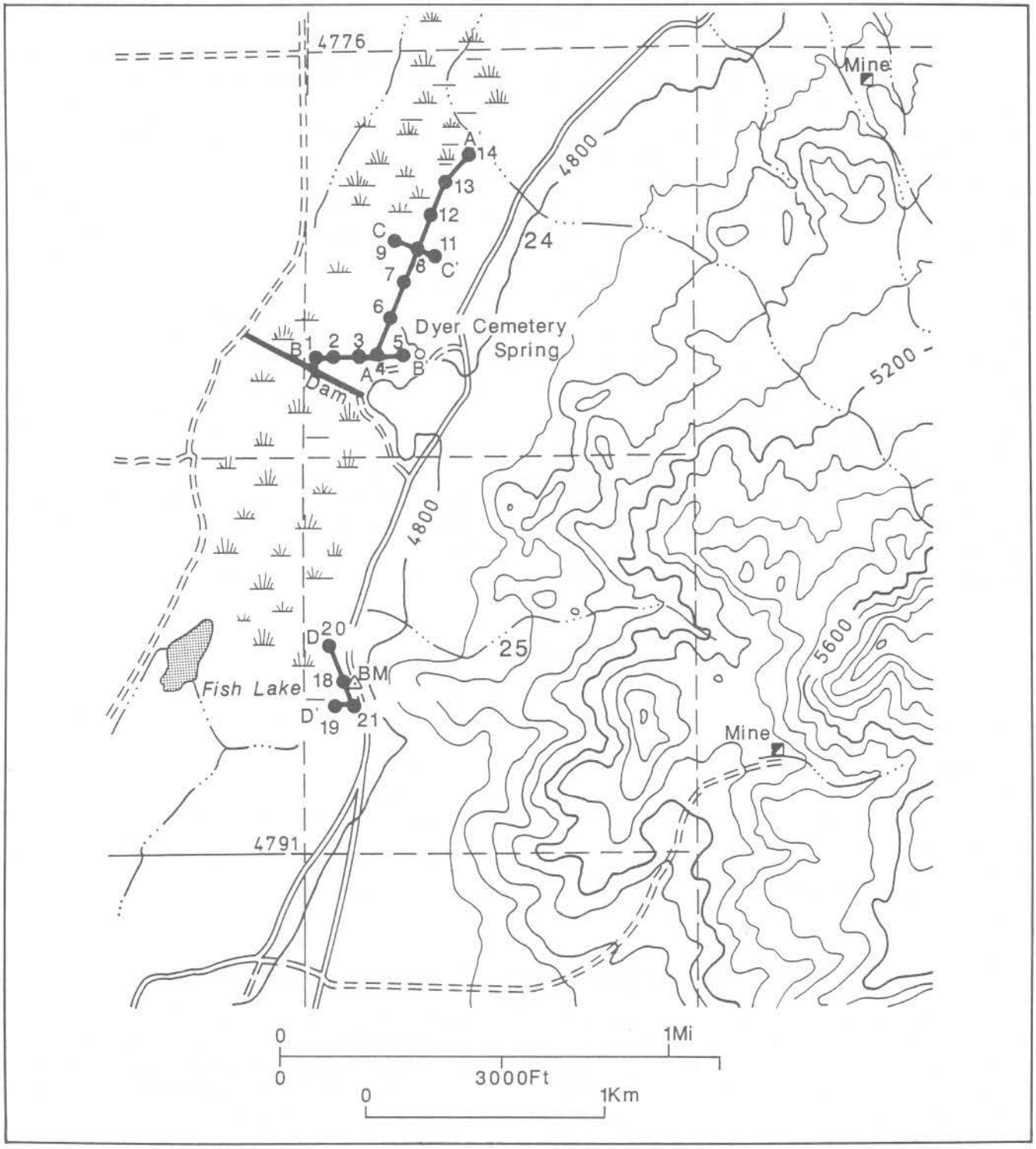


Figure 2 — Location of auger holes in Fish Lake marsh and lines of cross sections shown in figures 3 to 6. The natural pond at Fish Lake is directly east of location 18. The pond to the west of Fish Lake is man-made. The new dam (see text) floods the entire marsh area to a point approximately 300 m south of holes 19 and 21. Sections 24 and 25 are in T. 2 S., R. 35 E.

Field work for this report was conducted in the fall of 1985. A dam had been built across the marsh area during the previous winter (fig. 2) to provide irrigation-water storage. Ground and aerial photographs, as well as topographic maps of the area before the dam was built, indicate that a substantial area of marsh vegetation has been flooded by the reservoir.

Stratigraphy of the marsh area was sampled using a 25-mm-diameter soil auger; sample sites were less than 60 m to 150 m apart. Samples were analyzed for uranium and organic matter content (percent loss on ignition at 550°C). The cross sections (figs. 3A, 4A, 5A, and 6A) are based on field descriptions of the auger samples.

STRATIGRAPHY AND URANIUM DISTRIBUTION OF THE MARSH

The area sampled contains a remarkably consistent internal stratigraphy (figs. 3A, 4A, 5A, and 6A). Many of the individual units in the deposit can be traced across the entire study area. These units consist of a series of fining-upward sequences that can be traced by correlation of organic-rich layers. An idealized sedimentary unit in the deposit is composed of fine-grained clastic sediments at the base and is capped by marsh sediments consisting of either a thin peat or a siliceous, diatom-rich organic muck.

Organic layers in the deposit were classified on the basis of field descriptions. Organic matter content, as determined by loss on ignition at 550°C, roughly defines two groups of organic sediments. The most organic-rich group generally contains more than 20 percent organic matter; this includes peats and mucky peats, as described in the field. The second class of organic sediments generally contains 15 to 20 percent organic matter, and consists of mucks, and silty and clayey mucks. These two groups were combined into sedimentary unit "A" in the cross sections (figs. 3A, 4A, 5A, and 6A).

In the northern part of the marsh the highest uranium concentration is in hole 4. The depth interval from 1.8 to 2.4 m (figs. 3B and 4B) contains up to 591 ppm of uranium. High uranium concentrations also occur at depths of approximately 3.4 to 4.0 m, in a band that extends from hole 5 on the east to hole 3 on the west (fig. 4B). Uranium concentrations exceed 200 ppm in holes 3 and 5. In the northern transverse cross section (C-C'; fig. 5B), the highest concentrations of uranium are near the top and at the base of the section.

Uranium isopleths at the base of the southern end of cross section A-A' (fig. 3B) form a tabular shape; they extend from hole 4 northward to hole 6. In both the upper and lower zones, high uranium concentrations occur in an envelope defined by the 50-ppm uranium isopleth that extends downvalley as far as hole 12. The 50-ppm isopleth at the base of hole 8 appears to be separate from the upper zone of concentration, but does extend to the north as far as hole 12 and to the east as far as hole 11 (figs. 3B and 5B).

The highest uranium concentrations occur in the area adjacent to Fish Lake (fig. 6B) at depths of 4.3 to 5.2 m in hole 18. These apparently correlate with higher concentrations at 4.9 to 5.2 m in hole 20 and lower, but still elevated, concentrations at approximately the same depth in holes 19 and 21. A second horizon of elevated uranium concentrations occurs in the upper 0.6 m of the deposit in holes 18 and 19.

DISCUSSION

The sedimentation patterns, spring locations, and structural setting of the valley are the primary factors that control uranium distribution in the Fish Lake deposit. Numerous fine-grained organic-rich layers in the sediments and frequent inclusion of masticated plant material in clastic layers suggest that the marsh vegetation was frequently covered by silt and clay or drowned by the pond. Near the springs, individual depositional units fine upward into siliceous diatom-rich lacustrine sediments. These observations indicate that minor climatic variations resulted in variations in groundwater and/or surface runoff to the marsh, so that the area alternated between lacustrine and marsh environments. Marsh conditions are indicated by peats and organic-rich layers while shallow lake conditions are indicated by lacustrine clays. Coarser clastic layers probably represent fluvial sediments transported into the marsh during drier periods, when there was no dense vegetation at the upstream end of the marsh to trap such sediments. Some of the coarse sediments may also have been deposited during flash floods.

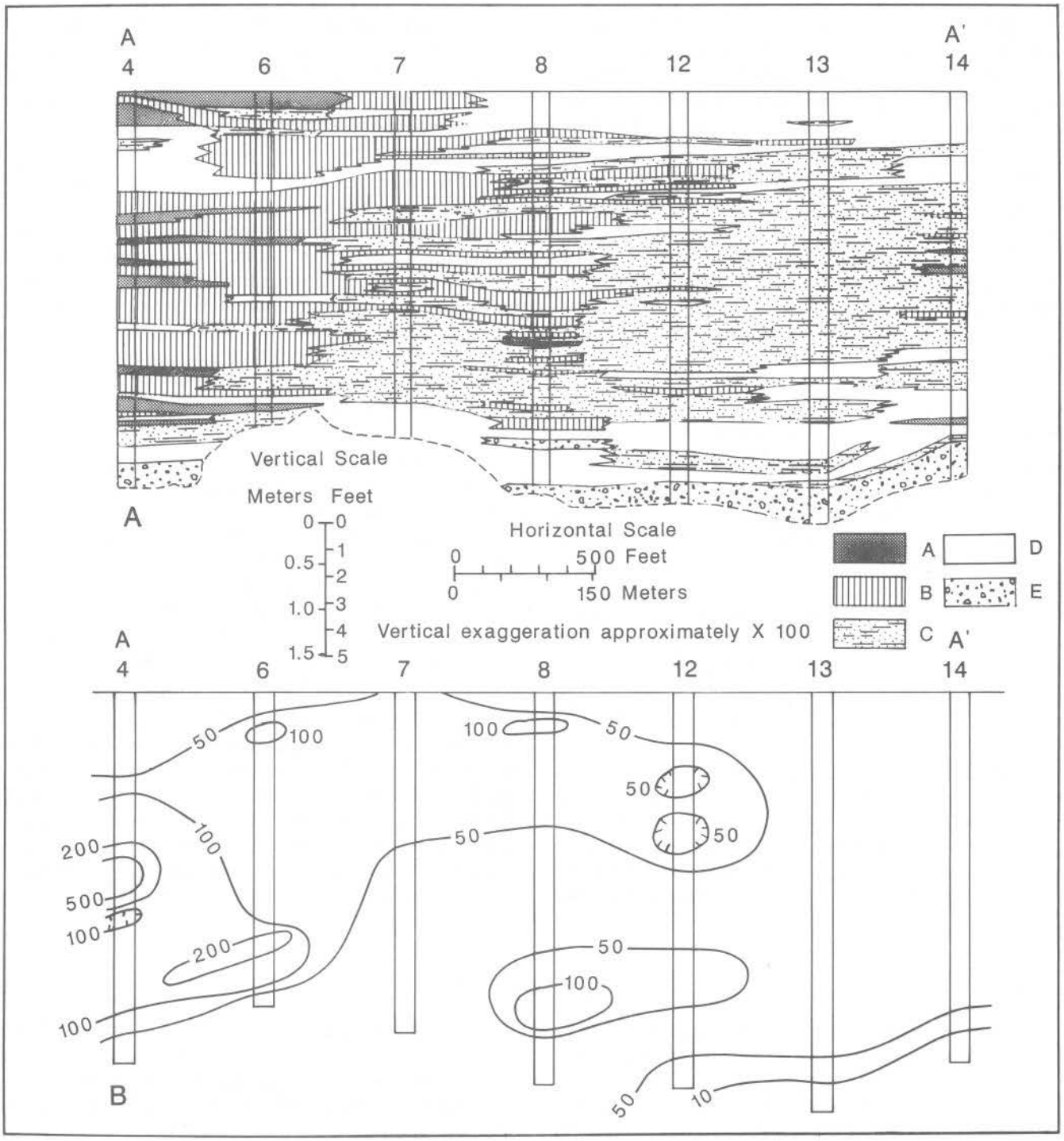


Figure 3 — (Map A) North-south sedimentary cross section A-A′ of of the northern marsh area. Explanation of symbols used: (A) Silty and clayey mucks and peats with greater than 15 percent organic material (determined by loss on ignition); (B) dark colored silts and clays containing up to 15 percent organic material; (C) clays and silty clays; (D) silts, clayey silts, and sandy silts; and (E) coarse sand, and silty and clayey coarse sands. (Map B) Uranium concentration, in ppm, for the north-south cross section. Samples were collected at approximately 0.3 m intervals. Concentrations contoured at various values. See figure 2 for location.

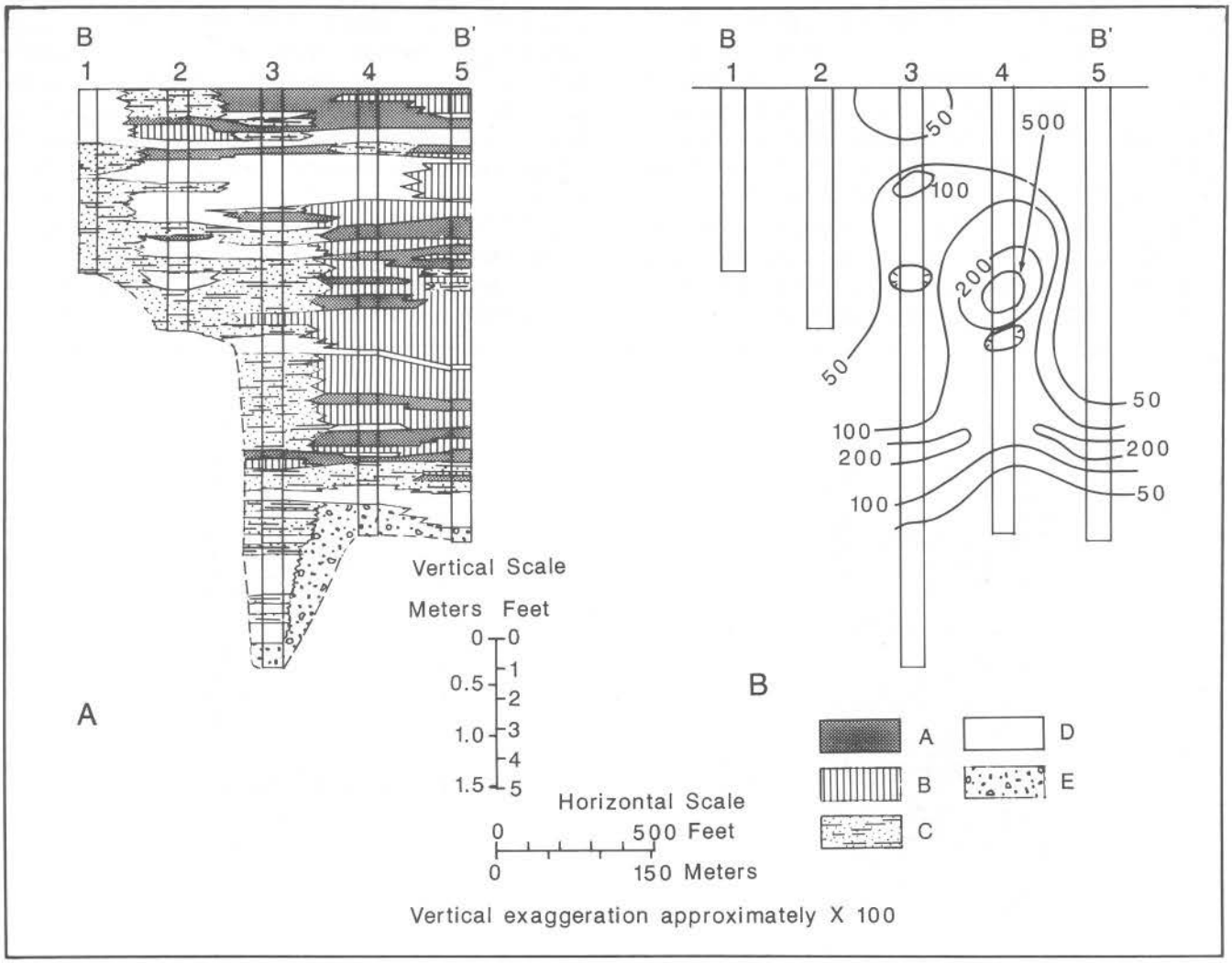


Figure 4 — (A) East-west sedimentary cross section B-B' of the northern marsh area. Units are the same as those in figure 3A. (B) Uranium concentration, in ppm. Concentrations contoured at various values. See figure 2 for location.

Probably due to its smaller discharge there is no permanent pond at Dyer Cemetery spring. Several small discontinous layers of organic-rich material in and around channels in the northern area (fig. 5A; see for example, hole 8), indicate that the presence and locations of channels were important factors that controlled the location and extent of organic accumulations north of the springs. Overall, however, the presence of springs was the principal factor that controlled accumulation of organic matter in the Fish Lake marsh. Marsh vegetation would not grow under the normal climatic conditions without a continuous inflow of groundwater.

The position of the valley's topographic axis is controlled primarily by alluvial fan deposition. The larger drainage areas, higher relief, and greater precipitation in the White Mountains have produced larger alluvial fans than those in the Silver Peak Range, and have caused the valley axis to shift toward the base of the Silver Peak Range. The bend in the Silver Peak Range at Fish Lake marsh causes drainages from these mountains to be diverted away from the marsh area, so that clastic sedimentation in the marsh is minimized.

Coarse-grained, pebbly sand at the base of the sections probably represents alluvial fan deposits over which the marsh sediments were deposited. At Fish Lake, the base of the organic-rich deposits slopes downward to the northwest and is deepest in hole 20 (fig. 6A), northwest of the modern pond. The steep

break in slope, between holes 21 and 18 (fig. 6A), on the alluvial fan surface that forms the base of the marsh deposit, corresponds to a similar break in slope, between holes 4 and 3 (fig. 4A), on the base of the deposit, and probably represents a fault scarp on the buried alluvial fan surface. Displacement on the fault is approximately 1 m in both locations.

According to Otton (1984), the highest uranium concentrations in spring-fed meadows along a valley slope would be expected closest to the springs, where uranium-bearing spring waters flow onto the meadow surface and soak into the organic material surrounding the springs. Uranium is normally concentrated in organic matter by absorption, adsorption (Johnson et al., 1987), or reduction, so surface enrichment takes place, and uranium concentration should decrease with depth. Localized minor surface enrichment has occurred in Fish Lake marsh (holes 7, 3, 11, 18, and 19; figs. 3B, 4B, 5B, and 6B, respectively) where surface waters ponded and soaked into the organic-rich surface sediments, but surface enrichment was limited by low uranium concentra-

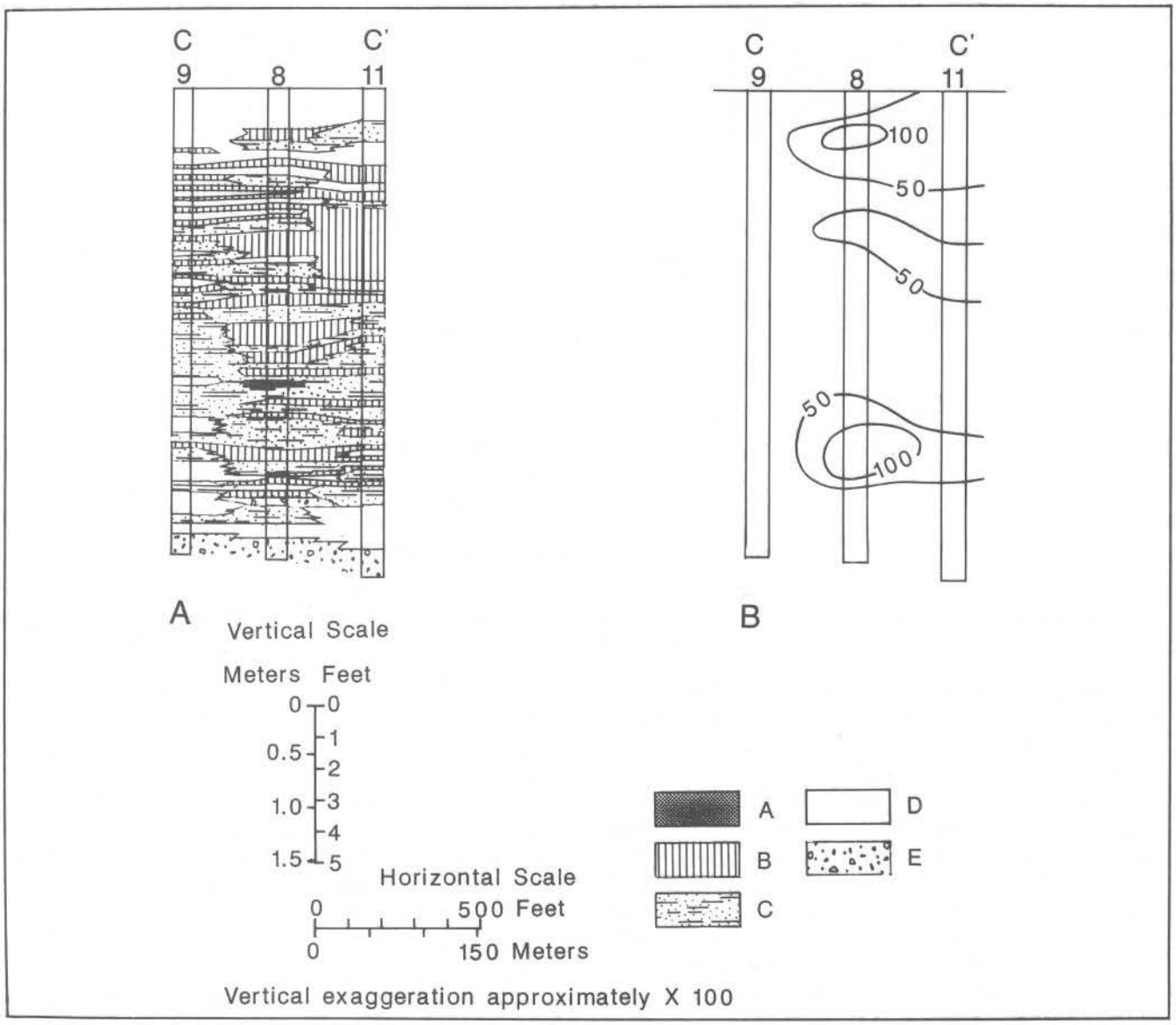


Figure 5 — (A) East-west cross sedimentary section C-C' of the northern marsh area. Units are the same as in figure 3A. (B) Uranium concentration, in ppm. Contoured at 50 ppm. See figure 2 for location.

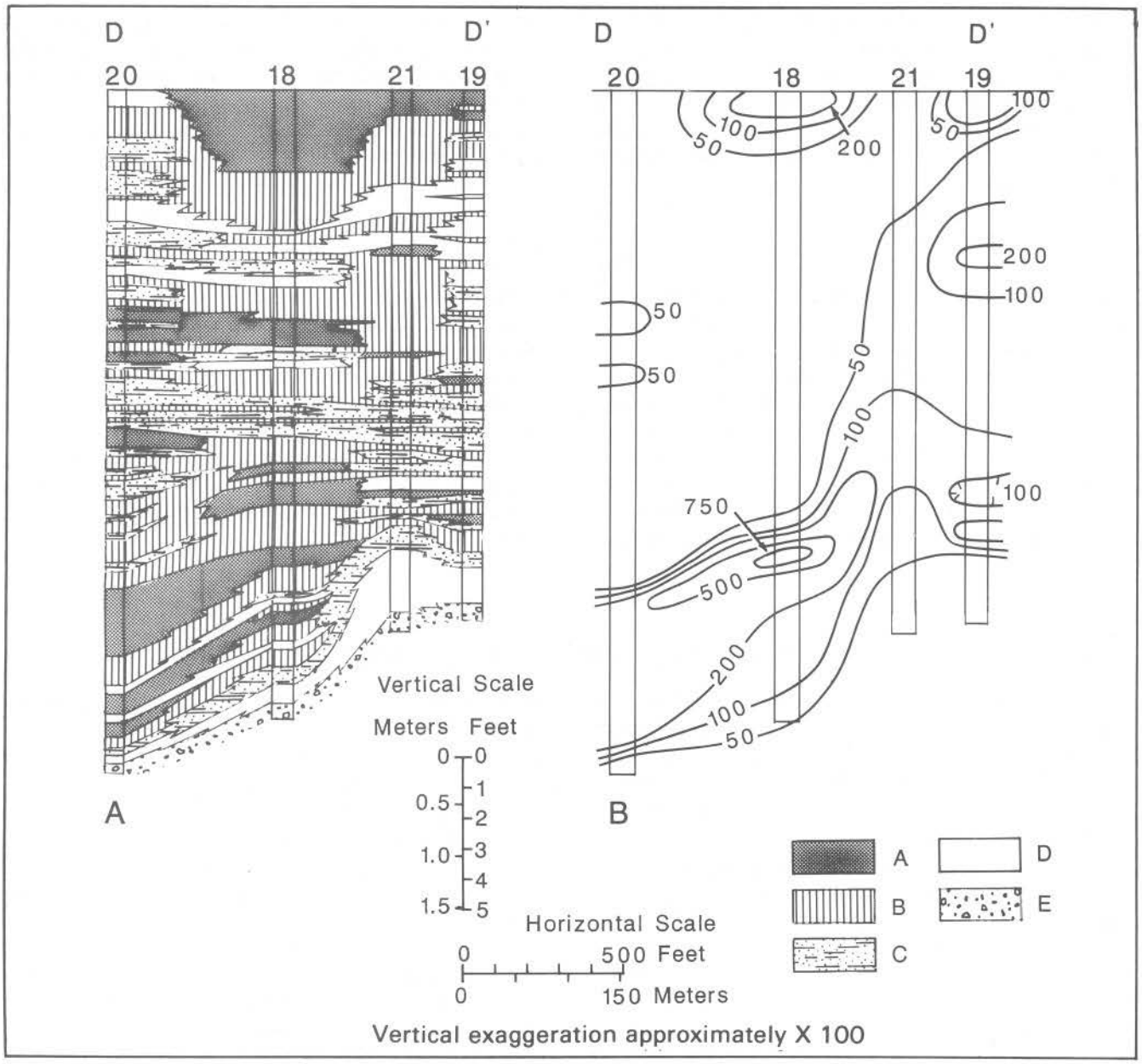


Figure 6 — (A) Sedimentary cross section D-D' of the southern marsh area. Units are the same as those in figure 3A. (B) Uranium concentration, in ppm. Concentrations contoured at various intervals. See figure 2 for location.

tions in the spring water. A somewhat different mechanism is suggested for higher uranium concentrations found at depth.

Upwelling goundwater from fracture systems beneath organic-rich valley-fill sediments has been suggested as a primary uranium enrichment mechanism in several known surficial uranium deposits (Culbert et al., 1984; Levinson et al., 1984; Zielinski et al., 1986). In such cases, groundwater enters the base of the deposit and moves upward through valley-fill sediments; uranium is concentrated in organic-rich layers along groundwater flow path. The shape of the uranium contour pattern in cross section B-B' (fig. 4B) strongly suggests that a plume of uraniferous groundwater moved upward through the deposit from a source below the valley-fill sediment. Enrichment occurred in organic-rich layers. The position of the plume corresponds to the position of the fault inferred

in the sediments underlying the marsh. A similar mechanism may be visualized for the uranium concentration represented in cross section D-D' (fig. 6B). In this case, groundwater moved upward until it encountered a relatively thick organic-rich layer capped by a thick impermeable clay (fig. 6A). Ponding below the clay cap formed a tabular zone of uranium enrichment in the underlying organic-rich layer. The zone of maximum enrichment is over a break in slope inferred to be a fault on the buried fan surface (fig. 6A).

Springs on the edge of the marsh probably have the same groundwater source as water flowing into the lower part of the marsh deposit. Some groundwater flows laterally through the coarse sediments at the base of the marsh deposit, and emerge as flowing springs where the water table intersects the ground surface at the edge of the marsh. Much uranium may be deposited in the basal marsh sediments, as indicated by minor enrichment (50-200 ppm) along the base of the deposit represented in cross sections B-B' (fig. 4B) and D-D' (fig. 6B), the two cross sections nearest the springs. Such enrichment suggests that groundwater welling upward into the marsh sediments probably has a higher uranium content than indicated by the uranium concentrations in the spring water samples.

The effect of climatic and hydrologic variability on sediment and water chemistry must also be considered. Changes in water and sediment salinity and alkalinity as the marsh fluctuated between wetter (lacustrine) and drier (marsh/meadow) conditions may have caused remobilization and redistribution of previously accumulated uranium. The present uranium distribution may therefore reflect more recent conditions rather than the original conditions of uranium emplacement. In any case, because organic material is the primary uranium host in the system, the pattern of uranium distribution will always be closely related to distribution of organic-rich sediments in marsh deposits.

SUMMARY AND CONCLUSIONS

Tectonic setting and groundwater hydrology and chemistry are key factors responsible for uranium and its distribution in the Fish Lake surficial uranium deposit. Specific combinations of these interrelated factors established the conditions necessary for formation of the deposit.

Fish Lake marsh is at a fault-controlled bend in the northern part of the Silver Peak Range. At the bend, sediment-laden runoff from the Silver Peak Range is diverted away from the marsh area, so that clastic sedimentation in the marsh is minimized and thereby allows the lacustrine/marsh environment to be maintained.

The fault zone defining the eastern edge of the valley provides an avenue of migration for uraniferous groundwater from rocks of the Silver Peak Range. The water moves upward along faults and into the base of the marsh deposits, where much of the dissolved uranium is trapped by organic-rich marsh sediments. Some water flows through coarser sediments at the base of the marsh deposits until it reaches the surface, where it forms springs at the marsh edge. The springs provide surface water to maintain marsh vegetation, which would not otherwise grow in the arid climate of the area.

Fluctuations in the groundwater discharge caused periodic flooding of the marsh and deposit of lacustrine clays. Marsh vegetation, reestablished during drier periods, forms the organic-rich layers in the deposit. Because uranium enrichment occurs preferentially in organic-rich sediments, the uranium enrichment zones generally are tabular shaped and follow the trend of the organic materials. Zones of maximum enrichment are in organic-rich layers nearest the groundwater source, which, in this case, are those layers directly above the fault zone.

Surficial uranium deposits are closely associated with the groundwater system. Uranium in these deposits may be easily remobilized; therefore, disturbance of uranium-bearing wetland deposits should be avoided to avert possible contamination of groundwater-fed domestic water supplies.

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RADIONUCLIDE DISTRIBUTIONS IN THE NATURAL ENVIRONMENT IN KANSAS — A REVIEW OF EXISTING DATA

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ABSTRACT

Recent emphasis on potential hazards associated with radon emanations focuses attention on the need to understand the distribution of radionuclides in both the aqueous and solid state in the natural environment. Radon anomalies are associated with concentrations of radium and, in many cases, with uranium. Little data on the distribution of radon and radium are available. The uranium content of a variety of natural solids has been determined during the past 15 years. Anomalous concentrations (up to 350 ppm U_3O_8) have been measured in thin, black, phosphatic Pennsylvanian shales in eastern Kansas. In central Kansas uranium anomalies are associated with the organic-rich basal parts of well-developed channels in the Cretaceous Dakota sandstone. Silcrete deposits, showing uranium-concentration ranges up to 125 ppm, occur in the Pliocene Ogallala Formation in western Kansas, most notably in Clark and Meade Counties. The uranium content is a function of the degree of silification; the silica is probably derived from dissolution of volcanic ash. Associated groundwater from Pliocene-Pleistocene aquifers shows a large regional anomaly; the uranium concentrations range from 2-172 ppb, with a mean of 9.5 ppb.

High radium levels (1500 pCi/L) are associated with oil brines in Cambro-Ordovician rocks in southeast Kansas. Basement-associated gas anomalies that are known to occur in association with the rift in central Kansas indicate a potential for radon anomalies along major rift faults.

INTRODUCTION

Recent emphasis on potential hazards associated with radon emanations focuses attention on the need to understand the distribution of radionuclides in both aqueous and solid states in the natural environment. To better understand the problems associated with the distribution of radon, one is forced to consider the parent-daughter relationships in the natural decay chain of uranium-238, which is the parent of the longest lived radon isotope, radon-222.

Because of its short half-life (3.825 days), radon-222 can travel or migrate only a short distance. It therefore seems clear that radon anomalies are associated with elevated concentrations of radium-226. Because of the long half-life of uranium-238 and its relatively high mobility, it is not clear if higher radium concentrations are directly related to elevated uranium levels.

In this paper we will briefly discuss current knowledge about concentrations and distributions of radionuclides in various environments in Kansas. No data are available on the distribution of radon-222 in the natural environment. A few scattered radon-222 measurements in homes have been reported.

Unfortunately, little is known about the distribution and concentration of the various isotopes in the natural environment in Kansas. Extensive surveys undertaken by the National Uranium Resource Evaluation (NURE) program, starting about a decade ago, contributed much data on the uranium content of groundwaters, stream sediments, and some of the lithologic units in a number of 1 x 2 degree quadrangles in Kansas (Dodge City, Hutchinson, Joplin, Manhattan, Pratt, and Wichita). A few area-specific studies were also conducted as part of this program.

Radium and uranium isotopes were also measured by the Kansas Geological Survey, in 77 producing wells from Mississippian and Cambrian-Ordovician aquifers in southeast Kansas and adjoining areas in Missouri and Oklahoma. Radium contaminant levels above accepted standards were recorded at several locations.

As part of chemical-quality studies of irrigation waters in western Kansas, conducted by the Kansas Geological Survey, uranium was analyzed in 1048 water samples. A survey of uranium concentrations in silicified Pliocene-Pleistocene sediments was also undertaken in the same region.

It is well known that many black, sometimes phosphatic, Pennsylvanian shales contain anomalous uranium concentrations. This is especially evident by examining gamma-ray logs of wells that penetrate rocks of that age. A number of studies have reported on the actual concentration of uranium in these shales.

DISCUSSION

Two commercial companies and the University of Pittsburgh, Kansas, provided results of radon-222 measurements in homes, mostly in the eastern part of the state of Kansas, to the Kansas Department of Health and Environment (KDHE). The information comprises a total of 148 measurements in 16 towns and some scattered localities. The highest concentrations were recorded in Shawnee, where eight samples gave a mean value of 14.9 pCi/L. Other localities having mean values greater than 5 pCi/L are Fairway (mean of 5.9 pCi/L: 4 samples), Lenexa (mean of 8.1 pCi/L: 19 samples), Mission (mean of 6.1 pCi/L: 4 samples), and Chanute (mean of 6.0 pCi/L: 1 sample). The KDHE, in cooperation with EPA, studied 1250 homes throughout Kansas during the first few months of 1987. No data are available at this moment.

As part of the NURE program, Union Carbide Corporation (1979a-e, 1980) published six reports detailing the chemical composition of several thousand groundwater samples from six of the 12 1 x 2 degree NTMS quadrangles that cover Kansas. Uranium analyses of samples from municipal, domestic, and livestock supplies in the Dodge City, Hutchinson, Joplin, Manhattan, Pratt, and Wichita Quadrangles range from less than 0.20 ppb to a maximum of 280 ppb in a sample from the Hutchinson Quadrangle; the mean is about 6.0 ppb. The anomalously high uranium concentration occurs in the western part of the Hutchinson quandrangle, part of an area containing several clusters of wells with high concentrations. The wells produce primarily from the Permian Nippewalla Group, the Cretaceous Kiowa-Cheyenne Sandstone formations, and Quaternary deposits. One of

those clusters forms a linear trend that follows the Smoky Hill River downstream from Kanopolis Reservoir where we identified anomalous radioactivity from drilling into what is believed to be a small paleochannel in the Cretaceous Cheyenne Sandstone. Other channels are common in this environment. Elevated concentrations of arsenic, molybdenum, selenium, and vanadium commonly accompany the high uranium concentrations (Union Carbide Corporation, 1979a-e). The next highest uranium concentration (177 ppb) was obtained in the Manhattan Quadrangle. Concentration ranges for all quadrangles are listed in table 1.

TABLE 1
Uranium values in ppb reported for 1 x 2 degrees NTMS quadrangles as part of the NURE program

Dodge City	<.2 — 106.00, mean 9.54
Manhattan	<.2 — 177.40, mean 5.91
Joplin	<.2 — 103.70, mean 2.94
Pratt	<.2 — 79.83, mean 5.31
Wichita	<.2 — 73.58, mean 8.70
Hutchinson	<.2 — 280.00, mean 5.35

All samples were taken from aquifers ranging in age from Cambrian-Ordovician in eastern Kansas to Pliocene-Pleistocene in western Kansas. Quaternary alluvial deposits associated with many of the major rivers and smaller streams are important sources of water throughout Kansas. High uranium concentrations occur in some alluvial aquifers, as in the Arkansas River valley in western Kansas.

Uranium was the only radioactive element measured in all samples. Nothing is known about the distribution of other radionuclides or the parameters that affect them.

In addition to aerial radiometric and magnetic surveys in five 1 x 2 degree NTMS quadrangles, a number of geologic studies were conducted in all 12 quadrangles in Kansas. Some of the data may be useful to delineate areas of higher near-surface radioactivity. The publications are available from the U.S. Geological Survey in Denver.

Hydrogeologic conditions and chemical quality of groundwaters from lower Paleozoic aquifers (Mississippian, Cambrian-Ordovician) in southeastern Kansas and adjoining areas of Missouri and Oklahoma (fig. 1) have been reported in publications by Hathaway and Macfarlane (1980), Macfarlane (1981), and Macfarlane and Hathaway (1987). The aquifers are primarily in carbonate rocks, used in the eastern part of the area as water sources for municipalities and rural water districts. In the western part of the area, the aquifers contain saline water and are not suitable for public water supplies. Hathaway and Macfarlane (1980) state that the aquifer systems are used with little general understanding of their regional hydrogeological and hydrogeochemical behavior.

Radium-226 and uranium levels in samples are given in table 2. In figure 1 the sample locations and the relative amounts of radium-226 are shown. Of the 77 samples analyzed (Macfarlane and Hathaway, 1987), 12 have radium-226 levels exceeding 20 pCi/L, another 11 contain between 5 and 20 pCi/L, and the rest (54 samples) contain less than 5 pC/L. The high radium-226 levels (>20 pCi/L) were measured in brine samples from oil wells or oil-field water-supply wells in the western part of the area. A direct relationship seems to exist between the amount of total dissolved solids and the radium-226 concentration in the water.

Further east the water is less saline and forms a transition zone between the saline and freshwater portions of the aquifer. As shown in figure 1, the eastern boundary of this zone coincides roughly with the top of the Mississippian outcrop. The western boundary of the transition zone is less well defined but trends northward more or less along the western boundaries of Cherokee, Crawford, and Bourbon Counties. Slightly west of the eastern boundary of the transition zone, sulfide levels in the water become greater than 0.2 mg/L.

A direct relationship exists between elevated radium-225 and sulfide levels greater than 0.2 mg/L, a circumstance that may reflect the long-term cumulative effects of reduction-induced deposition of uranium introduced by westward movement of freshwater into the zone (Macfarlane and Hathaway, 1987). At the same time the uranium concentrations decrease.

Concentrations of radium-226 between 5 and 20 pCi/L are common in the transition zone, but low levels are encountered in the freshwater portion of the aquifer. The high radium-226 concentrations measured in the saline portion of the aquifer, west of the transition zone, indicate that a different or additional source for radium-226 is present (Macfarlane and Hathaway, 1987). One possible origin for

TABLE 2

Radium and uranium data from wells tested in the Tri-State area (Kansas, Oklahoma, and Missouri)

Well name/location	Aquifer unit	Radium-226 pCi/L	Uranium ppb	Uranium-234/ Uranium-238
Arcadia #2 28S-25E-1bbd	M,O-C	3.4	—	—
Arma #2 29S-25E-5cdd	M,O-C	4.5	—	—
Baxter Springs #1 34S-24E-36cdc	O-C	1.7	0.493	7.48
Baxter Springs #5 34S-24E-36caa	O-C	2.3	0.280	8.30
Baxter Springs #6 34S-24E-36baa	O-C	12.0	0.350	7.10
Capaldo #1 30S-24E-1aca	P,M,O-C	4.8	—	—
Cherokee West 30S-24E-18dbd	M,O-C	3.2	—	—
Cherokee County RWD 1, #1 33S-25E-18daa	O-C	1.5	0.54	6.80
Cherokee County RWD 2 34S-25E-8cbc	O-C	1.2	—	—
Cherokee County RWD 3 34S-24E-17dcc	O-C	3.1	—	—
Cherokee County RWD 4 32S-24E-29bbb	M,O-C	4.1	—	—
Bill's Coal Co. Chetopa 34S-21E-28bcb	M	0.8	—	—
Columbus #6 33S-23E-13baa	M,O-C	5.5	—	—
Crawford County RWD 1 29S-25E-26cbc	M,O-C	3.5	—	—
Crawford County RWD 2 29S-24E-11daa	M,O-C	4.5	—	—
Crawford County RWD 4 30S-24E-28aaa	M,O-C	1.8	0.041	8.84
Crawford County RWD 5 30S-25E-23ccd	M,O-C	4.7	—	—

Aquifer units: P, Pennsylvanian; M, Mississippian; O-C or C-O, Cambrian-Ordovician
OFWS, oil-field water-supply well
OW, oil well

Table 2 (cont.)

Well name/location	Aquifer unit	Radium-226 pCi/L	Uranium ppb	Uranium-234/ Uranium-238
Crawford County RWD 7, #1				
29S-24E-5ddc	C-O	7.5	0.53	9.10
Diskin				
29S-21E-14ddd	C-O	2.7	—	—
Frontenac #1				
30S-25E-9bbb	M,O-C?	3.1	.033	9.44
Galena #1				
34S-25E-23aad	O-C	0.8	—	—
Bill's Coal Co. — Garland				
27S-25E-1acb	M	3.6	—	—
Girard — old well				
29S-23E-24acd	M,C-O	8.7	0.033	9.65
Gulf Oil				
34S-25E-4aca	C-O	1.5	—	—
McCune				
31S-22E-8ddc	C-O	7.5	—	—
Mulberry				
29S-25E-1aac	M,C-O?	3.6	—	—
Pittsburg #10				
30S-25E-28daa	C-O	1.9	.037	9.02
Emp. Dist. Elec. Riverton				
34S-25E-20bbd	C-O	2.6	—	—
Scammon #2				
32S-23E-7bdd	M,C-O?	1.9	—	—
Van Becelare, Pittsburg				
30S-25E-22ccc	M	2.1	—	—
Walnut #4				
28S-22E-20ccd	C-O	7.6	.016	8.80
Weir #1				
31S-24E-27cdc	M,C-O?	1.7	—	—
West Mineral #1				
32S-23E-6daa	C-O	6.4	0.010	5.40
Savonberg OFWS				
26S-21E-28baa	C-O	7.7	0.018	3.63
Tyro, OW6				
34S-15E-3dbd	C-O	970	0.014	3.17
Shaw, OW				
35S-16E-1ddc	C-O	220	0.005	3.10
Walnut, OFWS				
28S-22E-27bca	C-O	4.8	0.017	4.05
Johnson, OFWS				
28S-20E-23bdb	C-O	22	0.017	4.13

Aquifer units: P, Pennsylvanian; M, Mississippian; O-C or C-O, Cambrian-Ordovician
OFWS, oil-field water-supply well
OW, oil well

Table 2 (cont.)

Well name/location	Aquifer unit	Radium-226 pCi/L	Uranium ppb	Uranium-234/ Uranium-238
Trent, OFWS 28S-20E-22ddd	M,C-O	43	0.077	8.87
Flat Rock, OFWS 28S-21E-29abc	C-O	180	0.065	3.11
Mirriam, OW 33S-17E-8ddb	C-O	260	0.009	0.14
Adams, OFWS 28S-19E-4bca	C-O	41	0.034	4.62
Seefeldt, OFWS 26S-18E-34caa	C-O	28	0.006	2.05
Roberts, OFWS 26S-19E-23abb	C-O	43	—	—
Thompson, OW 33S-16E-12ccd	C-O	1.6	0.026	1.95
Fort Scott 25S-24E-36aac	C-O	5.6	0.400	4.85
Chetopa, OW 34S-20E-36adc	C-O	2.5	0.010	1.68
Wackerle, OW 35S-19E-1aab	C-O	40	0.013	1.46
Schreppel, OW 25S-20E-6bdb	C-O	25	0.100	2.08
Asbury #1 29N-34W-2bdd	C-O	1.5	0.584	7.24
Emp. Dis. Elec. #3 30N-33W-17cba	C-O	4.0	—	—
Well #1 32N-30W-27add	C-O	0.8	—	—
Well #2 32N-31W-17aaa	C-O	1.2	—	—
Well #1 31N-29W-17aab	C-O	1.1	—	—
Bronaugh #3 34N-32W-20baa	M,C-O	5.8	—	—
Carl Jct. #3 28N-33W-5cdc	C-O	1.5	0.335	8.72
Carthage #7 28N-31W-4bad	C-O	1.8	—	—
Diamond #1 26N-31W-3cab	C-O	0.9	—	—
Duenweg #2 27N-32W-10caa	C-O	0.9	0.416	10.37
Jasper #2 30N-31W-24ccc	C-O	1.6	—	—
Atlas Powder #6 27N-32W-1bbd	C-O	1.5	—	—

Aquifer units: P, Pennsylvanian; M, Mississippian; O-C or C-O, Cambrian-Ordovician
OFWS, oil-field water-supply well
OW, oil well

Table 2 (cont.)

Well name/location	Aquifer unit	Radium-226 pCi/L	Uranium ppb	Uranium-234/ Uranium-238
Farm Chem. Corp. east well, Joplin 27N-34W-2bcd	C-O	1.7	0.270	9.50
Liberal #2 32N-33W-2acd	C-O	2.4	—	—
Mindenmines #1 32N-33W-5bbb	M,C-O	2.3	—	—
Vernon Co. PWS #1 Well I 34N-32W-5aad	M,C-O	4.4	—	—
Nev. St. Hosp. #4 36N-31W-33bbd	M,C-O	7.3	—	—
Sheldon #2 34N-31W-35aad	M,C-O	2.1	—	—
Walker #1 36N-30W-15bcc	C-O	2.6	—	—
Webb City #11 28N-33W-24aac	C-O	1.0	0.325	10.60
Blue Jacket #1 27N-21E-20dcc	M,C-O	2.7	—	—
Commerce #3 28N-23E-6bac	C-O	0.8	—	—
Miami #5 28N-23E-32bab	C-O	2.2	—	—
Miami #7 28N-23E-28bbb	C-O	3.7	—	—
RWD 1 27N-24E-28cda	C-O	0.5	—	—
RWD 3 28N-24E-13aba	C-O	0.5	—	—

Aquifer units: P, Pennsylvanian; M, Mississippian; O-C or C-O, Cambrian-Ordovician
OFWS, oil-field water-supply well
OW, oil well

radium-rich oil-field brines was discussed by Bloch (1979), and Bloch and Key (1981), who attribute the disequilibrium conditions between uranium-238 and radium-226 in oil-field brines to the chemical properties of radium and the geochemical environment of the petroleum reservoirs. Under reducing conditions (low Eh values) the mobility of Ra^{2+} is increased and it can be released into the brine by petroleum-reservoir rocks.

Uranium concentrations were also determined in 1098 irrigation water samples as part of a study to characterize the quality of the water in the unconsolidated aquifers in western Kansas (Berendsen and Hathaway, 1981). Groundwater is mostly of the bicarbonate type, but sulfate becomes important along many drainages and a possible paleodrainage extending southward from Scott into Finney County. Uranium concentrations in the groundwater range from less than 0.5 ppb to about 25 ppb. In about 15 wells the uranium concentrations exceed 25 ppb. Most of these wells are in Hamilton, Ford, Scott, Finney, and Cheyenne Counties; the majority of them are associated with the major rivers and the Scott-Finney depression (Berendsen and Hathaway, 1981). Landis (1960) shows anomalous concentrations of uranium in the Smoky Hill River valley in Gove, Logan, and Wallace Counties. Analysis results agree with earlier data of Scott and Barker (1962). The uranium-234/uranium-238 activity ratio measured in nine samples (Cowart, 1978, personal communication)

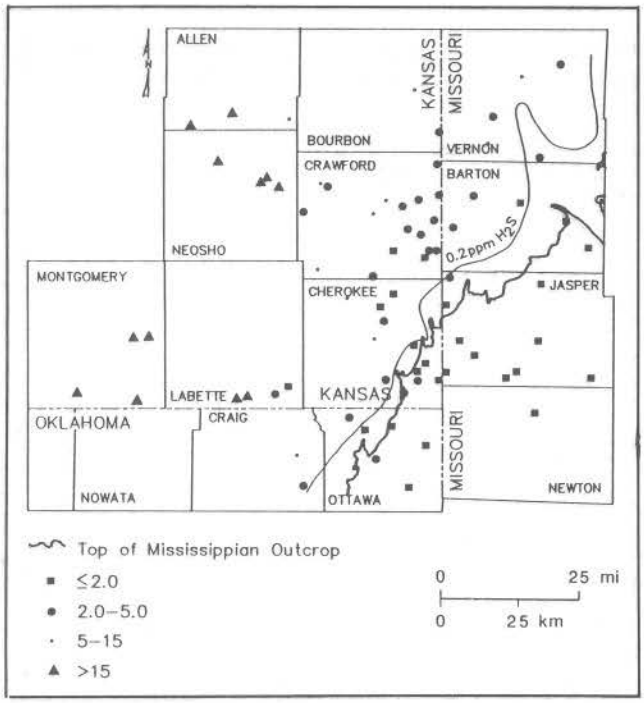


Figure 1 — Radium-226 distribution in groundwaters from Lower Paleozoic aquifers in Tri-State Region (Macfarlane and Hathaway, 1987).

was found to be near 1.0, which indicates an absence of reducing depositional environments. Concentrations of other uranium isotopes or radium were not measured in any of the samples. In a sample from Finney County (NW¼ NW¼ SE¼ sec. 3, T. 26 S., R. 33 W.), the uranium-234/uranium-238 activity ratio is 1.75 (Cowart, personal communication, 1978), which indicates that uranium is being precipitated from solution.

In several areas, secondarily silicified fluviatile sediments of the Pliocene Ogallala Formation contain anomalous uranium concentrations. Uranium content of the rocks directly correlates with the degree of silicification and can be visually assessed in the outcrops. Silica occurs as alpha-cristobalite, referred to as Opal-C by Jones and Segnit (1971). The most intensely silicified rocks contain up to 125 ppm U_3O_8. In eastern Meade and western Clark Counties in southwest Kansas, there is a 10-mi-long, 1.5-mi-wide, northwest-southeast-trending, continuously silicified outcrop belt (Berendsen and Hathaway, 1981). It was suggested that silica replaced preexisting sediments in a braided channel. Maximum thickness of the silicified material is about 10 ft near the center of the outcrop belt and thins to either side. To the southeast, erosion removed the sediments; to the northwest, younger loess deposits overlie the Ogallala sediments. The source of the silica and uranium may be the ubiquitous Pliocene-Pleistocene volcanic ash mixed with the sediments and which occurs in beds up to 30 ft thick (Carey et al., 1952).

Less intense and less extensively silicified Ogallala sediments occur in Scott and Cheyenne Counties. The greenish-colored quartzitic rocks in Philips County are of a different nature, generally showing little uranium enrichment.

Known radon anomalies in homes in eastern Kansas are generally attributed to the Pennsylvanian organic-rich, often phosphatic, and uraniferous black shales, most of which are less than 10 ft thick but are exposed for long distances along strike in a north-northeasterly direction. The most important shales (Runnels, 1949; Zeller, 1968) are listed in table 3.

TABLE 3
Pennsylvanian phosphatic black shales exposed in eastern Kansas

Heebner Shale Member
Eudora Shale Member
Muncie Creek Shale Member
Quindaro Shale Member
Stark Shale Member
Hushpuckney Shale Member
Pleasanton Group
Anna Shale Member
Little Osage Shale Member
Excello Shale Member
Shale above the Bevier coal
Shale above the Croweburg coal

Uranium and thorium analyses have been determined in 35 samples from a number of these shales. There is a direct positive correlation between the amount of phosphate present in a sample and its uranium content; therefore uranium is mostly concentrated in shales with discrete phosphatic nodules. The uranium contents of black shales that do not contain discrete phosphatic nodules, as well as those from which the nodules are separated, range from a low of about 15 ppm to about 100 ppm U_3O_8. Nodules separated from the shales have U_3O_8 concentrations ranging up to 350 ppm. Similar values have been reported by Runnels et al. (1953) for a number of phosphatic black shales. The thorium content of shales and nodules varies considerably; values range from near zero to about 30 ppm. The phosphate nodules contain up to about 25 percent P_2O_5. These shales are also enriched in selenium and molybdenum.

CONCLUSION

Much data are becoming available on radon-222 concentrations measured in homes constructed on a wide variety of geological materials in Kansas and across the U.S.A. Some data are presented on the distribution and concentration of uranium and thorium in geologic materials, but data for radium-226 are scarce. Because disequilibrium conditions seem to be common, it is difficult to calculate or predict the amount of radon-222 emanating from these environments, based on their uranium content.

Some data are also available on the distribution of uranium and radium in aquifers. Very high radium concentrations seem to occur in saline aquifers or brines associated with oil pools. The possible relationships between radionuclides in groundwater and radon emanating from it at the surface is unclear.

The activity of radon-222 measured in a home is largely a function of the type of construction and its maintenance record. The effect of geologically derived radionuclides upon tightly insulated homes needs further study.

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DISTRIBUTION OF RADIONUCLIDES IN MISSOURI GEOLOGIC TERRANES: A SUMMARY OF AVAILABLE DATA AND THE NEED FOR MORE DATA

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ABSTRACT

To evaluate the effects of naturally occurring radionuclides on health and the environment, background radiation values should be available in a standard usable format. Background values are needed to determine permissible radiation levels and to evaluate the effects of handling radioactive materials. To determine background values, types, sources, and levels of natural radiation must be quantified. To understand the natural distribution of radionuclides and radiation levels in our environment, surface geology is the most important factor to consider. Natural radiation, related to lithology and types of radionuclides in the rocks, can be evaluated by dividing the state into geologic terranes, combining rock types of similar lithology and origin, and evaluating each terrane individually for radionuclide content.

Missouri geologic terranes include 1) Precambrian igneous rocks, in two subterranes: plutonic rocks and volcanic rocks; 2) basal Cambrian rocks; 3) Devonian black shales; 4) post-Devonian diatremes; 5) exotic rocks associated with cryptoexplosion and volcanogenic structures; 6) pre-Pennsylvanian Paleozoic carbonate rocks and associated clastic rocks; 7) Pennsylvanian rocks; 8) Mesozoic and Cenozoic rocks; and 9) surficial materials such as alluvium, residuum, and glacial drift.

Terranes 1, 4, and 5 may contain radionuclides that are residual products of magma differentiation. Terrane 2 may contain enrichments of uranium mobilized from Terrane 1 and deposited in favorable lithologic intervals as well as indurated placer deposits composed of gravels derived from Terrane 1, pebbles of which may contain radiogenic mineral grains. Terranes 2, 6, 7, and 8 may host uranium mobilized from a primary source and deposited at favorable stratigraphic horizons. Terranes 3 and 7 may host uranium associated with carbonaceous matter and with phosphate nodules. Terrane 9 is expected to be void of radionuclide enrichments, because of dilution with other sediments and the removal of radionuclides by weathering; exceptions may be peat bogs, which may act as organic traps permitting uranium deposition. None of the terranes have been adequately evaluated for background radiation.

Other geologic influences on radionuclide distribution are geologic structure and the thickness of surficial materials. The first allows migration of radon from depth and of radionuclides in groundwater; the second prevents gamma-ray radiation from depth from reaching the surface and is itself depleted of radionuclides with respect to the bedrock of which it is the weathered residuum. This report describes sources of radiation expected in each terrane, summarizes available data, and stresses the importance of background radiation maps.

INTRODUCTION

Because of concern about radiation effects on health and the environment, the Missouri Department of Natural Resources wants to insure the safe handling of radioactive materials within the state. Some aspects of this problem currently include and could eventually include transportation of radioactive materials across the state, disposal sites for radioactive waste, existing problem areas of radioactive waste contamination (such as Weldon Spring), the generation of nuclear power, the mining and processing of nuclear fuels, and the amount of radionuclides in public drinking water supplies. The Division of Geology and Land Survey has qualified personnel capable of applying knowledge to these matters. The Geological Survey Program is particularly qualified to provide data concerning natural radiation sources in the state. It is important to determine such sources so that background values can be considered when determining permissible amounts of radiation that can be introduced into the environment. This report reflects some ideas the Geological Survey Program has developed in recent years about how to assemble and present background data in a format usable by the general public. We will examine regional geologic features that influence radionuclide distribution. The report includes data from the literature and new data.

In establishing background values it is best to relate the type of radioactivity measured to the source of radiation and, in turn, to relate the source of radiation to the containing medium. For purposes of constructing a statewide background radiation map, this can be done by relating sources of radiation, in each case, to surface geology of the immediate area. In Missouri, common lithologies can be combined into geologic terranes that comprise significant land areas.

Various lithologic units in the state can be combined into terranes that may differ for one purpose as compared to another. For instance, lead-zinc prospectors may group various lithologies differently than civil engineers. Likewise, persons concerned with background radiation may group the same lithologies differently than prospectors or civil engineers.

The terranes discussed herein contain rocks with common lithologies, some of which have a common origin. These terranes contain unique characteristics that influence radionuclide distribution; they include the following: 1) Precambrian igneous rocks divisible into volcanic and plutonic rock subterranes; 2) basal Cambrian rocks; 3) Devonian black shales; 4) post-Devonian diatremes; 5) exotic rocks associated with cryptoexplosion and volcanogenic structures; 6) Paleozoic carbonate rocks (including associated siliclastic sedimentary rocks and excluding Pennsylvanian rock units; 7) Pennsylvanian rocks divisible into marine and continental rock subterranes; 8) Mesozoic and Cenozoic rocks; and 9) surficial materials such as glacial drift, residuum, and stream drainage alluvium.

A brief discussion on how geologic structure and thickness of surficial materials influence radioactivity at the earth's surface is also included.

MISSOURI GEOLOGIC TERRANES AND RADIATION SOURCES
(known and potential sources)

PRECAMBRIAN ROCKS

The Missouri Precambrian igneous rock complex (fig. 1) comprises two subterranes: the plutonic rock subterrane and the volcanic rock subterrane. Most of these rocks were derived from late-stage magmas and residual fluids that tend to form granites and ash-flow tuffs. Uranium tends to favor these rock types and thorium, often accompanied by lesser amounts of uranium, tends to favor more basic-rock types, such as monzonites and calc-alkalic intrusives. Uranium in late-stage granites and volcanic rocks tends to be interstitial; in more basic rocks, uranium-thorium tends to be interlocked in rare-earth and accessory mineral grains. The average uranium content of granites is 4.0 ppm (DeVoto, 1978).

Uraniferous granites have been reported from Rossing, Nambia (DeVoto, 1978); Bokan Mountain, Alaska (DeVoto, 1978); and central Wyoming (Peterman and Hildreth, 1978). In Missouri, the Graniteville Granite is consistently enriched in uranium and thorium; assays using a Geometrics 410 portable

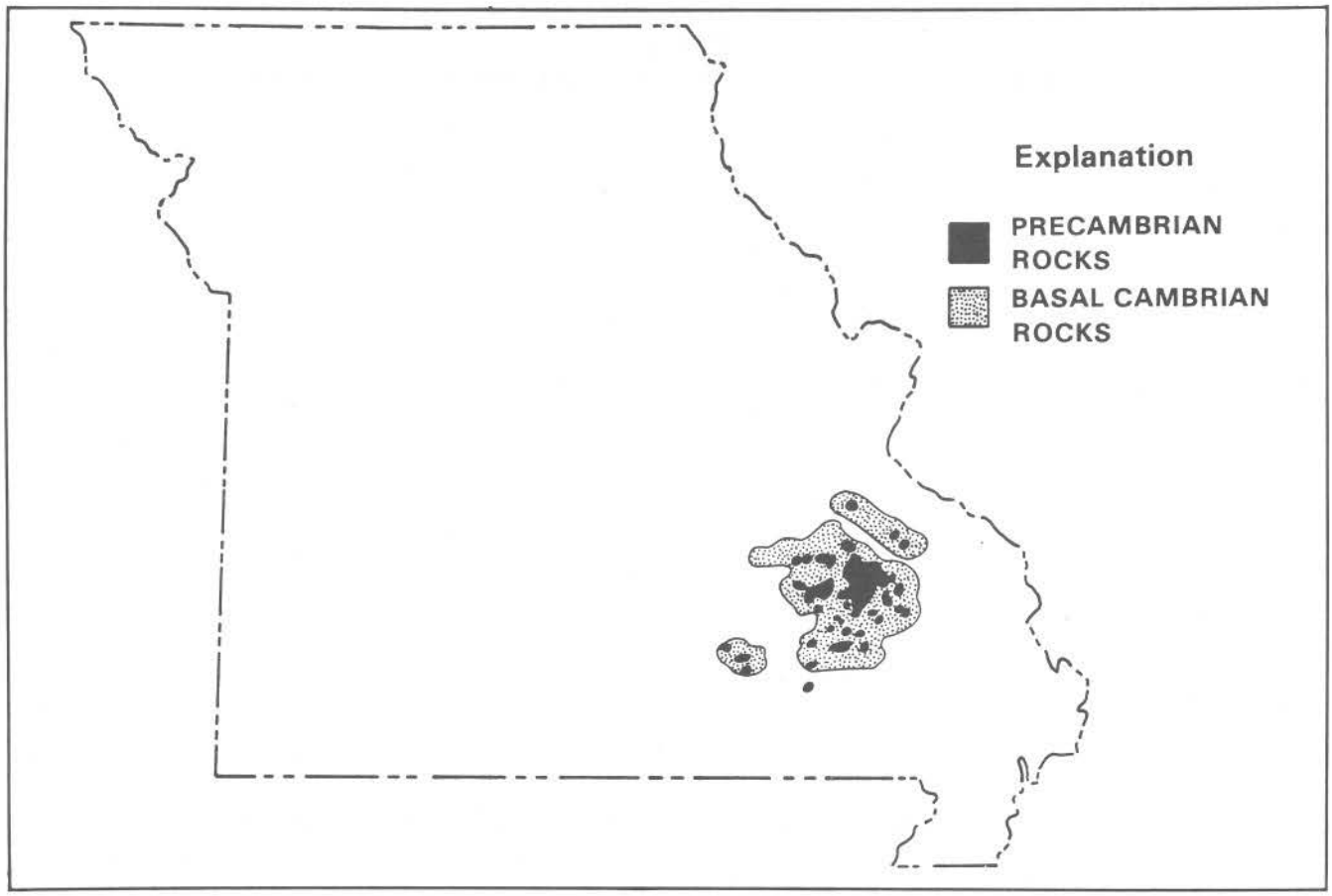


Figure 1 — Exposed Precambrian and basal Cambrian rocks in Missouri.

gamma-ray spectrometer with a 27-in^3 NaI detector show that it contains 8 to 38 ppm equivalent uranium and 34 to 111 ppm equivalent thorium (table 1). Neutron activation analyses show this granite contains up to 34.4 ppm uranium and 54.7 ppm thorium (Nash, 1977). O'Brien (1978) reports that the higher uranium contents are in island-like zones in the pluton and that thorium is more evenly distributed. He also states that late-stage magmatic fluids may have liberated uranium from mineral grains and transported this element and iron to sites favorable for deposition of late-stage, uranium-enriched magnetite, thereby concentrating uranium in the island-like zones. Other Missouri granites slightly enriched in uranium are the Breadtray and Butler Hill Granites, which average 6.2 and 5.6 ppm uranium, and 23.5 and 20.5 ppm thorium, respectively (Nash, 1977). Table 1 shows the uranium and thorium content of various Missouri granites.

Glass shards of ash-flow tuffs are uniquely leachable. Uranium on shard surfaces is leached early and uranium disseminated in the shards is leached upon divitrification or dissolution (DeVoto, 1978). Uranium tends to accumulate in vapor-phase (lithophysae) zones of ignimbrites, such as those of Sweden (Lindroos and Smellie, 1979). Uraniferous ash-flow tuffs, in addition to those of Sweden, include the Nopal and Escurada tuffs of Mexico (DeVoto, 1978) and the Erie Tuff of Nevada (Garside, 1973). Calderas, such as the McDermit caldera of northern Nevada, have proved to be hosts for uranium. Volcanic rocks make up a large portion of Missouri's exposed Precambrian rock terrane. Much of the volcanic rocks consist of ash-flow tuffs, some associated with identifiable calderas. Limited radiometric data on Missouri silicic volcanic rocks (table 1) give maximum yields of 7.0 ppm uranium and 18.5 ppm thorium (Malan, 1972).

BASAL CAMBRIAN ROCKS

Basal Cambrian rock units (fig. 1) constitute another geologic terrane having its own distinct

TABLE 1
Uranium and thorium content of various Missouri Precambrian rock units

Unit	Uranium min.	Uranium max. (ppm)	Uranium av.	Thorium min.	Thorium max. (ppm)	Thorium av.	Number of samples	Assay type	Source
Silicic plutonic rocks	2.5	17.6	5.9	5.1	49.0	17.6	27	eU	Malan, 1972
Bismarck Granite	3.9	4.81	4.36	13.8	16.0	14.9	2	DNA	Nash, 1977
Breadtray Granite	2.29	8.29	5.65	5.73	26.1	20.55	7	DNA	Nash, 1977
Butler Hill Granite	5.06	25.0	6.22	20.2	25.0	23.55	6	DNA	Nash, 1977
Graniteville Granite	8.0	38.0	20.0	34.0	111.0	67.0	17	eU	Nuelle et al., 1979
Graniteville Granite	4.1	36.3	16.3	30.0	72.0	53.0	110	eU	O'Brien, 1978
Graniteville Granite	7.41	34.4	16.98	25.7	54.7	42.66	10	DNA	Nash, 1977
Knoblick Granite	2.51	4.56	3.46	8.37	9.41	8.77	3	DNA	Nash, 1977
Silvermine Granite	0.0	1.0	.75	10.0	15.0	11.5	4	eU	Nuelle et al., 1979
Slabtown Granite	3.33	3.33	3.33	8.77	8.77	8.77	1	DNA	Nash, 1977
Stono Granite	2.85	2.97	2.91	7.77	8.7	8.24	2	DNA	Nash, 1977
Rhyolitic ash-flow tuffs	.9	7.0	3.1	2.5	18.5	10.1	45	eU	Malan, 1972
Unnamed rhyolite porphyry	2.0	6.0	3.6	14.0	18.0	15.6	3	eU	Nuelle et al., 1979
Unnamed lapilli flow-breccia	4.0	4.0	4.0	17.0	17.0	17.0	1	eU	Nuelle et al., 1979

eU — Equivalent uranium and thorium determined by gamma-ray spectrometer
DNA — Delayed neutron activation analyses

characteristics influencing radionuclide distribution. These rock units include the Lamotte Formation and basal conglomerates and arkoses, all of which may be contemporaneous. They could contain uranium leached from Precambrian igneous rocks or could contain indurated placer deposits of gravels derived from Precambrian rocks, pebbles of which may contain radiogenic mineral grains. Likely places for such occurrences are basins that received drainage from surrounding igneous rocks. Nash (1977) states that Lamotte sandstones may be more favorable for uranium deposited in an oxidizing environment rather than in a reducing environment. Iron-rich conglomerates and arkoses, on the other hand, may be favorable for uranium deposited in a reducing environment.

Because the Precambrian igneous rock complex was a positive region of relief during the Paleozoic, groundwater and surface-water drainage from it flowed into adjacent basins where Lamotte sediments, interpreted as an alluvial sequence of braided and fan fluvial deposits capped by thin marginal marine deposits (Houseknecht and Ethridge, 1977), were being deposited. Such fluid movement could concentrate uranium in favorable host-rock zones.

DEVONIAN BLACK SHALES

The Devonian Chattanooga Formation, which reaches 50 ft in thickness in southern McDonald County (fig. 2), is uranium enriched in various places outside Missouri. The higher uranium contents are associated with organic-rich shale layers (Connant and Swanson, 1961; Landis, 1962; Swanson and Landis, 1962). The organic-rich Gassaway Member of the Chattanooga in northern Tennessee contains as much as 0.33 percent uranium (Connant and Swanson, 1962). A uranium-enriched portion of the Chattanooga in north-central Arkansas contains as much as 0.71 percent uranium (Landis, 1962; Swanson and Landis, 1962). The only available radiometric assay of the Chattanooga Formation in southwestern Missouri yielded 0.001 percent uranium (Landis, 1962). More data are needed to evaluate the uranium content of the Chattanooga in southwestern Missouri, which may contain shale layers enriched in organic matter and uranium.

The Grassy Creek Formation is a dark olive-gray to brownish-black carbonaceous shale. Exposures are almost entirely restricted to the flanks of the Lincoln fold in northeastern Missouri (fig. 2). Its

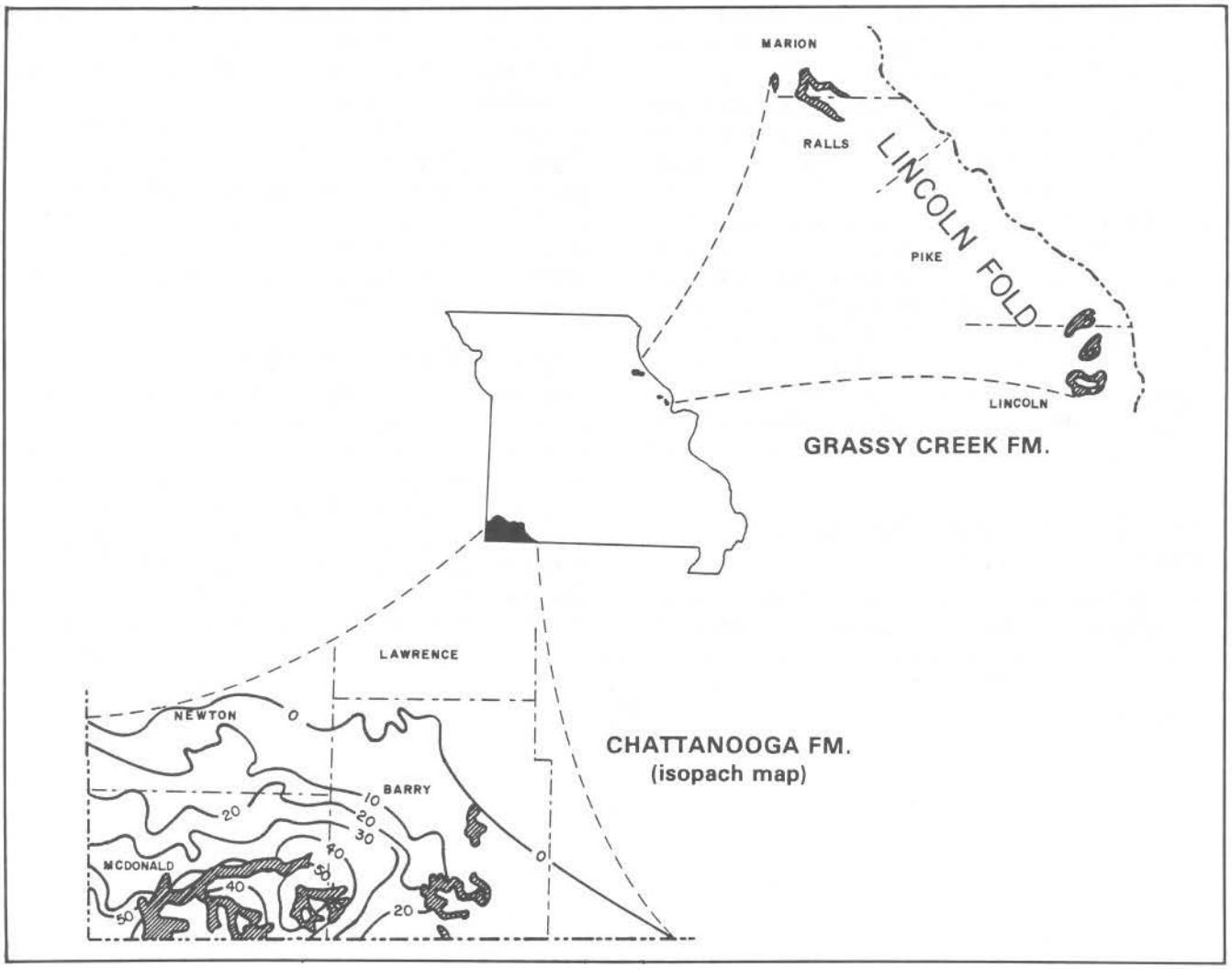


Figure 2 — Distribution of Devonian black shales in Missouri.

maximum thickness is 43 ft in northern Pike County; it thins rapidly southward and westward to less than 1 ft. The Grassy Creek extends into west-central Illinois and is equivalent to part of the Chattanooga of Tennessee and to the New Albany of Indiana and Kentucky. Only one fluorometric determination, 34 ppm uranium, is available for the Grassy Creek, but, because of its carbonaceous nature, it may contain slight amounts of uranium.

POST-DEVONIAN DIATREMES

Diatremes may host rare-earth and accessory minerals containing uranium and thorium. Some diatremes have associated uranium-copper mineralization like that of the Orphan mine, Grand Canyon, Arizona, where open-space fillings consist of uraninite and uranyl vanadates and phosphates (DeVoto, 1978). Over 100 post-Devonian diatremes are clustered in a relatively small area in Ste. Genevieve County, Missouri (fig. 3). One of them has associated sphalerite, galena, chalcopyrite, pyrite, and marcasite (Kidwell, 1947); however, no radiometric data for these diatremes are available.

CRYPTOEXPLOSION AND VOLCANOGENIC STRUCTURES

A number of structural features in Missouri lie along the 38th parallel lineament and were presumably derived from either volcanogenic or cryptoexplosive activity (fig. 3). Two features are of cryptoexplosive origin: the Decaturville structure

Krishnaswamy and Amstutz, 1960; Offield and Pohn, 1979) and the Crooked Creek structure (Hendricks, 1954; Kiilsgaard et al., 1963). Volcanogenic structures include the Dent Branch structure (Wagner and Kisvarsanyi, 1969) and possibly the Weaubleau Creek structural complex (Beveridge, 1951; Snyder and Gerdemann, 1965). Of these, the Decaturville structure has a central uplift of Precambrian granite pegmatite and a sulfide-bearing, clay-rich breccia. Radiometric data from these structures are unavailable, but they should be evaluated for possible radionuclide content. In particular, exotic rocks such as the sulfide-bearing breccia and the Precambrian granite pegmatite of the Decaturville structure, and the volcanic tuffs of the Dent Branch structure, may contain radioactive minerals.

PRE-PENNSYLVANIAN PALEOZOIC CARBONATE ROCKS

Pre-Pennsylvanian Paleozoic carbonate rocks and associated cratonic siliciclastic sedimentary rocks form much of Missouri's rock exposures (fig. 4). These rocks are expected to be essentially void of radiogenic minerals, but scattered occurrences have been reported, such as carnotite in a Mississippian limestone near Ste. Genevieve (Gableman, 1956; Muilenburg, 1957) and black radioactive carbonaceous matter in vugs and crevices in the Ordovician Roubidioux Formation and the Cambrian Lamotte Sandstone (Muilenburg, 1957). However, these appear to be chance occurrences of low concentration and limited distribution.

PENNSYLVANIAN ROCKS

Pennsylvanian rocks (fig. 4) would appear to be potential hosts for radionuclides, because many black shales, commonly associated with coal beds, are often enriched in uranium. Swanson (1956) reports that about 20 midcontinent black shales are abnormally uraniferous, containing from 0.003 to 0.010 percent and, locally, up to 0.017 percent uranium. Hyden and Danilchik (1962) divide these shales into 1) those that are soft and coaly in

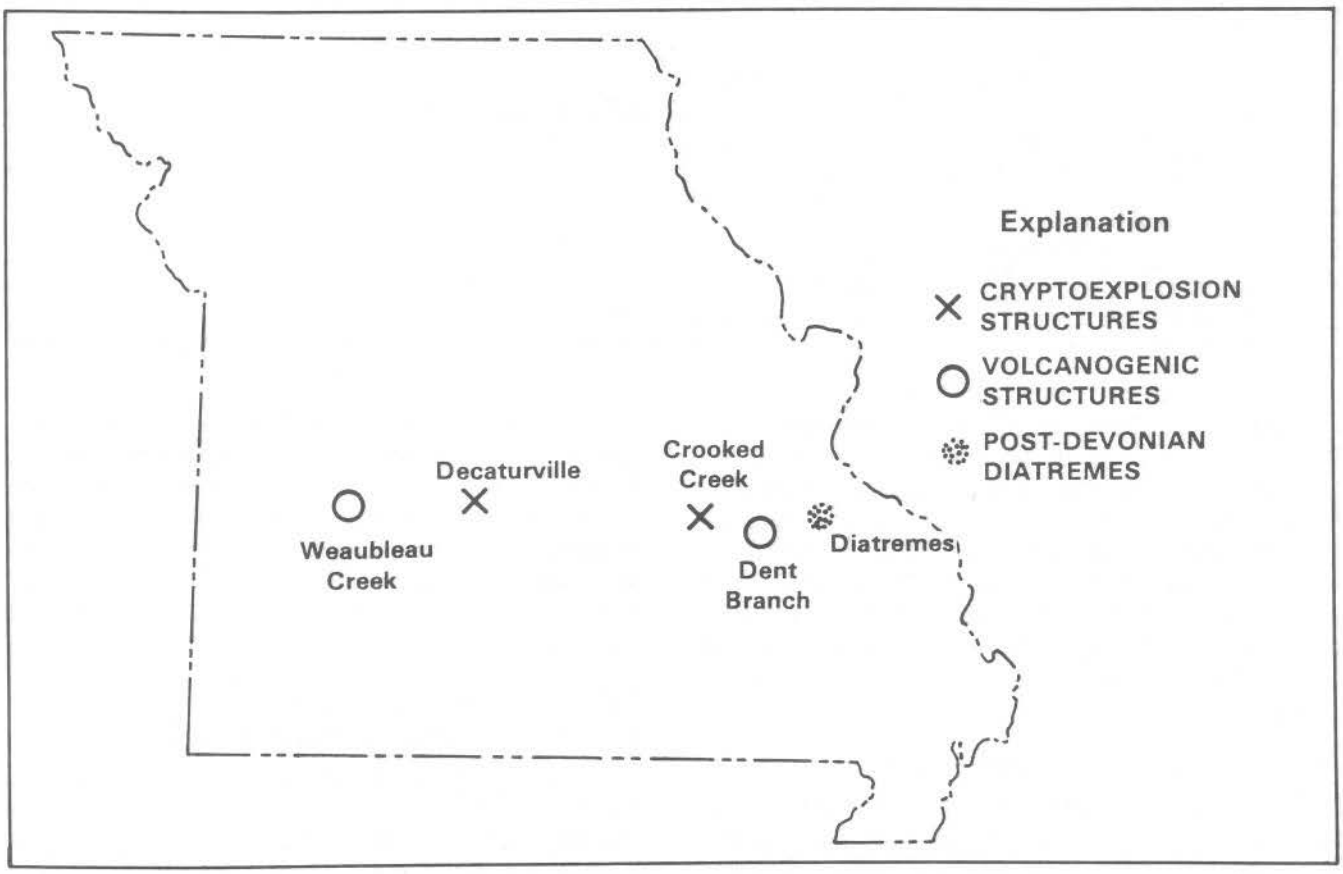


Figure 3 — Distribution of cryptoexplosion and volcanogenic structures along the 38th parallel lineament, Missouri.

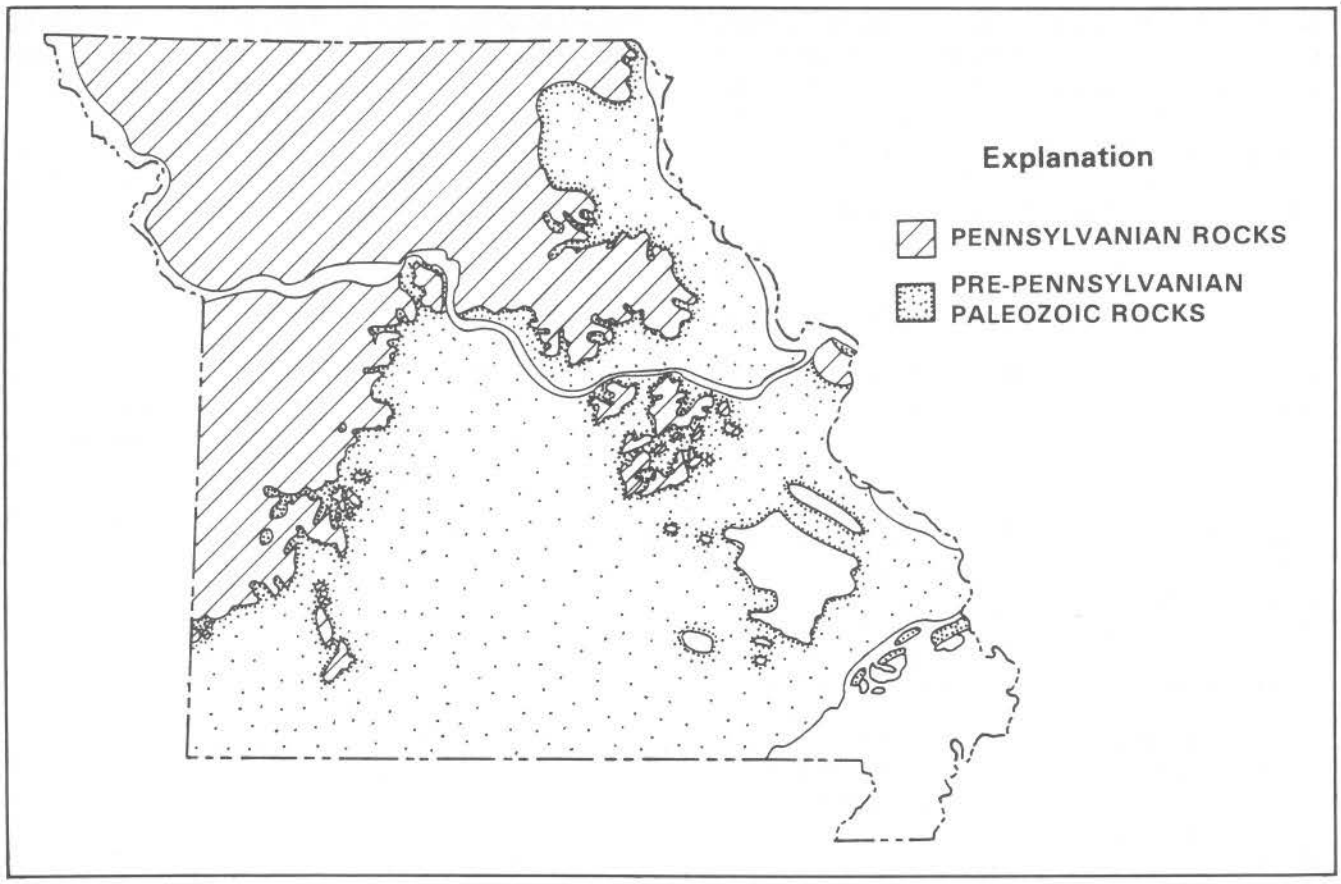


Figure 4 — Distribution of Paleozoic rocks in Missouri.

appearance and yield little or no oil upon destructive distillation and 2) those that contain phosphatic nodules and layers, are hard and brittle, and yield some oil upon destructive distillation. The average content of six stratigraphic units of the first type of shale is 0.001 to 0.002 percent uranium; that of eight stratigraphic units of the second type is 0.002 to 0.005 percent, with individual samples varying from 0.002 to 0.060 percent. Because uranium can substitute for calcium in the fluorapatite structure, the phosphatic nodules average 0.016 percent uranium (Hyden and Danilchik, 1962). The uranium content of various Pennsylvanian rock units are shown in table 2.

Emerson (1978) states that some Pennsylvanian channel-fill sandstones in Missouri and Kansas share numerous depositional and petrographic characteristics with uranium-bearing channel-fill sandstones of the Colorado Plateau and the Wyoming basins. He indicates that the Warner, Bluejacket, Warrensburg, Moberly, Englevale, Indian Cave (Permian) sandstones, and others unnamed fit this category. He comments, however, that they have less chance of radionuclide enrichment, because they lack the interbedded acidic tuffs of western United States sandstones. Nevertheless, these sandstones intersect uraniferous black phosphatic shales; hence, they may contain uranium accumulations from weathering of the shales. Radiometric data are unavailable for these units.

Some Pennsylvanian channel-fill sandstones in Missouri contain significant quantities of heavy oil and asphalt; enrichments of uranium are often associated with such rocks. Asphalt-bearing rocks in the western United States were examined as potential uranium sources by Hail et al. (1956). Samples of heavy oil ash recovered from sandstones in seven of the 45 regions examined contain significant uranium concentrations, averaging 0.028 to 0.376 percent (Hail et al., 1956). The average uranium content of heavy oil ash from 13

other regions not studied in as much detail was 0.020 to 0.068 percent (Hail et al., 1956). In the latter report, samples of tar sandstones from Vernon County, Missouri represent one of the seven uranium-enriched regions of asphaltic rock; the uranium content of the heavy oil ash is 0.011 to 0.40 percent. The samples were from a sandstone correlated with the Bartlesville Sandstone in Oklahoma; thus, they were probably collected from the Warner and/or Bluejacket Formations.

In addition to the potential radionuclide enrichments of Pennsylvanian rocks discussed above, torbernite has been reported from a sinkhole filled with Pennsylvanian fire clay (Keller, 1952;

TABLE 2
Uranium and thorium content of various Missouri Pennsylvanian-age rock units

A. Fluorometric determinations by Hyden and Danilchik, 1962

Unit	Lithology	Uranium (ppm) min.	Uranium (ppm) max.	Uranium (ppm) av.	Number of samples
Riverton Formation	black shale	11	11	11	1
Bluejacket Formation	sandstone with coal laminae	9	9	9	1
Bluejacket Formation	black shale	11	11	11	1
Drywood Formation	black shale	13	13	13	1
Scammon Formation	fossil hash	20	20	20	1
Verdigris Formation	limestone (Ardmore Ls. Mbr.)	27	35	31	2
Verdigris Formation	black platy shale	18	18	18	1
Verdigris Formation	black phosphatic shale	160	160	160	1
Verdigris Formation	phosphatic nodules	30	30	30	1
Excello Formation	dark-gray shale	30	30	30	1
Excello Formation	black phosphatic shale	24	28	26	2
Excello Formation	phosphatic nodules	100	180	132.5	4
Excello Formation	shale	20	20	20	1
Labette Formation	black claystone	8	8	8	1
Labette Formation	gray shale	11	11	11	1
Labette Formation	coal	28	28	28	1
Little Osage Formation	gray shale	15	15	15	1
Little Osage Formation	black phosphatic shale	29	60	43.4	5
Little Osage Formation	phosphatic nodules	40	170	125	4

B. Delayed neutron activation determinations by Wedge et al., 1976 and Wedge and Hatch, 1980

Coal seam	Uranium (ppm) min.	Uranium (ppm) max.	Uranium (ppm) av.	Thorium (ppm) min.	Thorium (ppm) max.	Thorium (ppm) av.	Number of samples
Rowe	2.2	11.8	7				2
Drywood	1.2	1.3	1.25				2
Weir-Pittsburg	0.6	0.6	0.6	2.3	2.3	2.3	1
Tebo	2.0	2.2	2.1	5.0	6.5	5.75	2
Fleming (?)	3.4	9.2	6.3	5.0	8.0	6.5	2
Fleming	2.2	3.3	2.75				2
Croweburg	0.2	0.9	0.55				4
Croweburg				1.8	1.9	1.85	2
Bevier-Wheeler	0.9	12.0	4.25				4
Bevier-Wheeler				3.6	6.9	5.33	3
Mulky	0.3	19.3	6.15	0.7	13.9	4.5	4
Lexington	1.2	5.1	2.92	5.0	9.1	7.04	5
Mulberry	1.8	3.0	2.4				2
Mulberry				79.4	79.4	79.4	1

Table 2 (cont.)

C. Delayed neutron activation determinations by Swanson, 1977 and 1978

Unit	Lithology	Uranium min.	Uranium max. (ppm)	Uranium av.	Thorium min.	Thorium max. (ppm)	Thorium av.	Number of samples
Bluejacket Formation	black shale	4.66	4.66	4.66	12.2	12.2	12.2	1
Drywood Formation	black phosphatic shale	5.09	5.09	5.09	17.2	17.2	17.2	1
Scammon Formation	black phosphatic shale	59.42	59.42	59.42	(14.61)	(14.61)	(14.61)	1
Robinson Branch Fm(?)	black phosphatic shale	4.58	4.58	4.58	15.5	15.5	15.5	1
Fleming Formation	black phosphatic shale	12.3	12.3	12.3	20.9	20.9	20.9	1
Verdigris Formation	black phosphatic shale	39.7	39.7	39.7	9.9	9.9	9.9	1
Excello Formation	black phosphatic shale	12.6	48.5	30.3	8.5	14.0	10.9	4
Little Osage Formation	brown shale	19.7	19.7	19.7	20.4	20.4	20.4	1
Little Osage Formation	black phosphatic shale	42.7	42.7	42.7	11.0	11.0	11.0	1
Labette Formation	black phosphatic shale	79.77	129.66	107.76	(10.82)	(29.76)	(20.23)	3

D. Fluorometric analyses for Nuelle, 1982

Unit	Lithology	Uranium min.	Uranium max. (ppm)	Uranium av.	Number of samples
Scammon Formation	black phosphatic shale	36	63	49.5	2
Verdigris Formation	black phosphatic shale	68	92	84.25	4
Excello Formation	brownish-gray shale	45	45	45	1
Excello Formation	dark-gray shale	161	161	161	1
Excello Formation	black phosphatic shale	44	53	48.5	2
Little Osage Formation	black phosphatic shale	69	82	75.5	2
Pawnee Formation Anna Shale Member	black shale	42	42	42	1
Pawnee Formation Anna Shale Member	black phosphatic shale	73	116	89.3	3

E. Fluorometric determinations of uranium in heavy oil ash in Krebs Subgroup sandstones (Hail et al., 1956)

Locality	Average amount of oil in samples (percent)	Average amount of ash in oil (percent)	Average amount of uranium in ash (percent)	Number of samples
Deerfield	4.63	0.79	0.006	7
Ellis	4.64	0.62	0.145	3
Sheldon East	3.99	1.46	0.016	4
Sheldon North	1.43	1.27	0.004	3
Dry Wood Creek	2.30	1.58	0.004	16

Muilenburg, 1957). Black carbonaceous radioactive substances have also been reported from other Pennsylvanian clays (Muilenburg, 1957). These occurrences are of restricted distribution.

MESOZOIC AND CENOZOIC ROCKS

Mesozoic and Cenozoic rocks in the bootheel (fig. 5) may also be potential sources of enriched radionuclides. Tibbs and Unfer (1979) indicate that Cretaceous and Tertiary rocks of the Mississippi embayment in southeast Missouri may contain fluvial facies that favor entrapment of uranium mobilized from Precambrian igneous rocks, but this matter has not been thoroughly investigated. Measurements of uranium and thorium in these rocks are presented in table 3, but the figures represent few analyses and cannot be considered typical of this terrane until more determinations are completed.

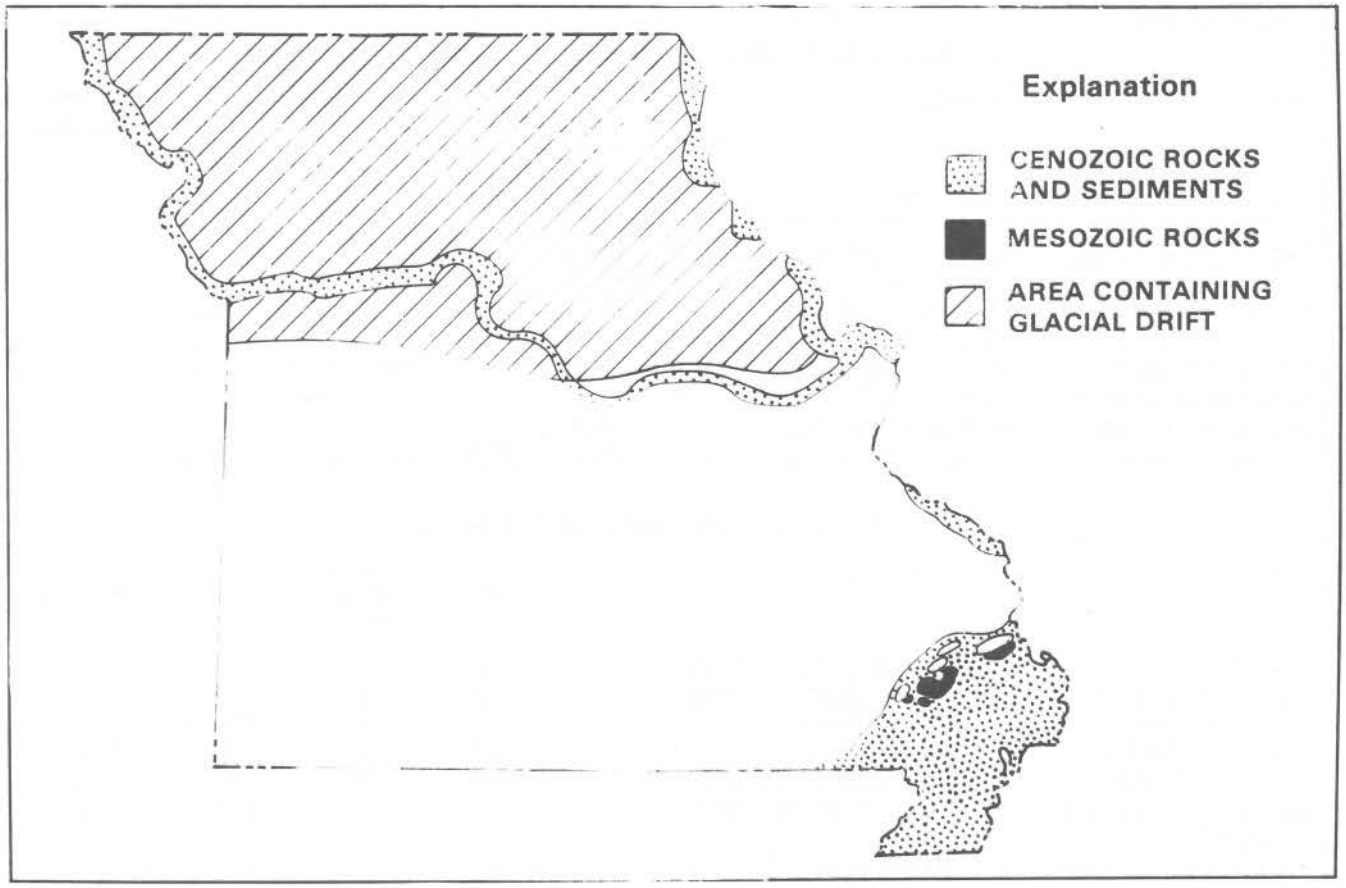


Figure 5 — Distribution of Mesozoic and Cenozoic rocks and sediments in Missouri.

QUATERNARY GLACIAL DRIFT, LOESS, AND ALLUVIAL SEDIMENTS

Although these sediments (fig. 5) have different origins, they can be included in the same geologic terrane for evaluating radionuclide content. These sediments, which result from mechanical erosion of pre-existing rocks, have been transported and mixed with sediments from other geologic terranes; thus, in sediments of this type, radionuclides tend to be dispersed, rather than concentrated in enriched zones. Exceptions may be recent peat bogs, some of which have been excavated for mastodon remains, which could contain organic traps favorable for uranium deposition.

TABLE 3
Uranium and thorium content of various Mesozoic and Cenozoic rock units in Missouri, determined by delayed neutron activation analyses (Hatch, 1978)

Unit	Lithology	Uranium (ppm)	Thorium (ppm)
McNairy	intercalated sandstone and claystone	1.42	7.45
McNairy Formation	intercalated sandstone and clay	1.30	6.60
Owl Creek Formation	sandy, fissile claystone	3.89	15.5
Owl Creek Formation	sandy, micaceous clay	3.48	18.0
Clayton Formation	sandy clay	2.65	21.5

OTHER GEOLOGIC INFLUENCES ON RADIONUCLIDE DISTRIBUTION

THICKNESS OF SURFICIAL MATERIALS

When rocks containing radionuclides are weathered, the radiogenic elements generally are liberated and transported away from the host rock. Thus, bedrock residuum is generally less radioactive than the solid bedrock. The thicker the residuum, or other surficial materials, the less radiation from the bedrock is detectable at the surface. Generally, about 1 m of cover is enough to block gamma-ray radiation from reaching the surface. Figure 6 shows the thickness of surficial materials in Missouri.

GEOLOGIC STRUCTURE

Geologic structures (fig. 7) can influence radiogenic enrichments in much the same way structures tend to mobilize and concentrate other metals in the formation of ore deposits. Fault systems that transect potential radionuclide hosts such as black shale terranes or igneous rock terranes may form groundwater plumbing systems capable of dissolving radioactive elements and transporting them to favorable deposition sites, where there may be significant enrichments in radiogenic minerals.

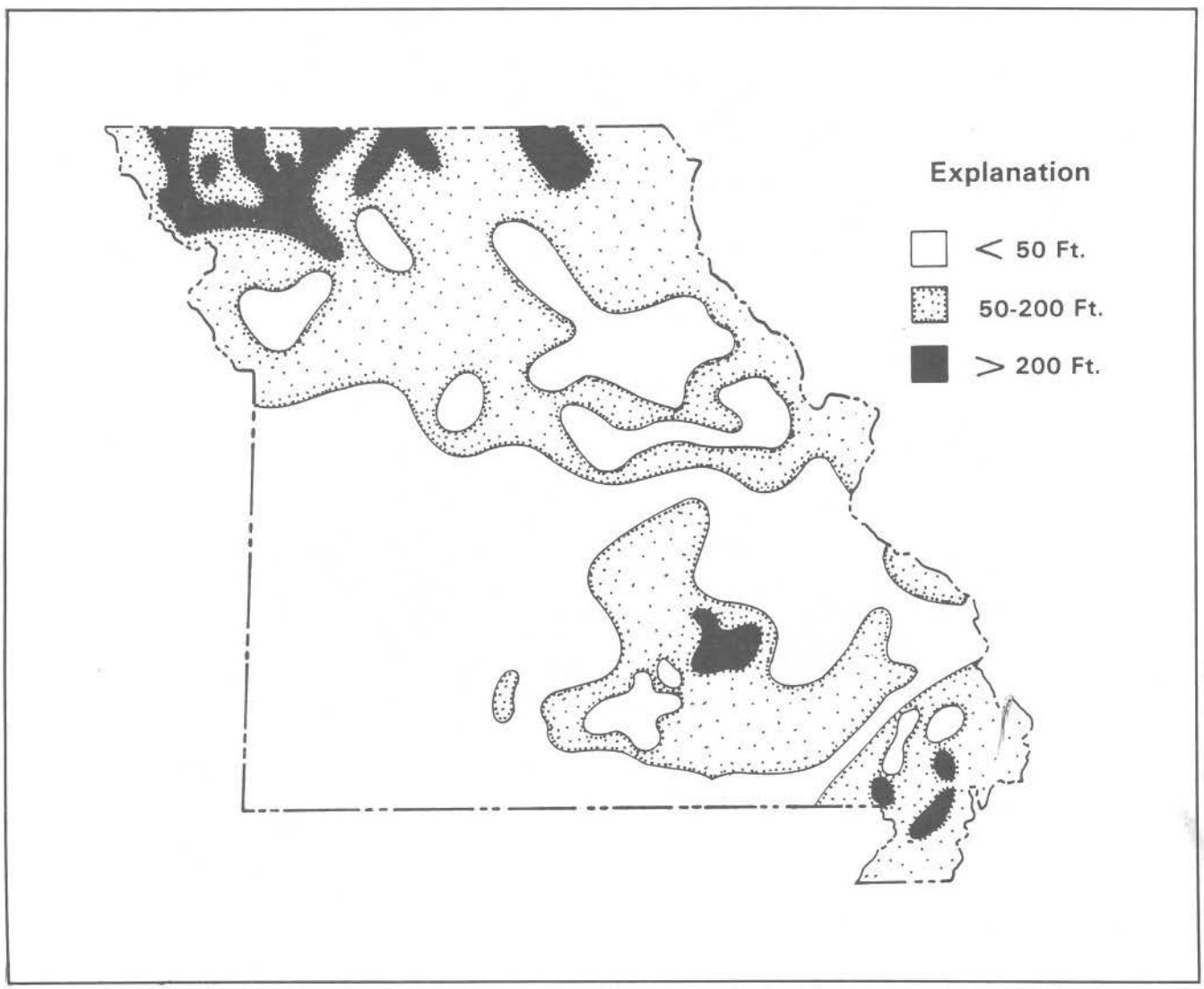


Figure 6 — Thickness of surficial materials in Missouri.

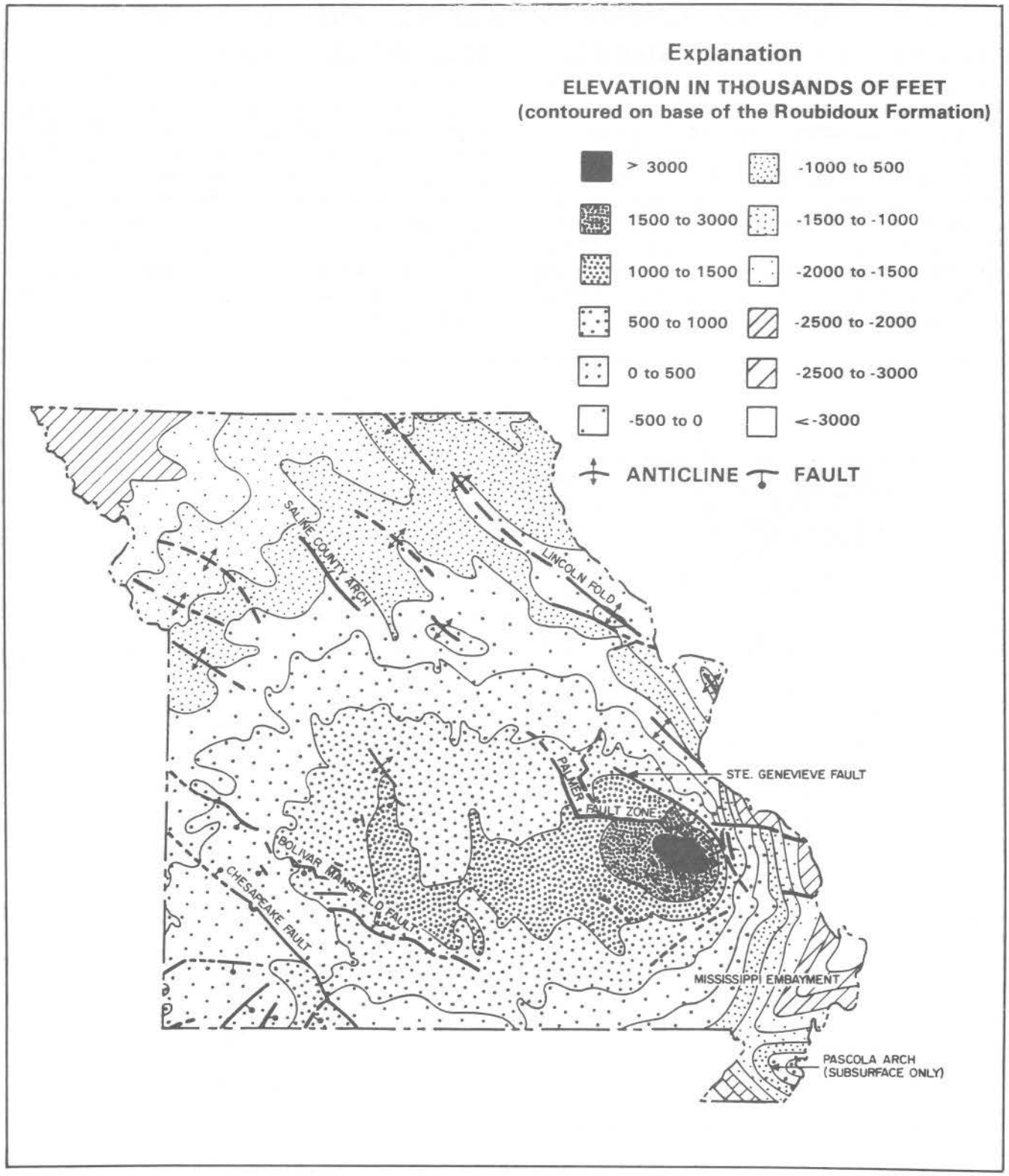


Figure 7 — Structural features map of Missouri (modified from McCracken, 1966).

RADON DISTRIBUTION

RADON IN SOILS

Radon can more easily reach the surface from depth than gamma-ray radiation. Soils derived from radiogenic-enriched rocks tend to emit radon as the radiogenic constituents decay. Radon is likely to be more of a health hazard in basements and earth-sheltered homes than in structures above the ground. For instance, in northwestern Missouri some homes in black shale terranes are earth sheltered. These homes may tend to have abnormally high radon concentrations because of the earth shelters and "tightness" from windows and insulation. Homes on the surface, however, tend to be spared radon buildups, because the gas is diffused into the atmosphere.

Another means of concentrating radon is through "plumbing systems" created by geologic structures. Some speculate that radon tends to migrate upward from depth along fault or fracture planes. If so, such regions include the Chesapeake fault system and the numerous faults in the bootheel. However, these radon sources probably present no health risks, because the gas is well diffused into the atmosphere once it reaches the surface. Some legitimate concern may arise, however, should basements and buildings be earth sheltered in fault and fracture zones.

RADON IN WATER SUPPLIES

Perhaps the largest concern with respect to radon in the environment is the amount in public water supplies. The more mineralized the groundwater, the more radon it is likely to contain, because dissolved salts in the water are readily available to form radiogenic complexes as the water passes through geologic terranes enriched in radionuclides. In Missouri, this is of particular concern in the northern and western portions of the state, where groundwater is particularly high in dissolved minerals. Some public water supply wells in these regions have radon levels above those permitted by the Environmental Protection Agency.

THE NEED FOR MORE DATA

From the above discussions it should be evident that no single geologic terrane in Missouri has been adequately evaluated for radionuclide content and distribution. A good start has been made by the U.S. Department of Energy's (DOE) National Uranium Resource Evaluation (NURE) program, for which DOE contracted for aerial radiometric surveys, data from which are available on 1° by 2° quadrangles from the U.S. Geological Survey. Because of the space between measurements and the altitudes at which surveys are flown, this data could be enhanced by supplementing it with ground radiometric surveys. Ground surveys could identify anomalies of limited distribution that may have been missed in airborne surveys. In some cases, ground surveys may even identify radiation sources more readily. A combination of ground surveys and NURE airborne surveys would provide excellent data for background radiation maps.

Background data are needed, because some geologic terranes pose potential health hazards from natural radionuclide concentrations. The Precambrian and Pennsylvanian rock terranes are those of most concern. Data indicate that certain rock units in them consistently register enriched concentrations of radionuclides. Of even greater concern is radon in public water supplies, because of the many people that depend on any one water supply. Some concern should also be shown for construction, particularly basements and earth-sheltered structures, in areas of high radon concentrations in soils.

In addition to background data for determining the amount of radiation in the existing environment, data are needed to evaluate effects of accidental spills of radioactive substances. For example, the spill of a low-level radioactive material where Graniteville Granite or Pennsylvanian black shales are the underlying bedrock may be more serious than a spill elsewhere. These two rock types are already enriched in radionuclides and the addition of low-level radioactive materials may increase the total radioactivity to levels above recommended health levels. A spill on Paleozoic carbonates may be less detrimental, because the bedrock essentially lacks naturally

occurring radionuclides. It may therefore be desirable to direct transportation routes of radioactive materials around regions containing abnormally high background radiation.

If a good data base exists for background radiation, radioactivity introduced after an accident can be quantified by subtraction of the background values. Such a technique was used in Germany, where background radiation maps were made before the Chernobyl accident. Background values were subtracted from the radioactivity measured following the accident. The true effects of the nuclear power plant disaster on the environment were thereby quantified.

Part of a good background data base would be radionuclide content of groundwater from various aquifers and public wells. Although not much can be done to change the natural concentrations of radionuclides in water supplies, monitoring wells can detect radionuclides introduced by cultural activities. For example, it would be possible to detect increased radionuclides in groundwater in an oil field after underground steam or chemical injection was used for enhanced recovery.

SUMMARY

The two geologic terranes most likely to pose at least minimal health hazards due to radionuclide content are those of Precambrian rocks and of Pennsylvanian rocks. Data for all the geologic terranes are sparse, but what little data there are indicate these terranes may be of some concern. Existing data, however, are much too sparse to evaluate these two terranes for radionuclide health hazards.

I suggest, that if we are truly concerned about the natural distribution of radionuclides and the effects of cultural introduction of radionuclides into the environment, it is time to compile an effective radiometric data base in an easy-to-use format that would be available to the public.

There are many ways to assemble such a data base. A standard format, adopted by each state would best serve the public interest. For example, one way of presenting background radiation concentrations would be a series of 1:100,000-scale maps covering the entire state. Considering the affordability of discriminating portable gamma-ray spectrometers, it would be relatively inexpensive to produce maps showing total count, and uranium, thorium, and potassium concentrations in either counts per second or as parts per million. Data could be collected by ground traverses and integrated with NURE airborne radiometric surveys. Formulation of the data could be calculated to give background radiation at 1 m above ground level. Surface geology could be shown on the base maps. For example, the Missouri Department of Natural Resources is trying to compile 1:100,000 geologic map coverage of the state. Background radiation maps (at 1 m above ground level) could be overlaid on geologic maps and the maps then combined into a single unit. Such maps would be easy to read for the public, including geologists, contractors, mining companies, environmental groups, and local, state, and national governmental agencies.

In a similar manner, background maps showing radionuclide content of groundwater could be constructed and combined with geologic maps and surface radiation maps. Such a combination of maps has been successfully used in formulating models for uranium exploration by various mining companies. Likewise, the combination of these maps could be used by health scientists for determining sources of radionuclides and for tracking migration routes of radionuclides in groundwater.

Such information should be compiled and made available as soon as possible, so that planning and the determination of acceptable radiation levels can be based on sound scientific data.

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CORRELATION BETWEEN GEOLOGY, RADON IN SOIL GAS, AND INDOOR RADON IN THE READING PRONG

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ABSTRACT

Detailed field studies of the Proterozoic metasedimentary rocks of Boyertown and Easton, Pennsylvania reveal a relationship between geology, radon (Rn) in soil gas, and the potential for indoor radon accumulation. Fault zones and lithologies with high concentrations of uranium (U) typically have high levels of radon associated with them. In contrast, lithologies with low uranium are not associated with high radon, even where soil permeability is high. The Environmental Protection Agency has established .02 Working Levels (W.L.), which is approximately equal to 4 picocuries per liter (pCi/L), as the maximum advisable level of indoor radon.

The Boyertown study area is underlain by hornblende gneiss and graphitic quartzite, which are low in uranium, and an interlayered quartz-feldspar and biotite gneiss (QFB), which is high in uranium. Correspondingly, houses and soils over the hornblende gneiss and graphitic quartzite have low radon ($\leq$.02 W.L. and $\leq$1000 pCi/L respectively), whereas homes and soils over the QFB generally have moderate radon (> .02 to 1 W.L. and <1000 to 2000 pCi/L). Where the QFB has been mylonitized by severe shearing of the rock, the radon in houses and soils is high (> 1 W.L. and > 2000 pCi/L).

The rock sequence in the Easton study area consists of biotite gneiss, quartz-feldspar gneiss, sillimanite gneiss, pyroxene gneiss, and marble. As in Boyertown, quartz-feldspar gneiss and some biotite gneiss underlie houses and soil with moderate to high radon. Fault zones and local occurrences of exotic uranium-bearing minerals, which are mostly found along lithologic contacts and in local intrusions in the marble, can also be correlated with high radon in soils and houses.

Physical and chemical properties of soils in both study sites are controlled by the geology. Hornblende gneiss and biotite gneiss soils have higher clay content and less permeability than soils developed on the quartz-feldspar gneisses, which are sandier and more permeable. Comparisons of uranium and radium (Ra) content in soils indicate that these two elements are in secular equilibrium. Most radon measured in soil gas correlates positively with radium measured in the horizon from which the soil gas was taken, and thereby indicates that the soils are directly producing radon and that other sources or parameters are not affecting it.

INTRODUCTION

The Reading Prong, a physiographic province in the northeastern United States, comprises three subprovinces: the Hudson Highlands in New York, the New Jersey Highlands in New Jersey, and the Reading Hills in Pennsylvania. The Proterozoic rocks underlying the Reading Prong are a sequence of volcanics and sediments metamorphosed and folded during the Grenville Orogeny (approximately 1.1 billion years ago) and syntectonically intruded by granites of different compositions. Parts of the Reading Prong were refolded and metamorphosed during the Paleozoic. Systematic faulting and jointing occurred regionally during the Proterozoic, Paleozoic, and Mesozoic Eras. (See Sims, 1958, for a thorough review of the geologic literature before 1958, and Offield, 1967; Baker and Buddington, 1970; Helenek, 1971; Dallmeyer, 1972; Grauch, 1978; Drake, 1984; and Gundersen, 1985, 1987, for more recent interpretations.)

Uranium is common in the rocks of the Reading Prong (fig. 1) and occurs in three general host rock associations: 1) magnetite-rich zones and deposits in gneiss and associated faults and fractures; 2) leucogneisses and pegmatites of igneous, volcanic, and sedimentary origin; and 3) marble (Grauch and Zarinski, 1976; Bell, 1983; Gundersen, 1984, 1985). Uranium occurs most commonly in the minerals uraninite, monazite, sphene, apatite, zircon, and allanite. The high concentrations of uranium in the Reading Prong rocks were caused by mechanisms that include primary deposition related to exhalative deposits of magnetite, igneous intrusive activity, anatexis during metamorphism, and fluid movement during deformation.

As uranium decays it produces radium, which in turn produces radon. Radon migrates into a house when a negative pressure differential exists between the house and underlying soil or bedrock. The high uranium content of the rocks, and several other contributing factors, such as permeability of soils and house architecture, may be responsible for the high levels of radon observed in houses in the Reading Prong. For this reason, several areas in the Reading Prong were selected for detailed study to examine the relationship between geology, radon in soil gas, and indoor radon. Two of these areas, Boyertown and Easton, Pennsylvania, will be discussed in this paper. In each area, soil, geologic, chemical, indoor radon, and architectural data were collected for comparison. The following sections describe the methods used and results of this study.

GEOLOGY AND RADON OF THE STUDY AREAS

BOYERTOWN

Houses with exceptionally high levels of indoor radon (Smith et al., 1987) are in Colebrookdale Township, near Boyertown, Pennsylvania. The area was remapped by the authors to produce the detailed geologic map needed for the study. The underlying rocks are a sequence of metamorphosed sediments consisting of the following mappable lithologies:

1) *Hornblende gneiss.* This rock is mostly quartz, plagioclase feldspar, and hornblende (at least 20 percent). Hornblende is always accompanied by either pyroxene or biotite, and iron sulfides are common accessories; it seldom contains more than 5 ppm uranium. Soils developed on it are silt loam to clay loam, and sandy clay loam at depth. Permeability is low.

Locally, graphitic quartzite forms thin interlayers (1 in. to 5 ft) in the hornblende gneiss, especially towards the contact with the QFB. Some quartzite (?) interlayers also occur in the QFB. The quartzite contains minor feldspar, biotite, and graphite. The areas underlain by hornblende gneiss with graphitic quartzite interbeds contain little uranium and form highly permeable silty and sandy loams.

2) *Interlayered quartz-feldspar gneiss and biotite gneiss (QFB).* These two rock types occur interlayered with each other over most of the study area. Layers are 10 to 100 ft thick. The quartz-feldspar gneiss comprises quartz, potassium feldspar, and sodium plagioclase; biotite, sphene, magnetite, allanite, monazite, and rare garnet are accessories. Undeformed quartz-feldspar gneiss forms permeable sandy loams and sands. Uranium contents of up to 25 ppm have been measured. Biotite gneiss contains quartz, sodium plagioclase, and biotite (at least 20 percent); potassium-feldspar, sphene, magnetite, and monazite are common accessories. Uranium content can be as

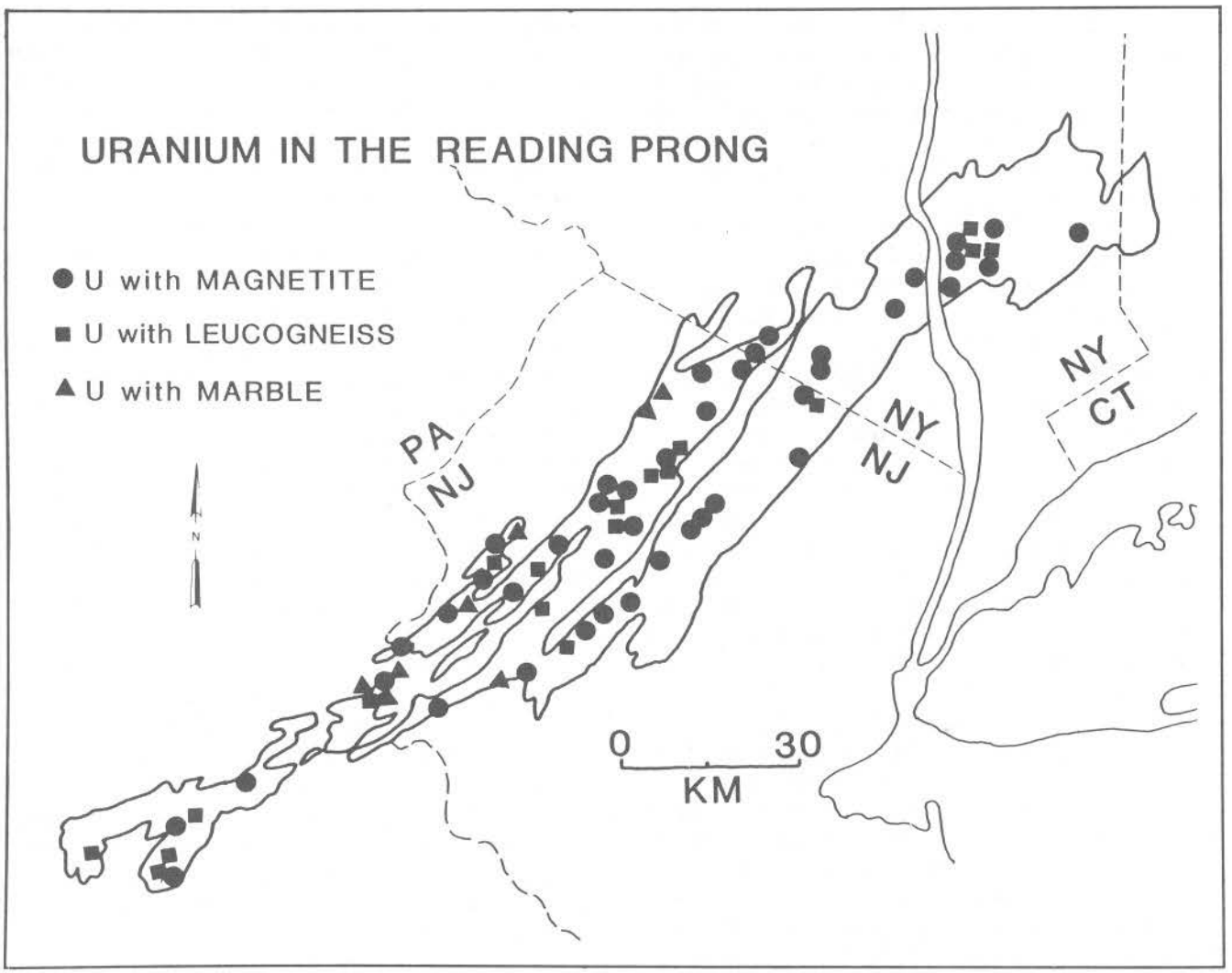


Figure 1 — Location of known uranium deposits in the Reading Prong.

high as 10 ppm. Silt and clay loams of low permeability are developed on this rock type. In both units, uranium-bearing sphene, allanite, monazite, and uraninite are sometimes concentrated in local anatexis zones.

3) *Mylonite.* Near its contact with the hornblende gneiss, part of the QFB has been mylonitized. The mylonite is mostly deformed quartz-feldspar gneiss and some minor biotite gneiss. It differs mineralogically from the undeformed QFB, because it contains abundant garnet, and there are dark, fine-grained, highly uraniferous layers throughout the rock. These layers are interpreted as a residue formed by migration of silica and sodium out of the layer during deformation. The soils developed on this rock type are sandy and highly permeable. Uranium contents as high as 50 ppm have been measured.

EASTON

Chestnut Hill in Easton, Pennsylvania, is a fault-bounded block of metamorphosed Proterozoic sediments, possibly representing an ancient reef assemblage. It is bordered on either side by the Cambrian Leithsville Formation. The geologic map used in studying this area has been slightly modified from Drake (1969). The main mappable rock types present in the area are the following:

1) *Marble.* Possibly correlative to the Franklin Marble that flanks the western edge of the Reading Prong,

this unit comprises dolomite, calcite, serpentine, tremolite, phlogopite, and talc. Uraninite and exotic uranium- and thorium-bearing minerals, such as thorianite, are concentrated where the marble has been locally intruded by albitic pegmatite. Pyroxene gneiss is interlayered with the marble along its northern contact. Soils formed over the marble are clayey and silty loams. A uranium content of 18 ppm was measured in one sample.

2) *Sillimanite gneiss.* This unit comprises quartz, potassium feldspar, sodium plagioclase, and sillimanite. Near its contact with the quartz-feldspar gneiss, it is intruded by a tourmaline-bearing pegmatite. Uranium content is low in the sillimanite gneiss, except near the tourmaline intrusions and the contact with the quartz-feldspar gneiss. The sillimanite gneiss weathers to a permeable sandy loam.

3) *Quartz-feldspar gneiss.* Potassium feldspar, quartz, biotite, and magnetite are the major constituents of this unit. Uraninite occurs in quartz-filled shears up to 2 ft long in a discontinuous zone subparallel to strike; it also occurs with uranium-bearing sphene, monazite, and zircon as accessories. This unit has uranium contents as high as 60 ppm and forms very permeable sandy soils. In the eastern part of the area, biotite gneiss forms a mappable layer in the quartz-feldspar gneiss. It comprises quartz, potassium feldspar, sodium plagioclase, biotite, and sometimes, significant amounts of magnetite. Local anatexis has produced coarse-grained quartz-feldspar knots with abundant uranium-bearing sphene and monazite similar to those observed in Boyertown. The biotite gneiss weathers more deeply than the quartz-feldspar gneiss, forms a clayey loam, and has little uranium, except in areas of local anatexis.

RADON MEASUREMENTS

In the Boyertown area, 170 soil-gas samples were measured with a calibrated alpha scintillometer modified to accept a 100-cm^3 Lucas cell and a controlled volume inlet (Reimer, 1977). Samples of 10 cm^3 were collected in plastic hypodermic syringes through an 8-mm-diameter hollow steel probe driven 0.75 m into the soil. Because the collection technique minimizes soil disturbance, a sample can be collected on placing the probe without waiting for soil-gas equilibrium to be re-established. Detailed sampling of specific home sites was on approximately 10-m centers, whereas reconnaissance sampling along the roads was on 50-m and 100-m centers. Indoor radon activities were determined by the passive alpha-track technique and are proprietary information.

Soil-gas radon and indoor radon activities plotted on the geologic maps of the Boyertown and Easton areas show a striking correlation between radon and geology. In Boyertown (fig. 2), soil-gas radon is low to moderate over quartz-feldspar and biotite gneiss, and low over the hornblende gneiss. High radon activities, up to 14,000 pCi/L, are found only in soil over the mylonite zone. As can be seen in figure 3, only homes built over the mylonite zone have greater than 1 W.L. Moderate levels are mostly found in houses over the interlayered quartz-feldspar and biotite gneiss; the lowest levels are found over the hornblende gneiss. Lithology of the QFB is more heterogeneous than in the hornblende gneiss and mylonite; this heterogeneity is reflected in the greater variation in measured radon activities in soil and houses.

In the Easton area (fig. 4), soil-gas high radon activities (up to 22,250 pCi/L) occur in the quartz-feldspar gneiss and along its contacts with the sillimanite gneiss. In the eastern part of the study area, high radon activities are associated with uranium mineralization related to albitic intrusions in the marble. In the southern part of the study area, high radon activities are associated with silica-filled uraniferous fractures in the Leithsville. The majority of indoor radon data for Easton (fig. 5) was collected from houses over the quartz-feldspar gneiss and biotite gneiss and correlates directly with the soil-gas data. Two houses with low radon activities are reported from the sillimanite gneiss and three houses with moderate radon activities from the marble. These radon activities correlate well with the concentration of uranium in underlying rocks.

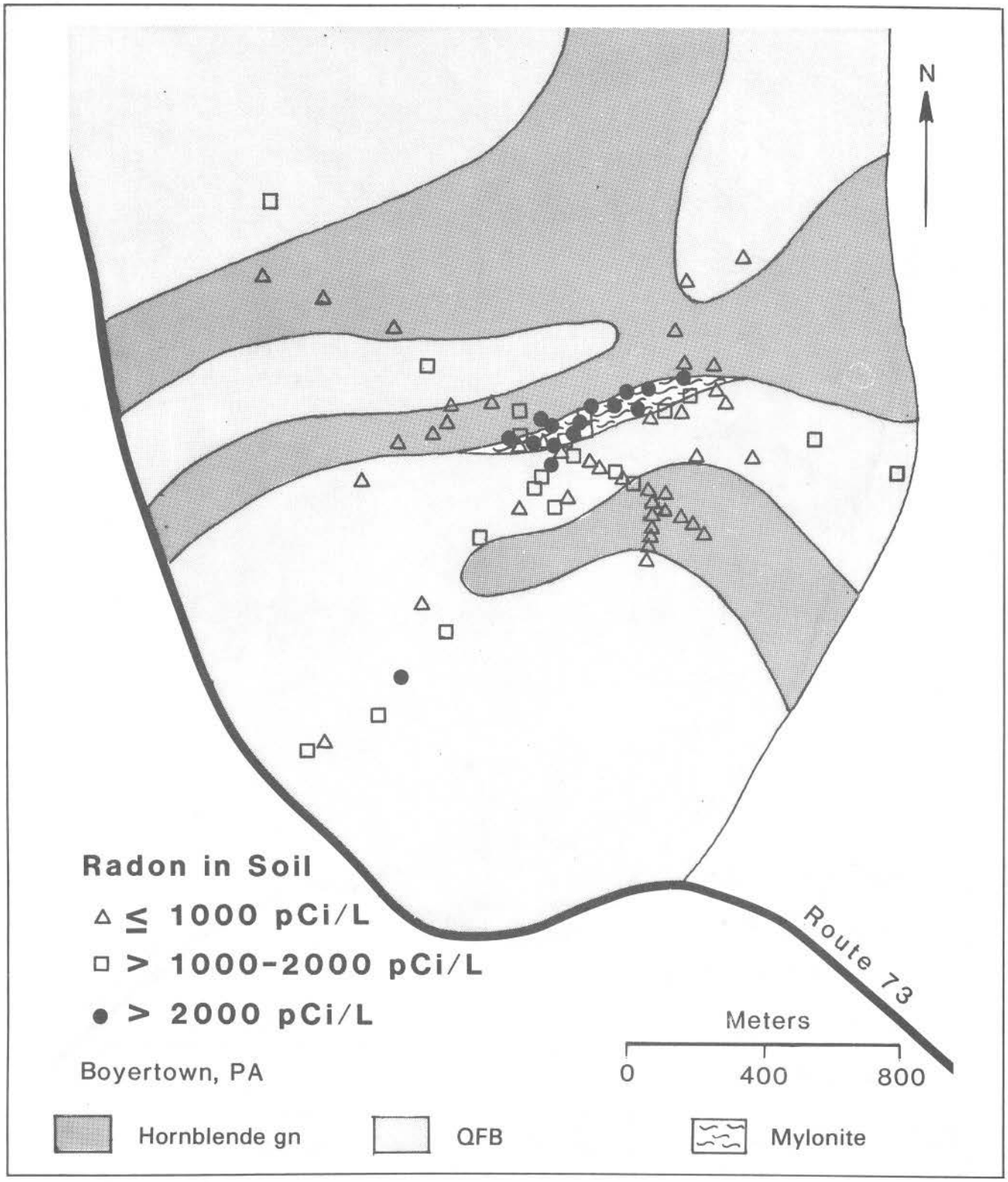


Figure 2 — Soil-gas radon activities measured in Boyertown, Pennsylvania.

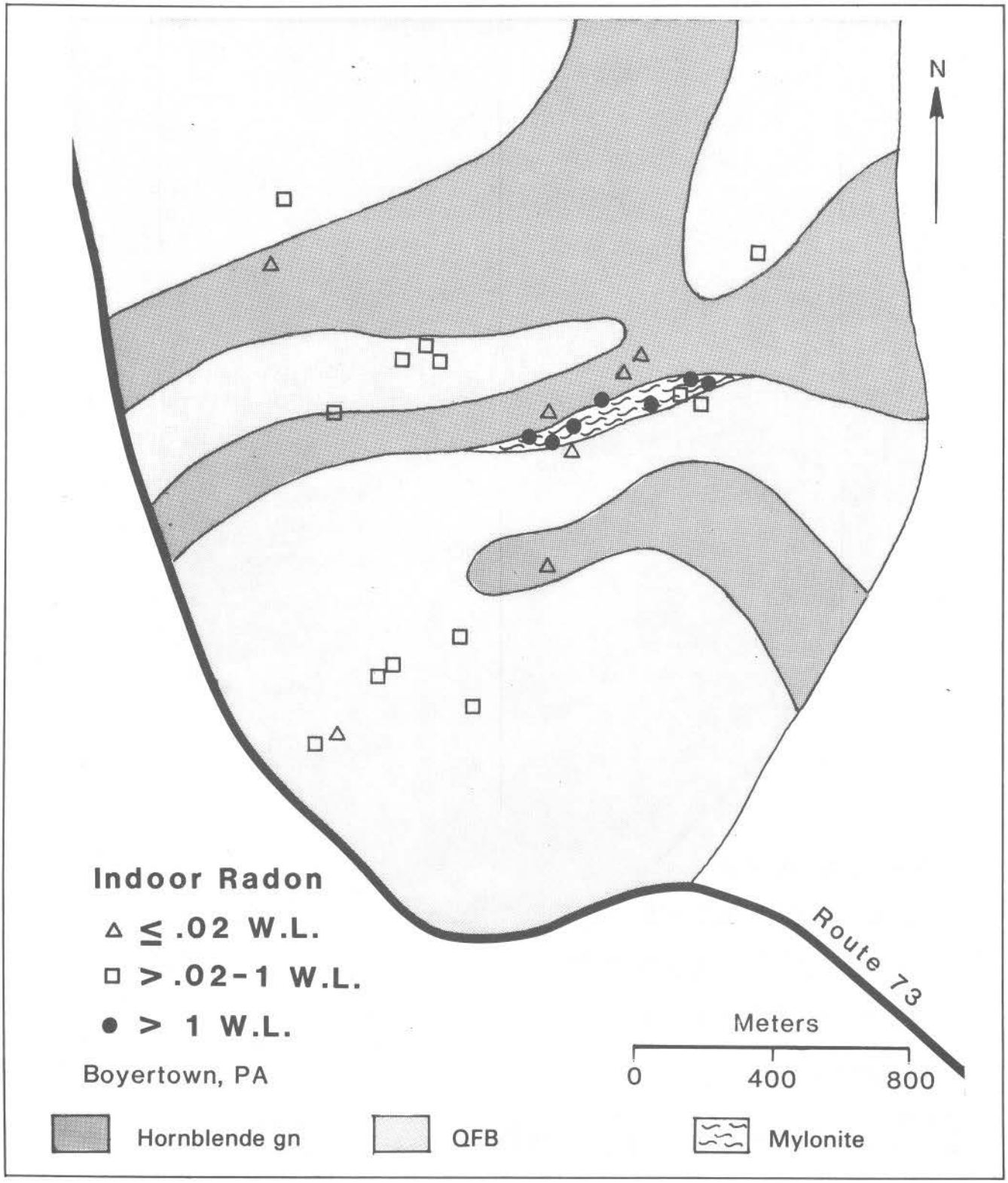


Figure 3 — Indoor radon activities in Boyertown, Pennsylvania.

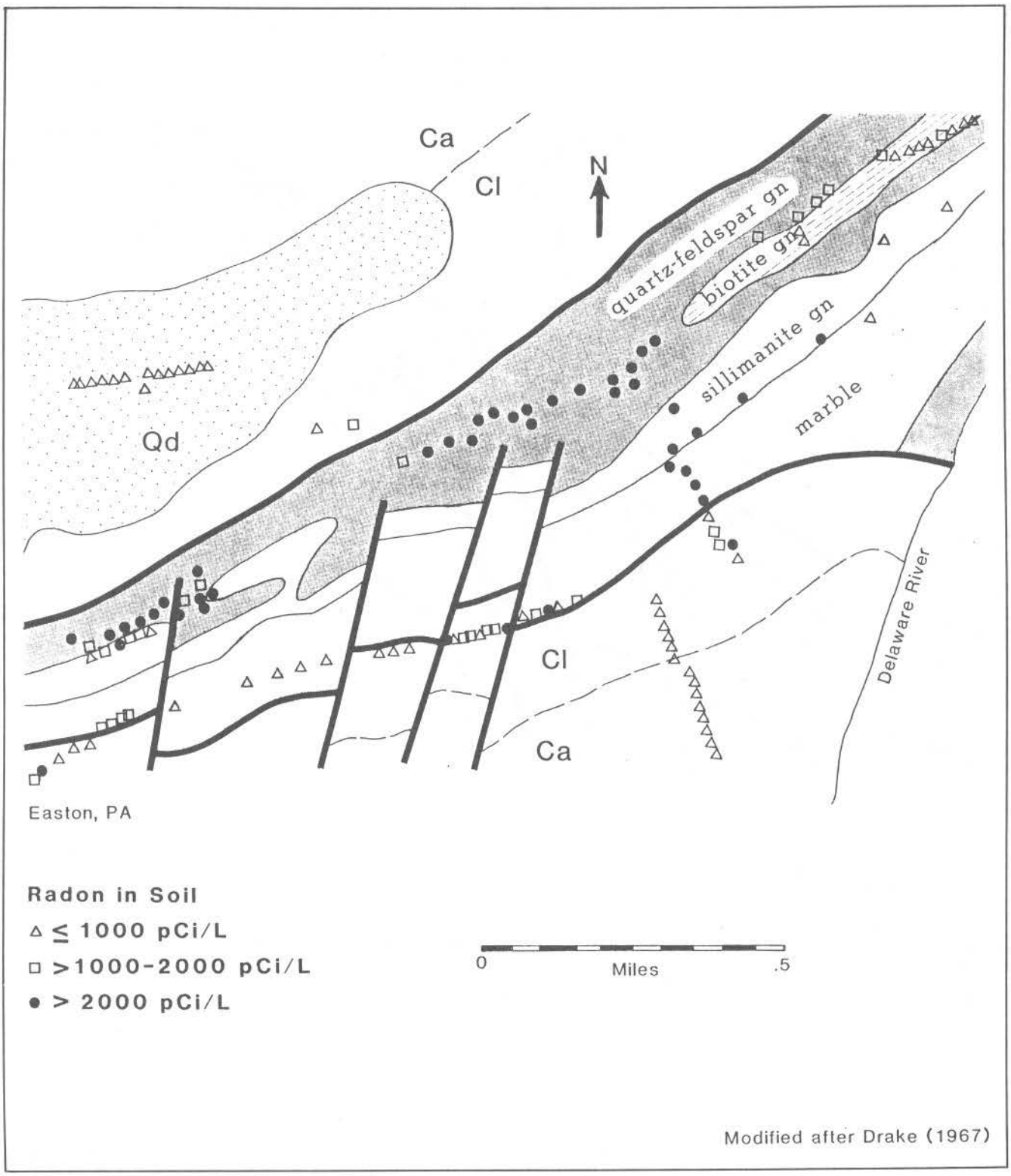


Figure 4 — Soil-gas radon activities measured in Easton, Pennsylvania. Cl is the Cambrian Leithsville Formation, Ca is the Cambrian Allenton Dolomite, and Qd is a Quaternary deposit.

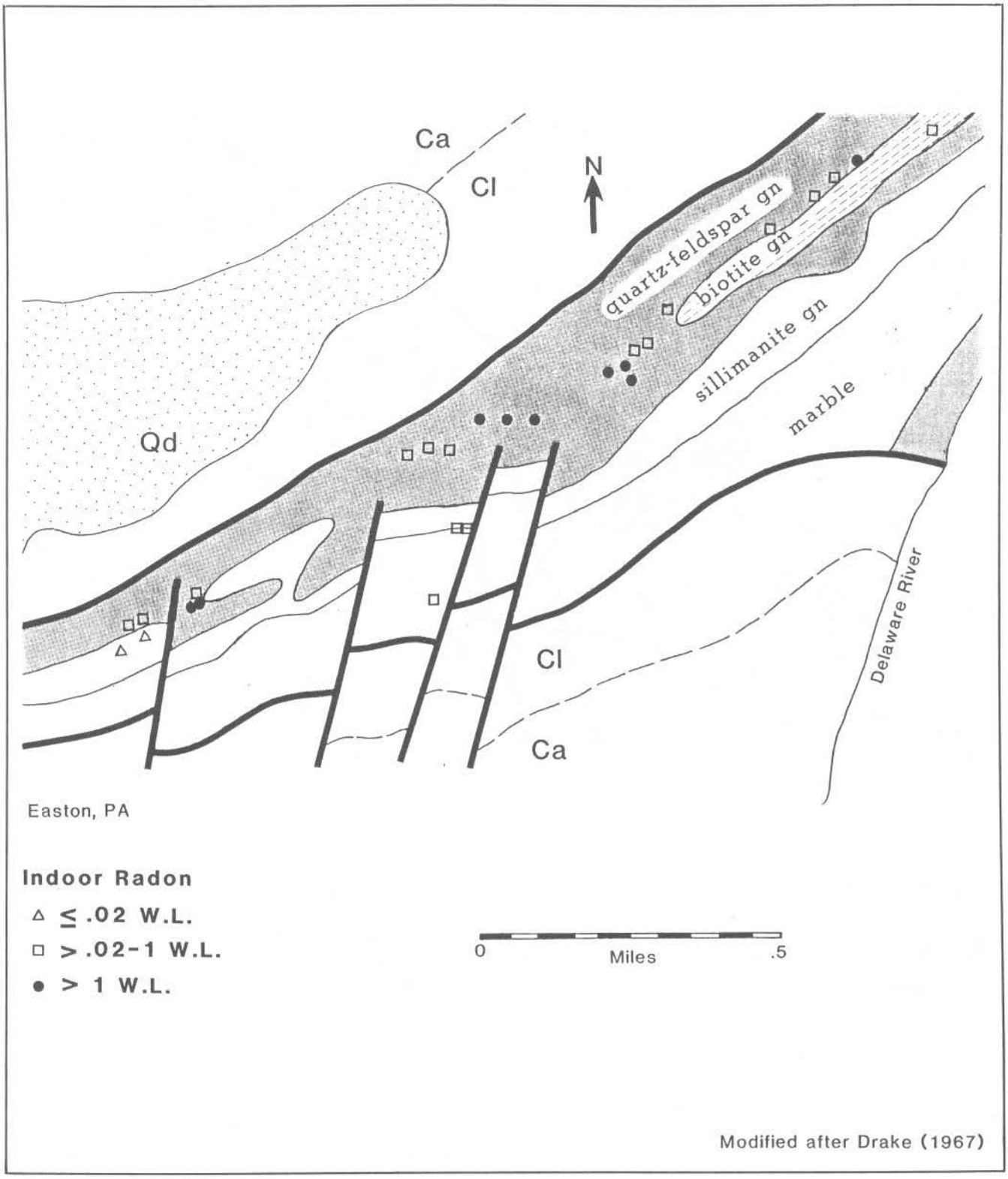


Figure 5 — Indoor radon activity in Easton, Pennsylvania. Geology is the same as in figure 4.

SOIL MORPHOLOGY AND CHEMISTRY

Soils from Boyertown and Easton have the general profiles illustrated in figure 6. Soil profiles were described from hand augers, cut banks, and hand-dug pits. Thinner soils are developed over the quartz-feldspar gneiss than over the biotite and hornblende gneisses. Tables 1 and 2 show uranium, thorium, and radium contents for several soil profiles, and the radon activity measured at a depth of 75 cm in each profile. Figures 7 and 8 show graphically the most important aspects of these data. Uranium and radium in soils from both areas (fig. 7) are near secular equilibrium; therefore, the soils have remained closed with respect to uranium and radium. Radium concentrations correlate positively with *in-situ* radon activity measurements (fig. 8), except for the highest radon activity of 22,250 pCi/L, a measurement from an area where high permeability may have contributed to the much higher reading. The samples in figure 8 that show a positive correlation reflect the fact that only the soils are producing radon and that transient radon from other sources is not a factor. Soils from Easton generally have more uranium and radium than those from Boyertown. In both areas, radium and uranium in soils may decrease or increase with depth.

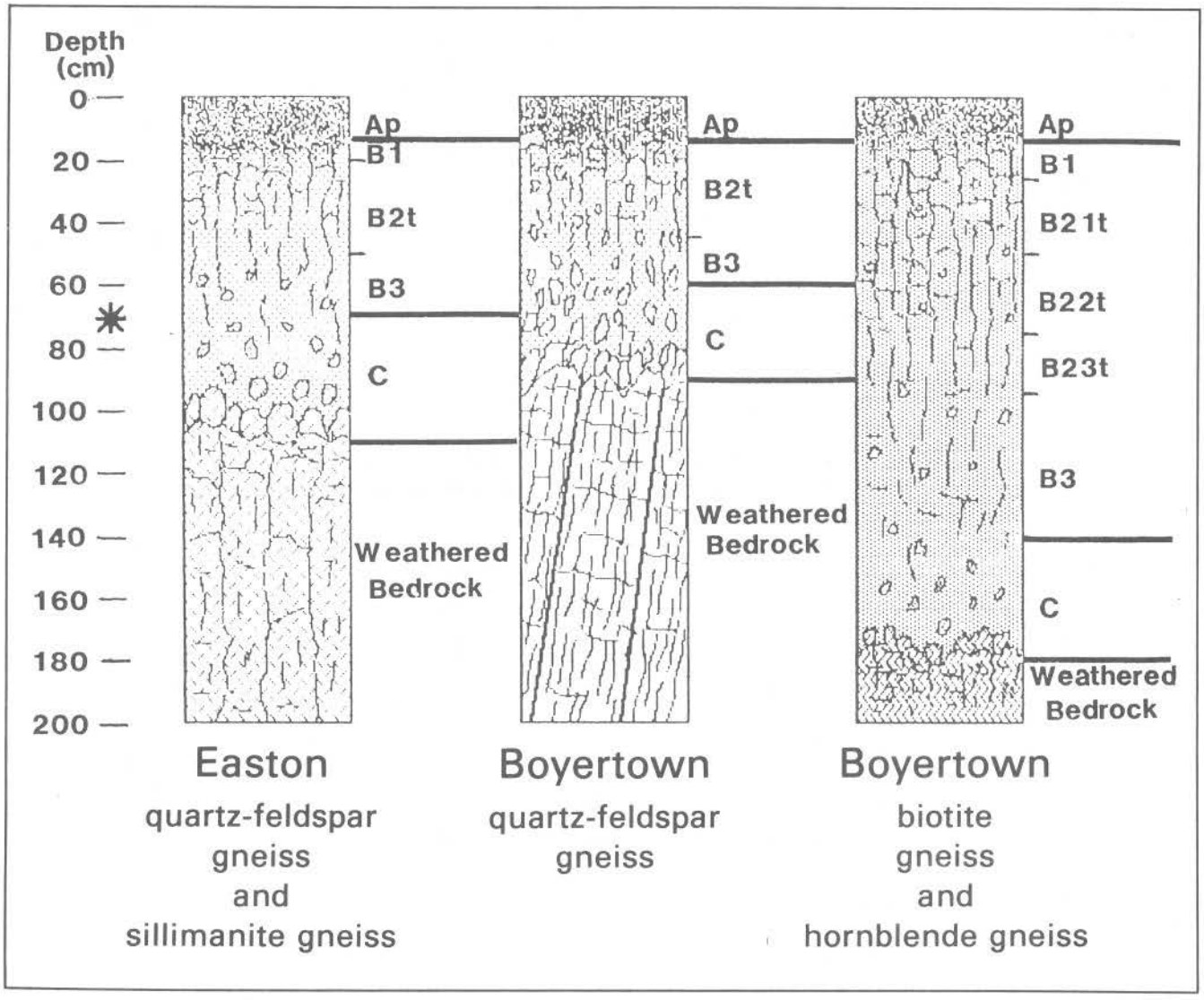


Figure 6 — Generalized soil profiles for Boyertown and Easton, Pennsylvania.

TABLE 1
Chemical uranium, radium, and in-situ radon measured in soils from Boyertown, Pennsylvanian (eU calculated from radium-226)

Sample	Rock type	U	eU	Radium-226 pCi/g	Soil-gas radon pCi/L
G-6B(A)	hornblende-	9	8	2.7	500
G-6B(B1)	biotite gneiss	9	9	3.1	
G-6B(B21t)		7	6	2.0	
G-6B(B22t)		5	3	0.9	
G-6B(B23t)		5	4	1.5	
G-6B(B3)		3	2	0.8	
G-8D(Ap)	quartz-	12	11	3.8	5,000
G-8D(Bt)	feldspar	10	10	3.4	
G-8D(C)	gneiss	16	18	6.0	
G-8D(75)		25	26	8.6	
G-9A(B1)	biotite gneiss	1	2	0.8	500
G-9A(B22t)		2	2	0.6	
G-9A(B32)		2	5	1.6	
G-9A(C)		10	9	3.1	
G-10(B)	mylonite	35	42	14.0	7,250

TABLE 2
Chemical uranium, radium, and in-situ radon measured in soil from Easton Pennsylvanian (eU calculated from radium-226)

Sample	Rock type	U	eU	Radium-226 pCi/g	Soil-gas radon pCi/L
Ch-3B(40)	quartz-feldspar	35	30	10	8,000
CH-3B(75)	gneiss	26	27	9.1	
CH-3B(180)		20	22	7.4	
CH-9A(Ap)	quartz-feldspar	44	47	16	22,750
CH-9A(B21t)	gneiss	39	35	12	
CH-9A(B22t)		40	45	15	
CH-10A(B3)	quartz-feldspar	48	52	17	11,000
CH-10A(C)	gneiss	46	54	18	
CH-10C(20)	quartz-feldspar gneiss	60	61	20	12,000
CH-11	marble	18	29	9.8	8,500

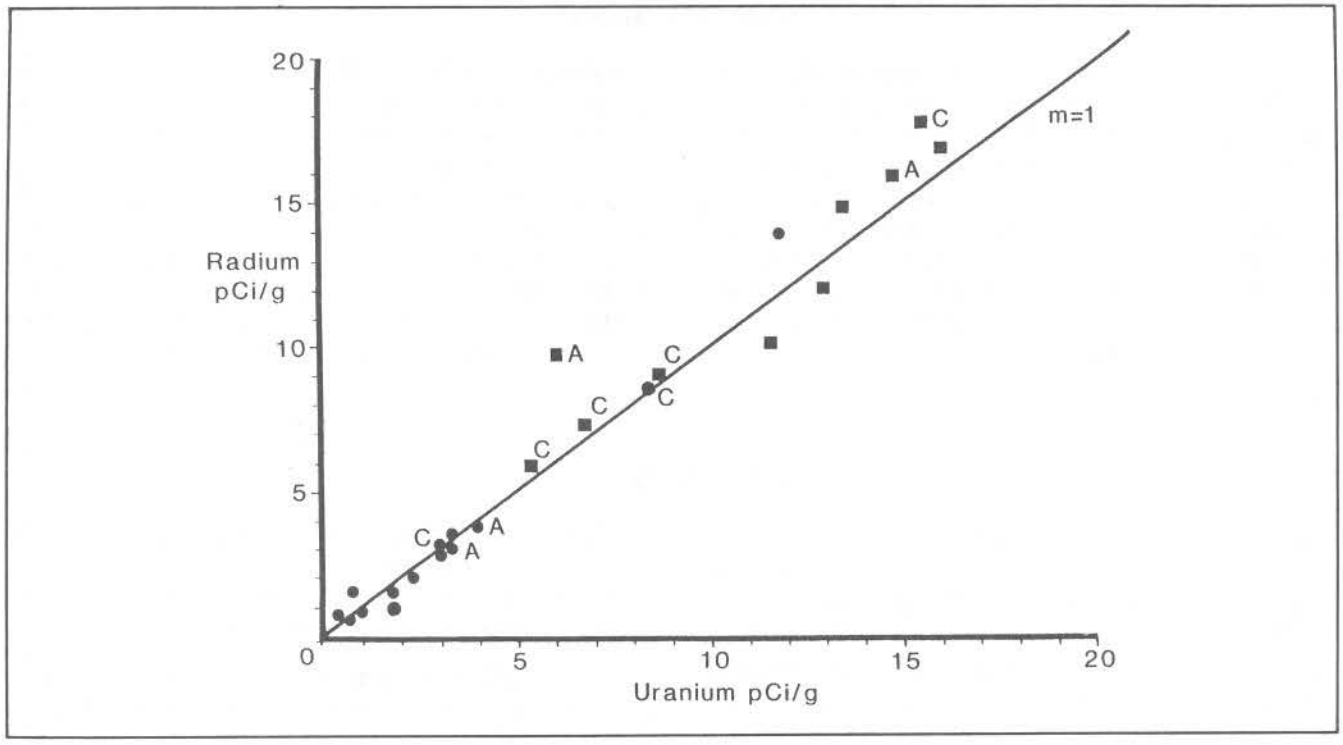


Figure 7 — Uranium activity versus radium activity (in picocuries per gram) for soil samples from Boyertown (●) and Easton (■) Pennsylvania.

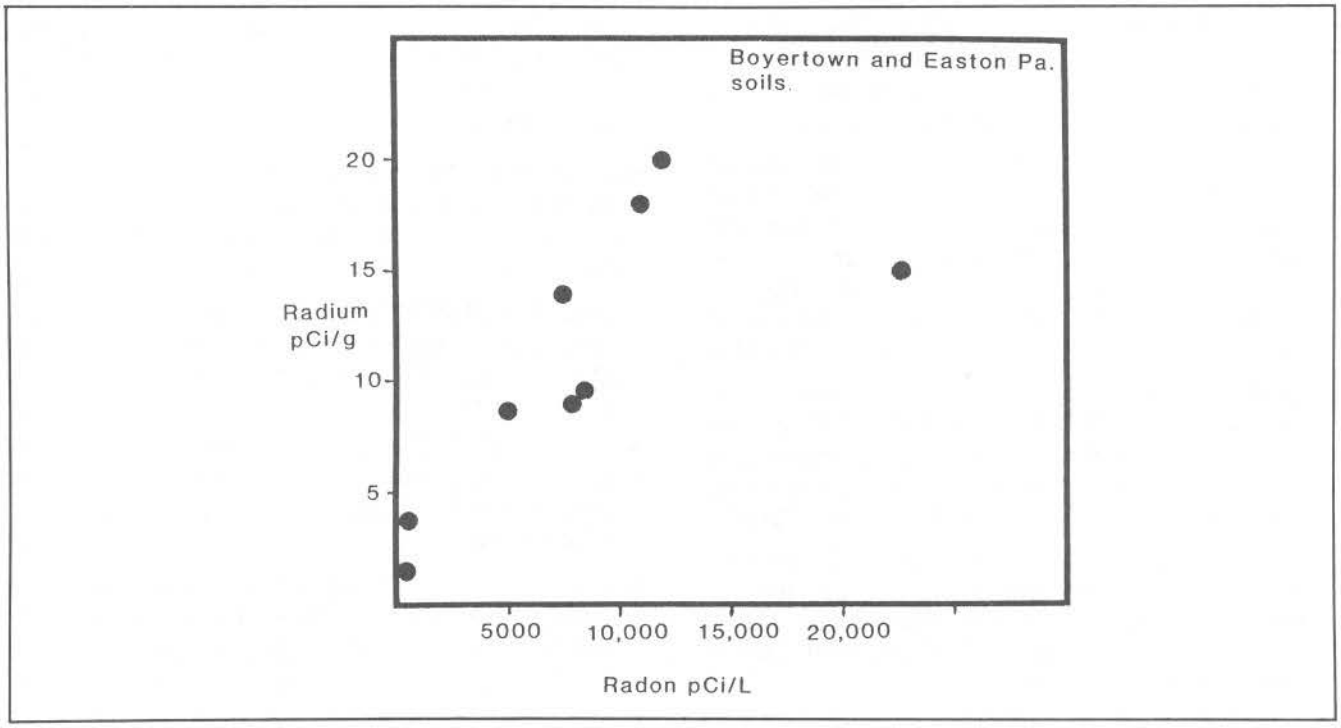


Figure 8 — Radium activity versus radon activity; both measured in the soil at 75 cm.

CONCLUSIONS

This study shows a clear correlation between geology, soil-gas radon, and indoor radon. Physical properties of the soil and the concentration of uranium, radium, and radon are controlled almost exclusively by the nature and composition of underlying bedrock. Furthermore, this control is so localized that adjacent houses may differ by orders of magnitude in their indoor radon measurements. Permeability does not appear to be as strong a control of indoor radon activity as previously thought.

Geology and soil gas can be used to predict radon availability in unglaciated saprolite terranes. Because of daily and seasonal radon variations and the heterogeneity of soil and rocks, several measurements of soil gas, accompanied by an understanding of the geology and mode of occurrence of uranium, are needed to characterize a geologic unit fully. Geology and soil-gas measurement of radon can be used together to assess developed land and be useful in future environmental planning and land development.

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ANOMALOUS MISSISSIPPI VALLEY LEADS: ANOTHER SUGGESTION

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ABSTRACT

We have developed a model to account for anomalously high values of lead-206/lead-204, lead-207/lead-204, and lead-208/lead-204 from ore deposits in Lower Paleozoic sedimentary rocks of the Mississippi Valley region. Transport of ore fluids for these deposits occurred in Cambrian and Ordovician rocks that form part of the aquifer system providing water to industries and municipalities throughout the area. One possible explanation for the anomalous lead is that a radiogenic component was contributed by decay of elements in the aquifer during ore transport. This analysis deals specifically with the systematics of uranium-238 decay through intermediate uranium-234 to produce lead-206.

A study of Illinois public drinking-water supplies that exceed the EPA water quality standards for radiation (Gilkeson et al., 1984), reveals unsupported uranium-234/uranium-238 activity ratios of approximately 40 in some water samples from the Cambrian-Ordovician aquifer system of the state. Uranium can be concentrated along aquifer surfaces in places where oxygenated uranium-bearing groundwaters encounter organic matter in the rock. Radioactive decay then produces daughter isotopes, which can be ejected or leached into the waters of the aquifer system.

Using published or reasonable estimates of flow rates, lead and uranium concentrations in solution, and system porosity, we calculate that the 25 percent anomaly observed in lead-206/lead-204 ratios of Mississippi Valley deposits could have been produced by isotopes derived from uranium-rich zones in the aquifer during or before ore tranport.

INTRODUCTION

Galenas in the Upper Mississippi Valley (UMV) base-metal district contain an anomalously high component of radiogenic lead. Attempts to date these "J-type" leads by single-stage lead-evolution models result in negative, or future, ages (fig. 1). The UMV district is further characterized by a lead isotope zonation across the district, with an increase in radiogenic lead from southwest to northeast (fig. 2).

The anomolous ores are primarily concentrated in carbonate units in the Middle Ordovician Galena and Platteville Formations, which are part of the Cambrian-Ordovician aquifer system (fig. 3). It is believed that the ore minerals were precipitated from fluids that moved through Cambrian-Ordovician aquifers, from the Illinois Basin to the south (Bethke, 1986; Cathles and Smith, 1983) and/or the Forest City Basin to the west (Heyl et al., 1974) (fig. 2).

Various models have been proposed for the generation of the isotopic patterns in the UMV district. Heyl et al. (1974) suggested a model in which brines bearing normal leads became progressively more contaminated with selectively leached radiogenic lead from the aquifers and basement rocks. Similar models have been proposed by Doe and Deleveaux (1972) for the Southeast Missouri Lead district, and by Kanasewich (1962), Heyl et al. (1966), and Doe et al. (1983) for the UMV district. Heyl et al. (1974) also suggested a reversed model, by which excessively radiogenic lead-bearing solutions migrated upward through fractures in the aquifer system in the northeast corner of the district, and spread out laterally through aquifers to the south and west, depositing more radiogenic lead near the source of upwelling and less radiogenic lead further from the source. The radiogenic lead component of the fluids would become contaminated by ordinary lead leached from the aquifers during lateral migration.

A third model, proposed by Rose (1981), suggested that naturally occurring high concentrations of radioactive radon, radium, and other uranium and thorium decay daughters, existing both as weakly adsorbed cations on grain surfaces in modern aquifers and in solution, generate sufficient radiogenic lead over 10 to 100 million years to account for the anomalous leads. We explored a variant of this model, focusing particularly on uranium, and conclude that under the proper set of conditions, at least the anomalous lead-206 values observed in the UMV can be generated by such a mechanism in 3000 to 250,000 years. This period agrees with estimates of the duration of ore deposition in the UMV, of 2000 to 250,000 years, made by McLimans et al. (1980) and Lavery and Barnes (1971).

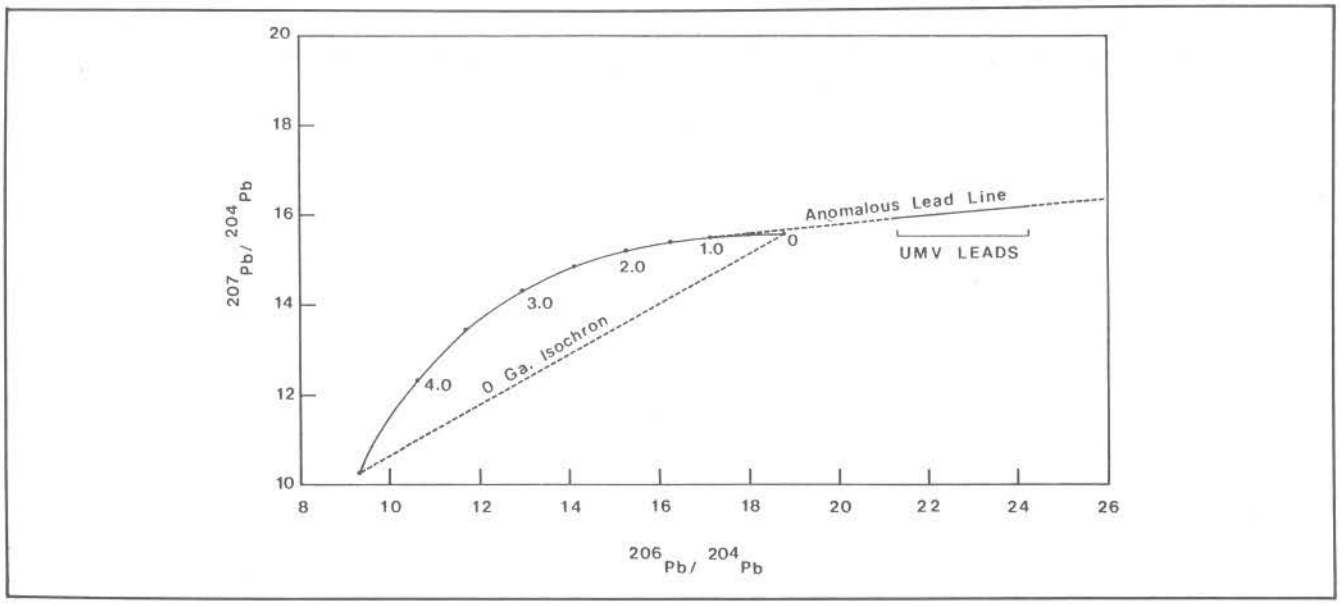


Figure 1 — Plot of lead-207/lead-204 versus lead-206/lead-204, showing range of anomalous lead values relative to a single-stage lead growth curve (modified from Faure, 1986).

THE MODERN SYSTEM

An examination of conditions in the modern aquifer is a necessary preliminary step to definition of the conditions of the model. Much work has been done on the chemical conditions in the modern Cambrian-Ordovician aquifer system in northern Illinois. As seen in figure 3, the Cambrian and Ordovician rocks of northern Illinois are divided into several hydrostratigraphic units, each of which may locally act as a single aquifer; regionally there is considerable communication with adjacent hydrostratigraphic units. The Maquoketa Shale separates the Cambrian-Ordovician aquifer system from overlying aquifer units and is an effective aquiclude.

Figure 4 illustrates the bedrock/subcrop relations in northern Illinois. Modern recharge of the Cambrian-Ordovician aquifers occurs where these rocks exist in surficial outcrops or pre-Pleistocene subcrops in north-central Illinois. Present groundwater

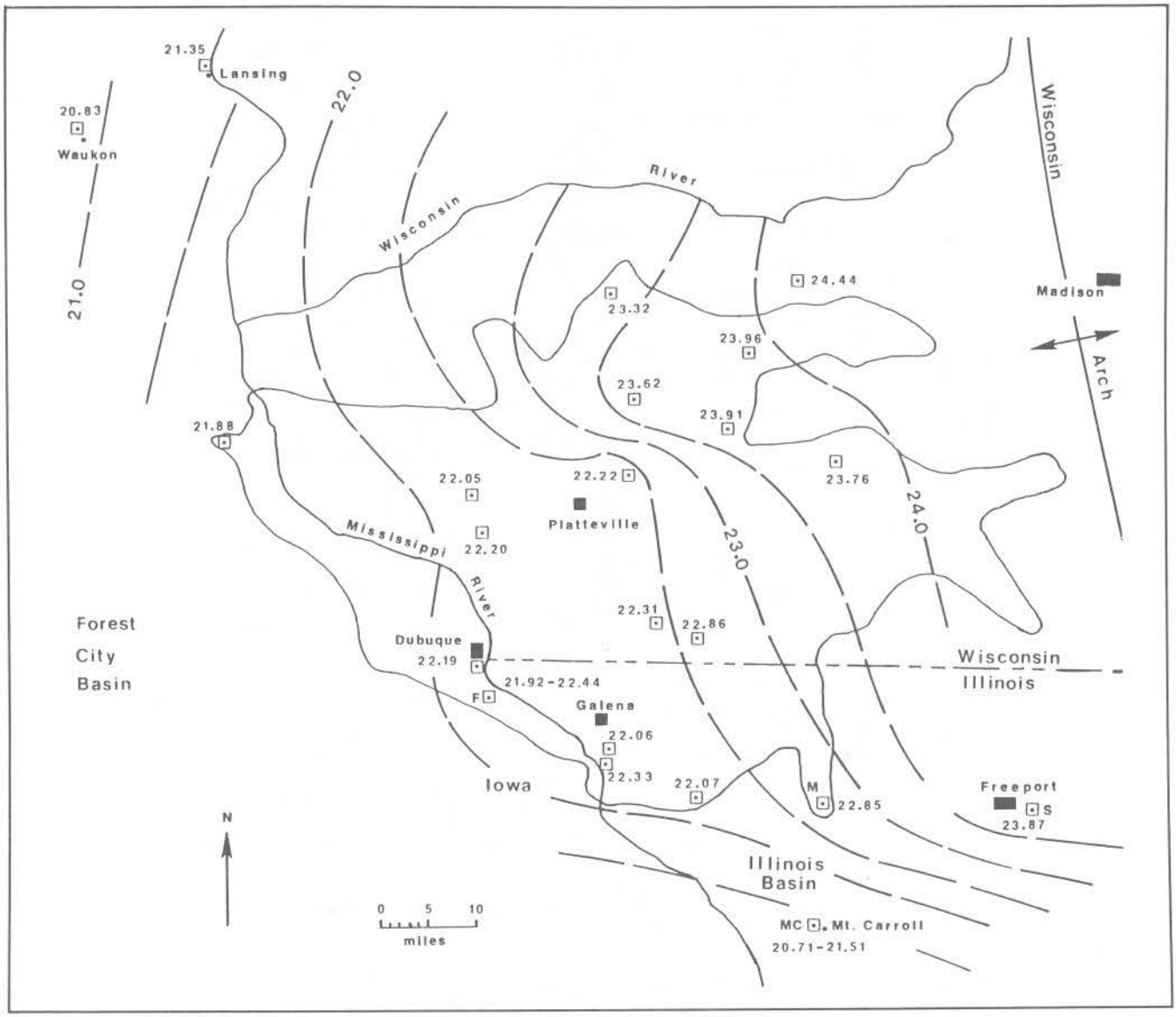


Figure 2 — Contour plot of lead-206/lead-204 values for galenas in the Upper Mississippi Valley Lead-Zinc District (modified from Heyl et al., 1966). All data points from Heyl et al. (1966) except the following taken from Millen and Ludvigson (1987): F = Fessler Mine; M = Morseville Lead diggings; MC = Mt. Carroll lead mines; S = Stebbins Mine.

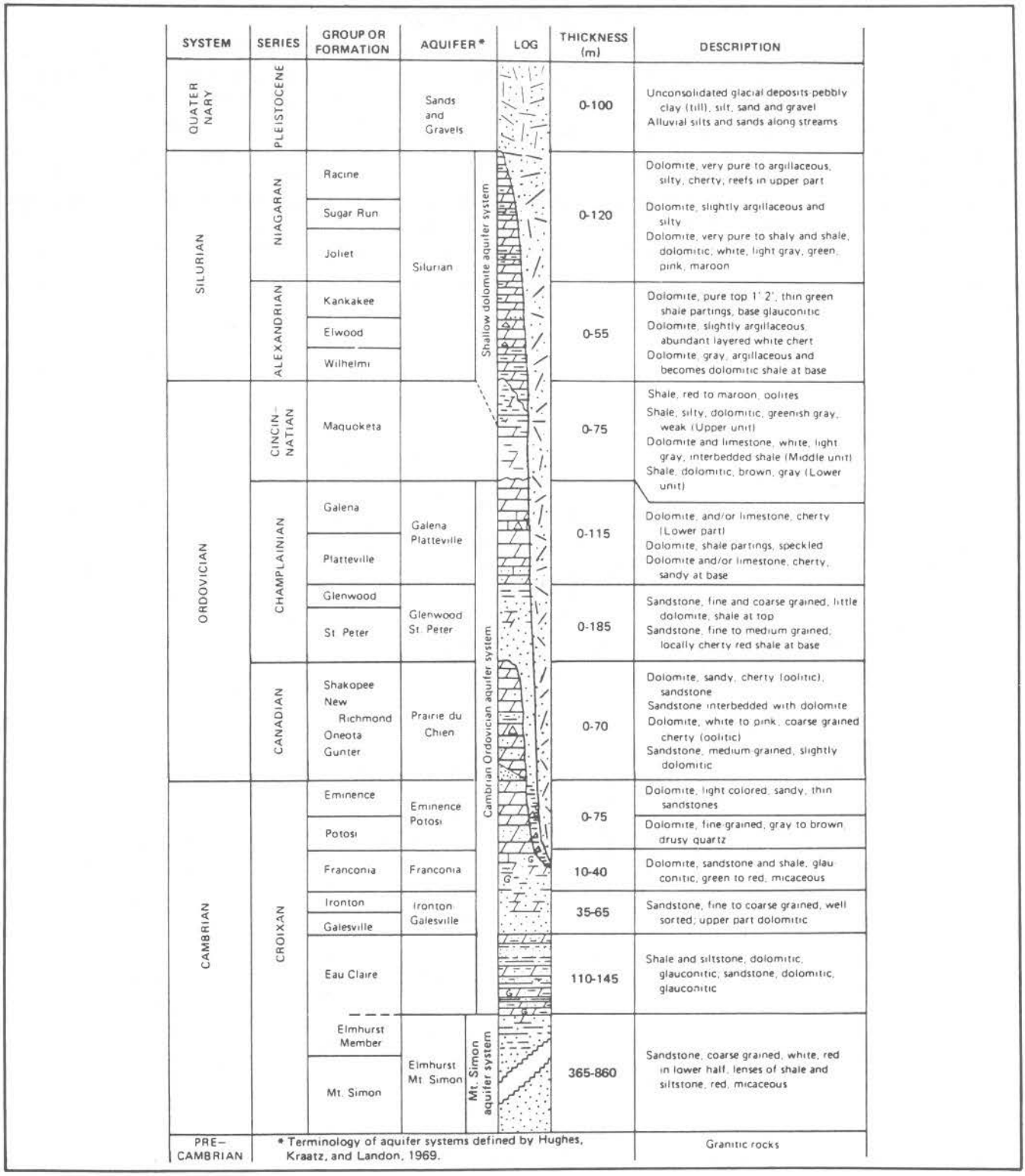


Figure 3 — Generalized geologic column for lithostratigraphic and hydrostratigraphic units in northern Illinois (from Gilkeson and Cowart, 1982).

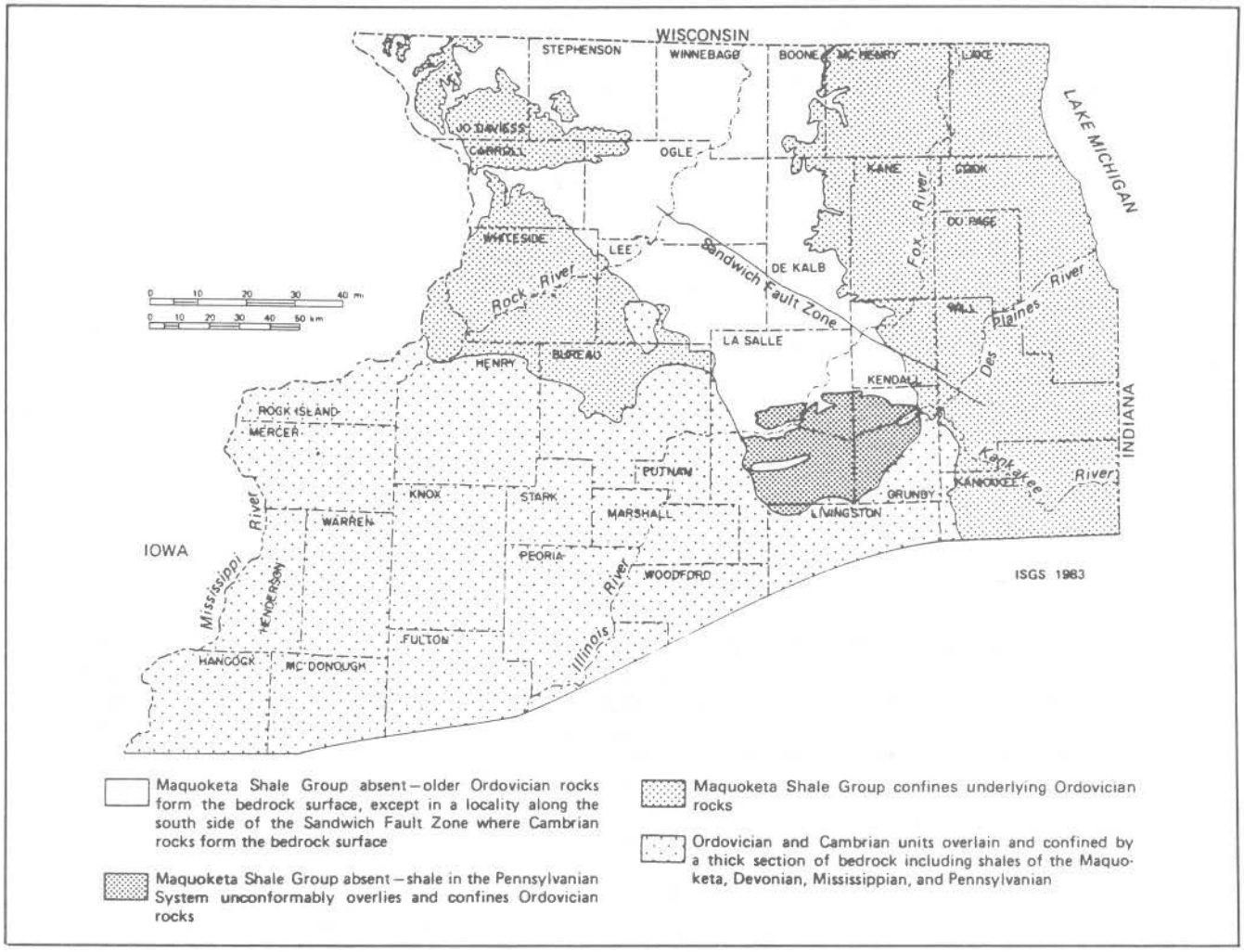


Figure 4 — Generalized geologic map of bedrock units in northern Illinois (from Gilkeson et al., 1984, after Willman et al., 1967 and Willman et al., 1975).

flow in the Cambrian-Ordovician aquifers is radially down dip (generally southward) from the recharge zone toward the confined portion of the aquifers. Gilkeson et al. (1984) and Gilkeson and Cowart (1982) have demonstrated that there are high radium activities (fig. 5) and uranium disequilibria (figs. 6-8) in the modern aquifer system in northern Illinois. Total dissolved radium in the aquifers often exceeds the EPA maximum of 5 picocuries/liter (pCi/L), a matter that causes concern to the region's population, which depends on these aquifers for domestic water supplies. The uranium-234/uranium-238 activity ratios of dissolved uranium exceed one (secular equilibrium) in northern Illinois; a few wells approach uranium-234/uranium-238 activity ratios of 40.

The mechanisms that generate elevated uranium-234/uranium-238 activity ratios are best described by Davidson and Dickson (1986). Briefly stated, either 1) uranium decay within mineral grains of a source rock ejects daughter products directly into the groundwater, where they stay in solution or are adsorbed on grain surfaces, or 2) alpha recoil during decay produces crystallographic defects, from which daughter products can be dissolved more readily than the parent isotope. These mechanisms are represented schematically in figure 9. Dissolved uranium concentrations in the modern system range from 0.003 micrograms per liter to over 15 micrograms per liter (Gilkeson et al., 1984, p. 28); the lower concentrations coincide with a zone of reduced water (figs. 7 and 8).

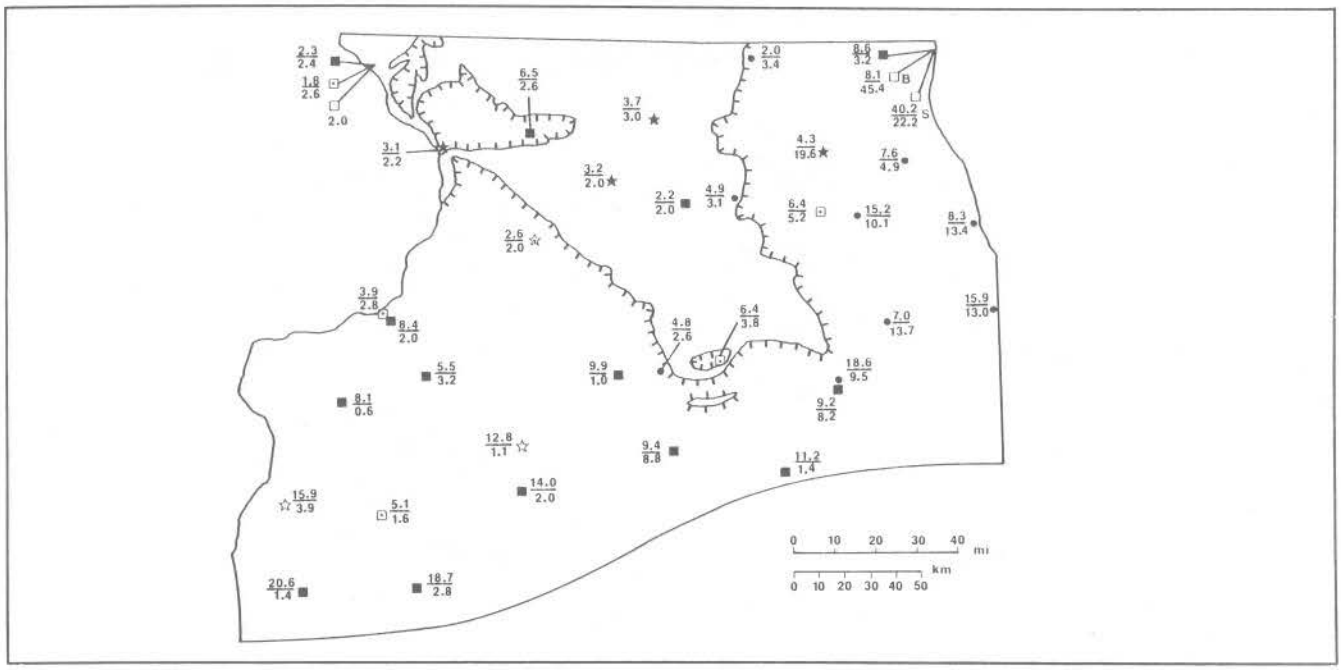


Figure 5 — Distribution of radium-226 and radium-228 in groundwaters from wells in the Cambrian-Ordovician aquifers (modified from Gilkeson et al., 1984). Symbol key: ☆ = Galena-Platteville waters; ■ = St. Peter waters; ● = Galena-Galesville waters; □ = Ironton-Galesville waters; ✶ = Galena-Mt. Simon waters; □ = Mt. Simon waters; ☆ = Ironton-Mt. Simon waters; B = Brackish water; S = Saline water. Upper values are for radium-226 (pCi/L) and lower values are for radium-228 (pCi/L). Hatchured line is the approximate limit of confining shales.

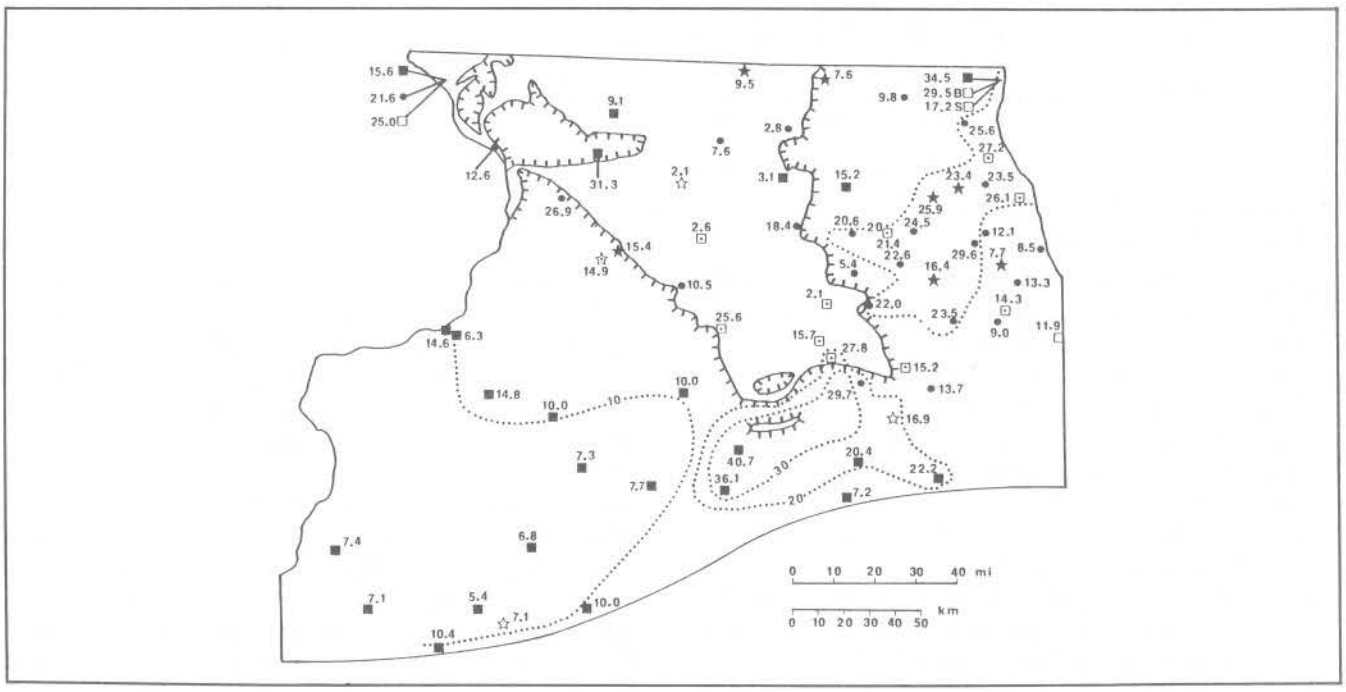


Figure 6 — Distribution of uranium-234/uranium-238 activity ratios from wells in Cambrian-Ordovician aquifers (modified from Gilkeson et al., 1984). Symbols are the same as in figure 5.

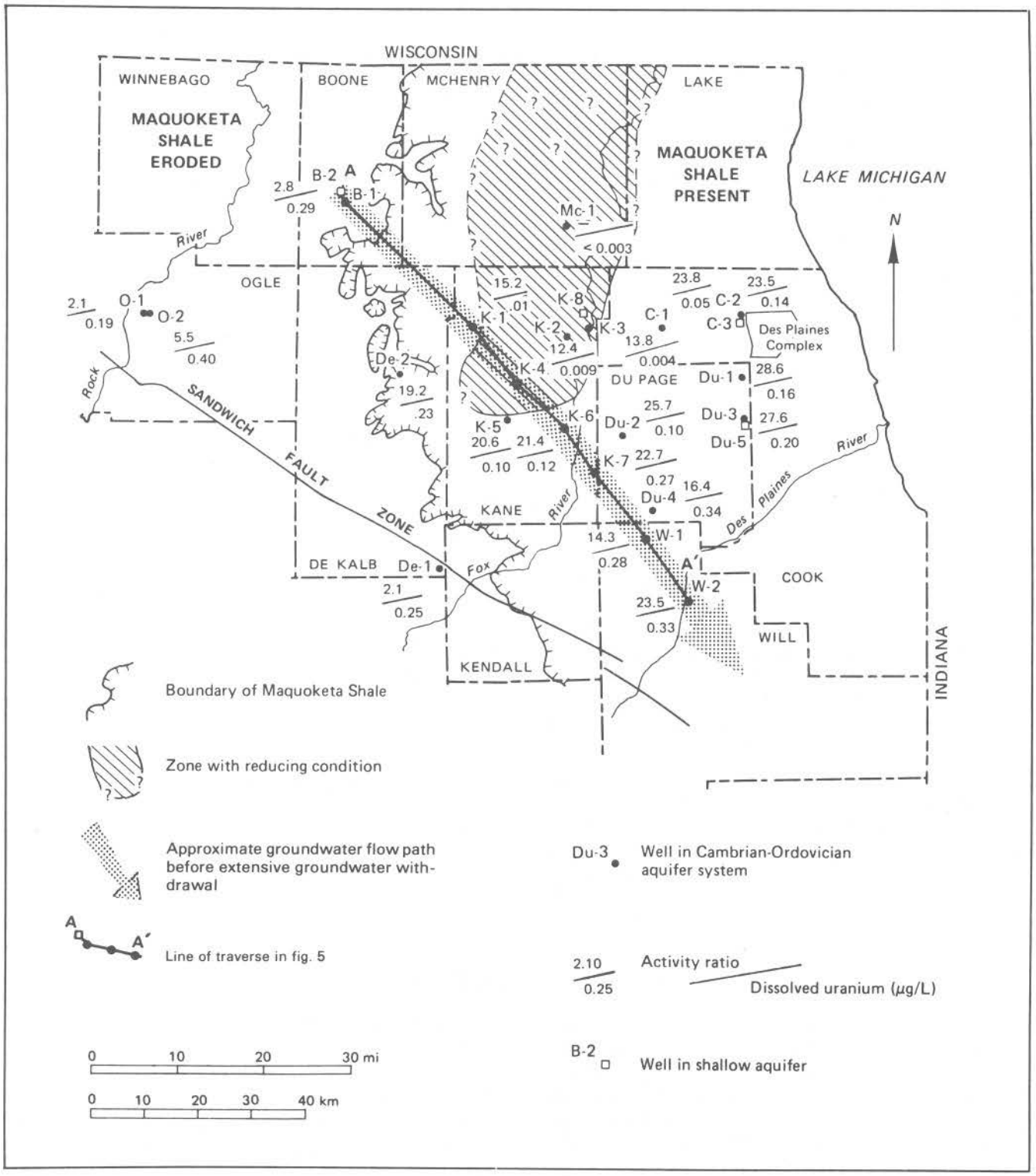


Figure 7 — Map of northeastern Illinois showing uranium-234/uranium-238 activity ratios (upper value) and uranium concentrations (lower value) in relation to the observed reducing zone in Cambrian-Ordovician aquifers (from Gilkeson and Cowart, 1982). Note elevated activity ratios in confined zone.

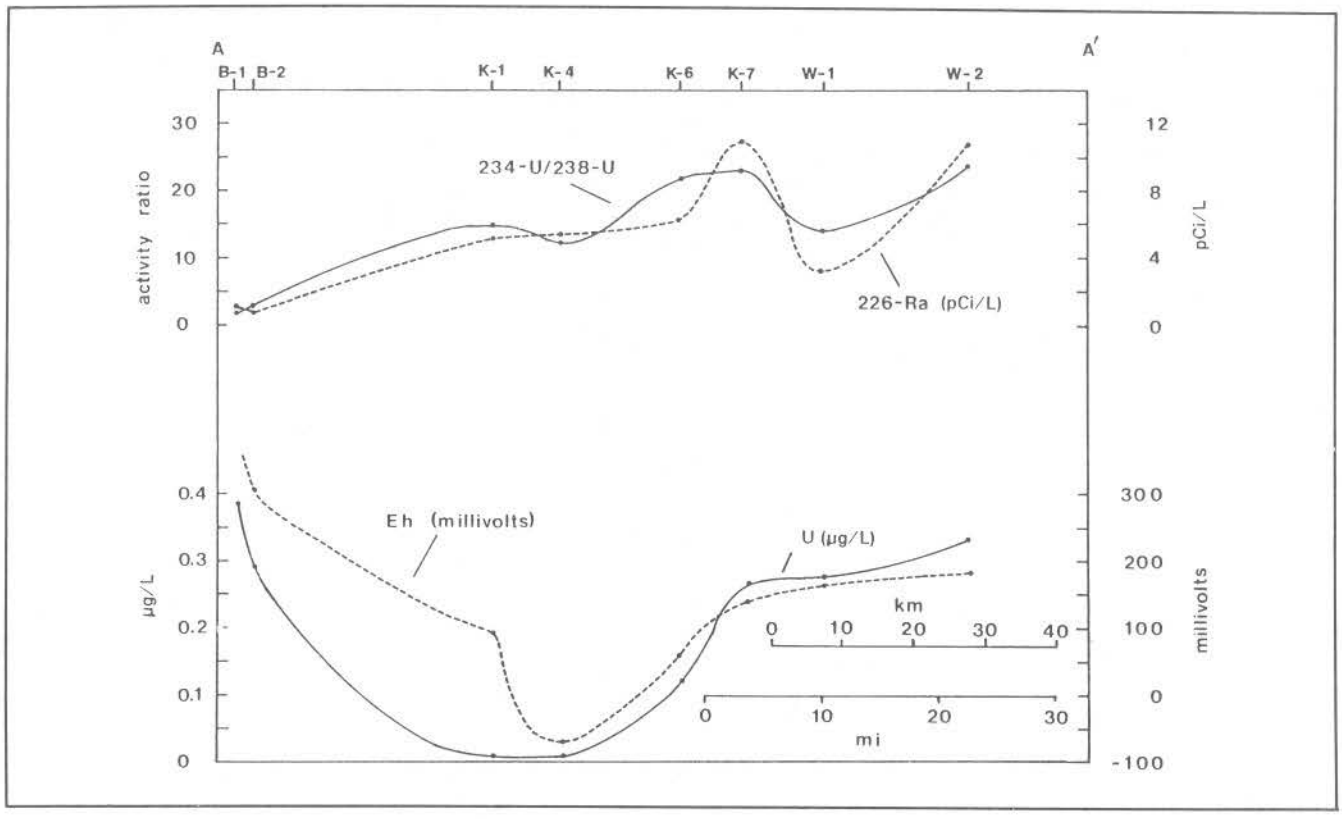


Figure 8 — Plot showing changes in uranium-234/uranium-238 activity ratios. Radium-226 activities, uranium concentrations, and redox potential along line of section A-A' from figure 7. Line of section is subparallel to the modern groundwater flow path (from Gilkeson and Cowart, 1982). Note drop in uranium concentration with reduction in Eh, and close correspondence of trends of uranium activity ratios and dissolved radium-226 activity, indicating little independent migration of radium-226 from uranium-238.

As oxidized uranium (U^{6+}) is easily dissolved and reduced uranium (U^{4+}) is immobile in aqueous solutions, dissolved uranium is "plated out," or deposited, on grain surfaces on entering this zone of reducing waters. This becomes an effective means for concentrating uranium, and thus its daughter products, in aquifers. We use this concentration mechanism in our model to account for generation of significant quantities of radiogenic lead over geologically reasonable periods of time.

MODEL ASSUMPTIONS

As most available data on modern groundwater systems deal with nuclides of the uranium-238 decay chain, and lead-206 is the ultimate decay product of this chain, we first explored the potential for lead-206 production in our model. Use of this model to produce isotopes lead-207 and lead-208 from uranium-235 and thorium-232 is more speculative, owing to the general lack of data on the behavior and concentration of these nuclides and their intermediate daughter radionuclides.

In developing our model, the following assumptions were considered reasonable:

1) Ore-fluid migration occurred 250 million years before present (mybp) (McLimans et al., 1980). The model, which depends on the initial lead isotope ratios of the lead in solution, is insensitive to the actual timing of ore-fluid migration, within broad limits; common lead isotope composition changed very slowly with time in the Phanerozoic.

2) In the Cambrian-Ordovician aquifer system there was a reducing zone similar to that documented by Gilkeson et al. (1984), in which uranium was "plated out" on grain surfaces and concentrated.

3) The location of the reducing zone could have migrated with respect to the eventual ore district, due to changes in fluid-flow rates and directions during basin dewatering and migration of erosional and depositional surfaces. A basinward shift in the location of the reducing zone would result in an increased lead-206/lead-204 ratio at a given depositional site, whereas a shift in the opposite direction would result in a lower lead-206/lead-204 ratio at a given depositional site. Migration of the reducing zone could explain the observed zonation of lead isotope compositions in galenas from the Viburnum Trend, Missouri, and the Tri-State District (Cannon et al., 1963; Sverjensky et al., 1979; Hart et al., 1981; Deloule et al., 1986).

4) The ore fluid has a density of 1 g/cm^3. As the ore fluids are basinal brines, this assumption obviously does not accurately reflect conditions, but the error generated by underestimating the fluid density is small and certainly less than that generated by the assumed starting and final lead isotope ratios.

5) A groundwater flow rate of 10 m per year (Bethke, 1986) was maintained in the aquifer during the period of ore emplacement. This value is a maximum calculated flow rate for the ore fluids. A decrease in the flow rate to 5 m per year would double the lead-206 production rate and thus halve the time required to produce the desired anomalous lead-206/lead-204 ratio.

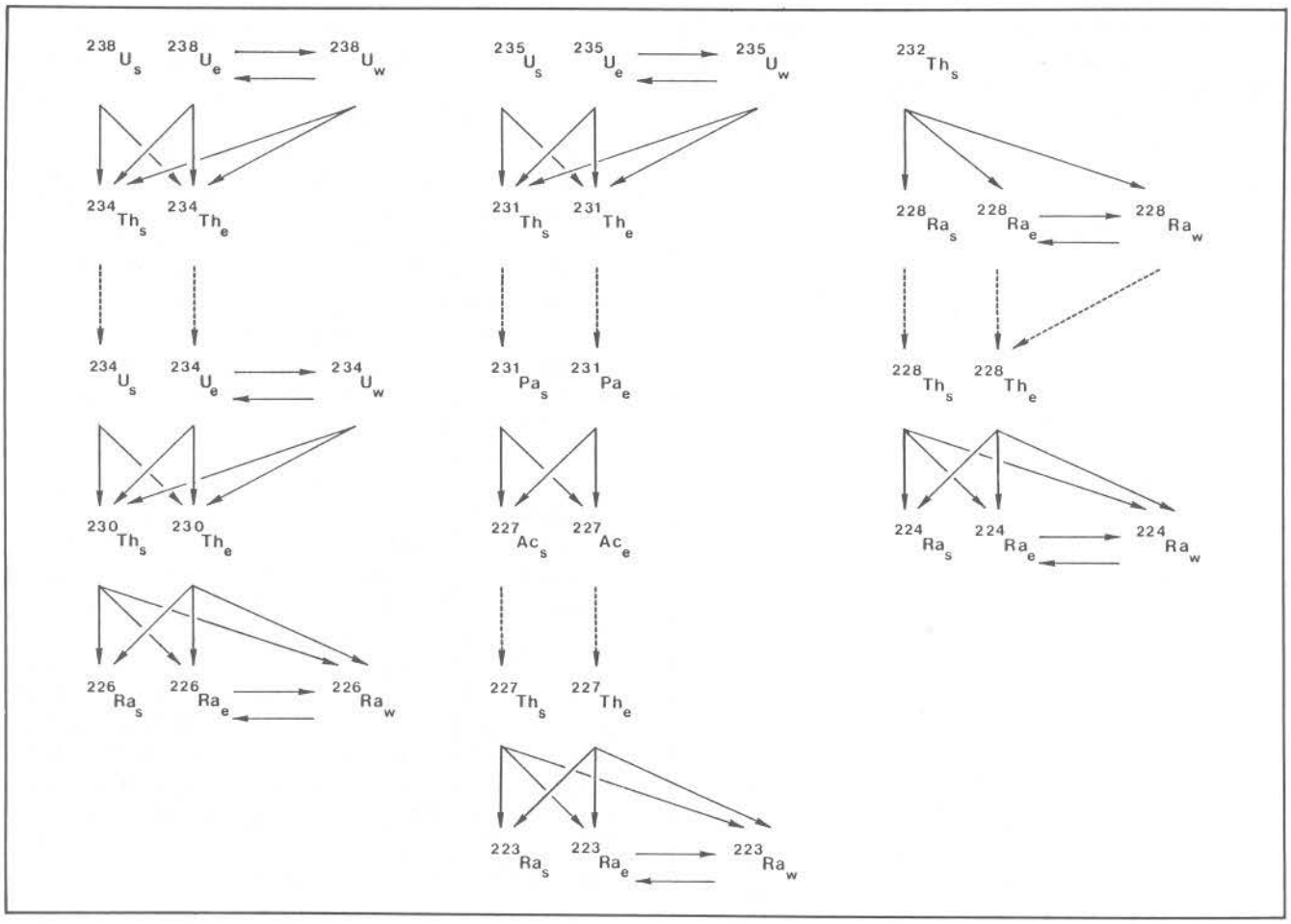


Figure 9 — Partial schematic diagram illustrating nuclide transfer cycles between solid (subscript s), grain surface (subscript e), and solution (subscript w) for uranium-238, uranium-235, and thorium-232 decay series (modified from Davidson and Dickson, 1986). Solid arrows represent alpha decay and dashed arrows represent beta decay.

6) Concentrations of 100 ppm uranium were achieved and maintained in the reducing zone for the duration of ore formation. We assume all uranium was on grain surfaces in contact with migrating ore fluids. This results in 270 g of total uranium in each cubic meter of aquifer of density 2.7 g/cm^3. Although the uranium concentration assumed is reasonable for reduced sediments (Coveney et al., 1987), the concentration of uranium on grain surfaces, rather than disseminated in them, favors the model. Reducing available uranium on grain surfaces to 50 ppm reduces the lead-206 production rate by a factor of two, and doubles the time required to produce a desired anomalous lead-206/lead-204 ratio.

7) Excess lead-206 is produced directly by decay of uranium-234 (fig. 10). Other intermediate uranium-238 daughters are assumed to be immobile in the aquifer (e.g., thorium-230, half-life = 7.52 x 10^4 y) or of sufficiently short half-life that they are considered to decay instantaneously relative to uranium-234. The intermediate daughter radium-226 is sufficiently long lived (half-life = 1.6 x 10^3 y) that radium migration during fluid flow could remove significant quantities of radium-226 from the reducing zone before conversion to lead-206 could occur. If there were conditions in the aquifer that would make both radium and uranium immobile, however, the model is not hurt by the long radium-226 half-life.

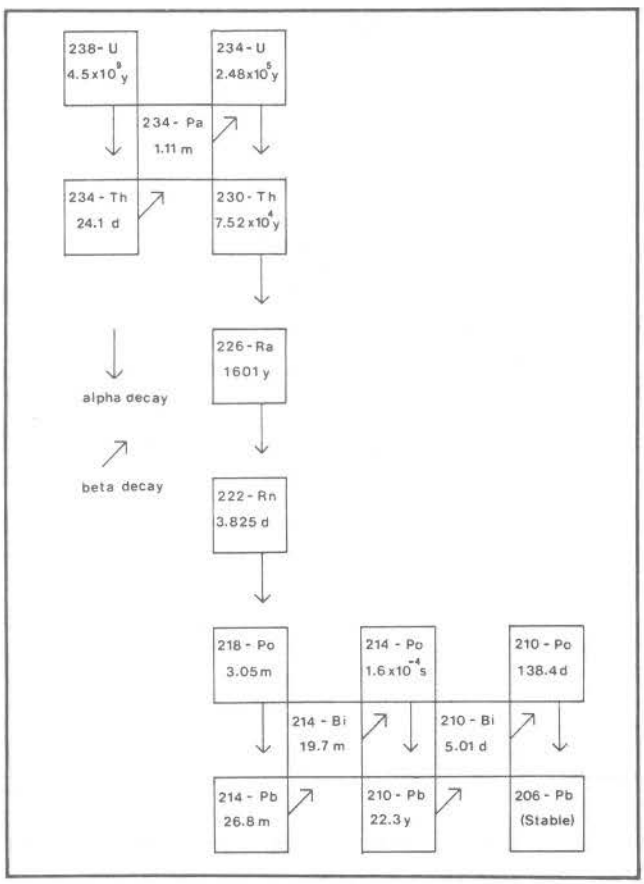


Figure 10 — The radioactive decay series of uranium-238, showing half-lives of radionuclides.

8) All excess lead-206 produced by uranium-234 decay during ore-fluid migration through the reducing zone goes directly into solution. To the extent that this condition is not satisfied, the time required to produce the anomalous lead in solution is lengthened.

9) A uranium-234/uranium-238 activity ratio of 40 in this zone of reduction was maintained during ore formation. This choice of activity ratio corresponds approximately to the maximum value measured by Gilkeson et al. (1984), in modern groundwaters of the Cambrian-Ordovician aquifer. This number seems large but may actually be conservative. If an activity ratio of 20 is used, the production rate of lead-206 is cut in half, and the time required to produce the desired lead-206/lead-204 anomaly is doubled.

10) The initial ore fluid contained 1 ppm total lead (Sverjensky, 1981, p. 1868) with a normal contemporary lead isotope composition: lead-206/lead-204 = 18.20, lead-207/lead-204 = 15.75, and lead-208/lead-204 = 38.00 (Russell and Farquhar, 1960). This assumed initial concentration of lead is a minimum value for most models of these ore fluids. If an initial lead concentration of 10 ppm is used, a ten-fold increase in the amount of time required to produce the desired anomalous lead-206/lead-204 ratio is needed.

11) The final anomalous lead isotope compositions are lead-206/lead-204 = 24.44, lead-207/lead-204 = 16.33, and lead-208/lead-204 = 43.95 (galena values from the Demby-Weist mine determined by Heyl et al., 1966). From assumption 9, this means a 25.5 percent increase in the lead-206/lead-204 ratio, a 3.6 percent increase in the lead-207/lead-204 ratio, and a 14.5 percent increase in the lead-208/lead-204 ratio. Our choice of final lead isotope ratio values is a worst case for the model, as the range of lead isotope ratio values reported by Heyl et al. (1966) in UMV galenas is 20.83-24.44 for lead-206/lead-204, 15.96-16.33 for lead-207/lead-204, and 40.45-43.95 for lead-208/lead-204.

From these assumptions, we shall show that an ore fluid containing ordinary lead in solution can be converted to an ore fluid with anomalous lead isotope ratios in a geologically reasonable time.

THE MODEL

Natural uranium mostly comprises three isotopes, uranium-238, uranium-235, and uranium-234. Taking a 1-gram sample of total uranium (atomic mass = 238.03), which converts to 4.201×10^{-3} moles, or 2.530×10^{21} atoms of uranium, the total number of uranium atoms in our 1-gram sample at the time of ore deposition is expressed in equation 1:

$$(1)\quad N_{total} = N_{238t} + N_{235t} = N_{234t},$$

where N_{238t}, N_{235t}, and N_{234t} are the number of uranium atoms of the respective uranium isotopes at t=250 mybp.

Values for N_{234t} and N_{235t} can be expressed in terms of N_{238t} in equation 1, so that the total number of atoms of the individual isotopes can be determined. From assumption 9 (uranium-234/uranium-238 activity ratio = 40) we can determine N_{234t} as a function of N_{238t} as follows:

$$(2)\quad \text{Activity ratio of } {}^{234}U/{}^{238}U = N_{234t}\lambda_{234}/N_{238t}\lambda_{238} = 40,$$

where λ_{234} and λ_{238} are the decay constants for uranium-234 and uranium-238.

Rearranging equation 2 yields

$$(3)\quad N_{234t} = 0.0022 N_{238t},$$

which can be substituted into equation 1.

To determine the value of N_{235t} in terms of N_{238t} we must express the decay of uranium-235 in terms of uranium-238:

$$(4)\quad N_{235}/N_{238} = N_{235t}(e^{-\lambda 235t})/N_{238t}(e^{-\lambda 238t}) = 1/137.88,$$

where N_{235}/N_{238} is the modern ratio of these uranium isotopes and N_{235t}/N_{238t} is the corresponding ratio at t=250 mybp. Rearranging equation 4 yields

$$(5)\quad N_{235t} = 0.0089 N_{238t},$$

for substitution into equation 1. Results of these substitutions yields the numbers of atoms of uranium-238 ($N_{238t} = 2.502 \times 10^{21}$ atoms/g uranium), uranium-235 ($N_{235t} = 2.225 \times 10^{18}$ atoms/g uranium and uranium-234 ($N_{234t} = 5.505 \times 10^{17}$ atoms/g uranium) per gram of total uranium in our system at 250 mybp. Therefore, in our 1 m^3 volume of aquifer, we have 6.755×10^{23} atoms of uranium-238, 6.013×10^{21} atoms of uranium-235, 1.486×10^{21} atoms of uranium-234.

In this model, the amount of lead-206 produced in each cubic meter of rock primarily depends on uranium-234 decay. From equation 6,

$$(6)\quad {}^{206}Pb^* = {}^{234}U(1 - e^{-\lambda 234 T}),$$

we can determine the number of radiogenic lead-206 atoms (lead-206*) produced in each cubic meter of rock for the time a packet of ore fluid is in contact with each cubic meter of rock. T is 0.1 year. From equation 6, we find that 4.170×10^{14} atoms of lead-206 are contributed to the ore fluid from each cubic meter of rock per 0.1 year. As each cubic meter of aquifer ($1\ m^3 = 10^6\ cm^3$) contains 10 percent pore space, or $10^5\ cm^3$ of fluid at an assumed $1\ g/cm^3$, this translates to an addition of 4.170×10^9 atoms of lead-206 per cm^3 ore fluid per 0.1 year (4.170×10^{10} atoms/g fluid/y).

From assumption 9, the ore fluid initially contains 1 ppm total lead. A solution of equation 7 will yield total concentration of the individual lead species in the initial fluid.

$$(7)\quad Pb_{tot} = [{}^{206}Pb/{}^{204}Pb + {}^{207}Pb/{}^{204}Pb + {}^{208}Pb/{}^{204}Pb + {}^{204}Pb/{}^{204}Pb] \times {}^{204}Pb.$$

The normal lead isotope ratios of assumption 10 yield atom fraction values of the individual lead species of 0.2495 for lead-206, 0.2159 for lead-207, 0.5290 for lead-208, and 0.0137 for lead-204 in our initial ore fluid. Thus, in a 1 ppm $lead_{tot}$ solution (5.846×10^{15} atoms lead), there are 7.294×10^{14} atoms lead-206/g of ore fluid. Compared to the number of atoms of lead-206 added to the solution per year (4.170×10^{10} atoms/g fluid/y), the quantities of lead added by this process are not insignificant. An addition of 1.860×10^{14} atoms is required to increase the lead-206/lead-204 ratio from the initial 18.20 to the final 24.44 of assumptions 10 and 11. Dividing this required increment of lead-206 by the lead-206 production rate shows that only 4460 years are needed to produce the desired change in the lead-206/lead-204 ratio, from the initial 18.20 to the final

24.44 of assumptions 10 and 11. This result is well within the 2000 to 250,000 year estimates for ore formation (McLimans et al., 1980; Lavery and Barnes, 1971). Using this value, a flow rate of 10 m/y would require a reducing zone approximately 45 km wide, which is close to the width of the reducing zone in the modern system (see fig. 7). Note that even if less favorable assumptions are made in 5, 6, 9, and 10 of the previous section, resultant times required for the production of the anomalous lead-206/lead-204 are within the range of estimates for the duration of ore formation.

SPECULATIONS ON ANOMALOUS LEAD-207 AND LEAD-208 PRODUCTION

As previously stated, relatively little has been published on the uranium-235 decay chain in modern groundwater systems. Low concentrations and low activities of these isotopes relative to the uranium-238 decay products make them both more difficult to analyze and less significant as health hazards. If we consider the uranium-235 decay chain (fig. 11), we see that the intermediate daughter isotopes do not have sufficiently long half-lives to control lead-207 production. Also, uranium-235 does not have an intermediate uranium daughter that can be concentrated like uranium-234 in the proposed reducing zone; thus, lead-207 is controlled primarily by uranium-235 decay. Additionally, there are no means by which our system can be selectively enriched in uranium-235, relative to the other uranium isotope species. In spite of its greater concentration in the system, therefore, the much longer half-life of uranium-235 relative to uranium-234 is reflected in a much lower lead-207 production rate than that of lead-206. From figure 1 and assumption 11, however, it can be seen that the lead-207/lead-204 enrichment need be only 4 percent instead of the 25 percent needed in lead-206/lead-204 to produce UMV-type leads. From the previously stated assumptions, it can be shown that an anomalous lead-207/lead-204 ratio of 16.33 can be produced from a solution with normal lead-207/lead-204 ratios in 384,000 years. A reduction in the uranium-234/uranium-238 activity ratio to 20 does not significantly increase the uranium-235 concentration from equation 1. Migration of radium-223, due to its short half-life (11.4 days), should have essentially no effect on lead-207 production. Although 384,000 years is longer than the maximum amount of time estimated for the duration of ore deposition, 250,000 years (McLimans et al., 1980), it is of the same order of magnitude. Agreement between the time required to produce anomalous lead-206/lead-204 and lead-207/lead-204 could be achieved by significant radium-226 fractionation, resulting in a much reduced lead-206 production rate. Alternatively, it may be necessary, in addition, to invoke a limited amount of selective radiogenic crustal lead contamination to reconcile the observed anomalies and the time required.

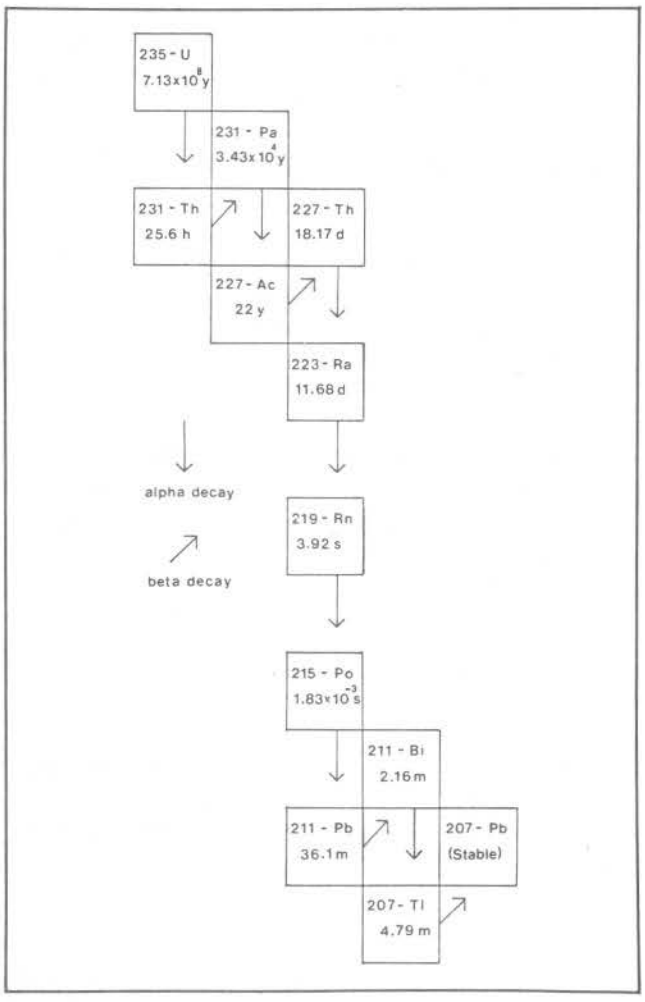


Figure 11 — The radioactive decay series of uranium-235, showing half-lives of radionuclides.

More information exists on the thorium-232 decay chain than on that of uranium-235, particularly on the occurrence of radium-228 (Gilkeson et al., 1984; Kraemer and Reid, 1984). However, thorium is considered immobile in aqueous environments and would not be easily concentrated by the same methods used to concentrate uranium. Nevertheless, the model can indicate something about anomalous lead-208 production.

From figure 12, we can see that the longest-lived daughter isotope of thorium-232 is radium-228 with a half-life of 5.75 years. Although high radium concentrations have been observed in oil-field brines (radium-228 = 1509 pCi/L maximum, Kraemer and Reid, 1984, table I, p. 158-159), this excess radium is insufficient to generate the quantities of lead-208 necessary to satisfy the model. Because thorium-232 is so long-lived relative to its daughter nuclides, its decay controls the production of lead-208, as well as the intermediate daughter products (see assumption 7). By comparison, intermediate steps in the decay of thorium-232 are geologically instantaneous. Assuming a 10 ppm thorium concentration on the grain surfaces (see assumption 6), the production rate of lead-208 calculated from equation 6 is a factor of 10^9 greater from thorium-232 than from excess radium-228 in solution at the above maximum measured concentration. Thus, decay of thorium-232 would produce greater quantities of excess lead-208 in less time than decay of unsupported radium-228. Even at this concentration of thorium in the aquifer, thorogenic lead production is much slower than uranogenic lead production (12.6 million years), due to the much longer half-life of thorium-232 (1.39×10^{10} y). As with lead-207, some radiogenic crustal lead contamination might also be necessary to account fully for the anomalous leads observed in the UMV district.

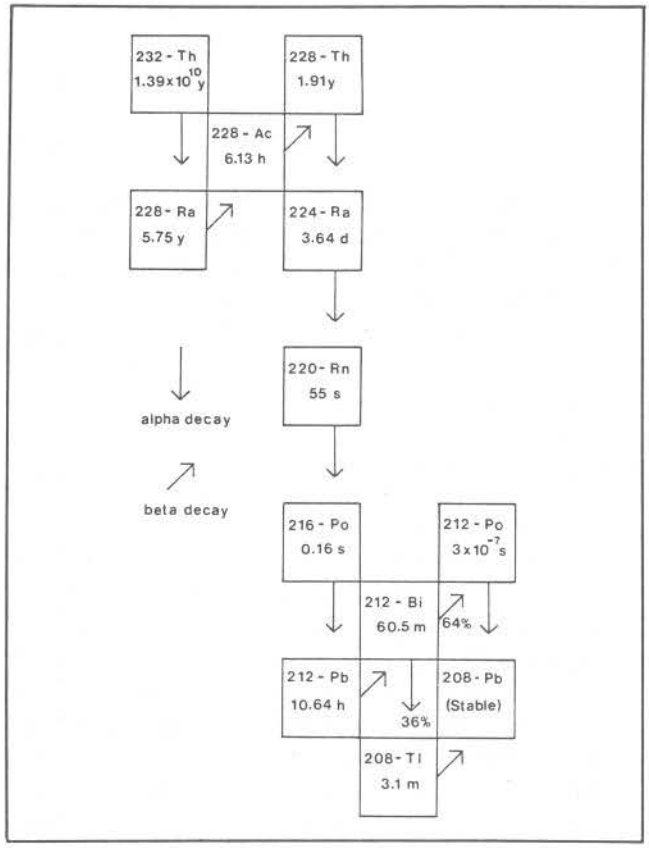


Figure 12 — The radioactive decay series of thorium-232, showing half-lives of radionuclides.

CONCLUSIONS

A model has been developed to account for the anomalous lead-206/lead-204 values of galenas in the UMV district. These lead ratios are believed to occur through decay of uranium-234 deposited on grain surfaces in the aquifer, over geologically reasonable periods of time. Using uranium geochemistry in the modern Cambrian-Ordovician aquifer in Illinois as an analog to conditions during ore-fluid migration, and assuming a reasonable uranium concentration for the system, we have determined that in a reducing zone 45 km wide, ordinary lead isotopes in solution would have sufficient lead-206 added to them solely by uranium-234 decay to produce the anomalous lead-206/lead-204 ratios observed in the UMV in less than 4500 years. This is well within accepted (2000-250,000 year) limits placed on the duration of emplacement by McLimans et al. (1980) and Lavery and Barnes (1971). Insufficient data exist on the uranium-235 and thorium-232 decay sequence to constrain a similarly detailed model for the production of lead-207/lead-204 and lead-208/lead-204 anomalies; a radiogenic crustal lead component may also be required for these. However, the extreme anomalies in lead-206/lead-204 can be fully accounted for through our model.

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GEOMORPHIC AND GEOCHEMICAL ENHANCEMENT OF RADON EMISSION IN MIDDLE TENNESSEE

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ABSTRACT

A special stratigraphic sequence, involving the uranium-rich Chattanooga Shale (30-40 μg/g) and underlying phosphatic limestones of the Nashville Group (Upper Ordovician), combined with a sloping topography (the escarpments of the Central Basin) provides a physical setting for subsequent chemical mobilization, reprecipitation, and enrichment of uranium and its alpha-emitting daughters as secondary phosphates, near the base of a relatively thin cover of residuum-colluvium.

Secondary enrichment of uraniferous phosphate would occur on the surface of pre-existing grains. Subsequent daughter recoil from alpha decay would likely deposit the daughter near the surface and favor enrichment of the mineral surfaces with the daughter also, as both thorium-230 and radium-226 are compatible with phosphate minerals. Thus, radium-226 should become relatively enriched on mineral surfaces, and thereby increase the probability that its daughter, radon, will be emitted into the soil atmosphere.

Although the Chattanooga Shale contains higher concentrations of uranium than the phosphatic limestones, its asphaltic organic matter seals in the radon to produce a relatively closed system. During weathering, oxidation of pyrite in the shale produces acidic leachates that can dissolve UO_2 and oxidize it to uranyl complexes, which can precipitate on residual phosphate grains accumulated from weathering of the underlying phosphatic limestones.

Thus, uranium dissolved from either the Chattanooga or residual phosphates during weathering can be enriched downslope in the residuum. Mass movement aids downslope transport and tends to bring the uranium-enriched material toward the surface for renewed weathering. If uranium and its daughters, thorium and radium, follow phosphate through the weathering cycle, processes that enrich the phosphatic residuum to commercial-grade phosphate deposits would also enrich uranium and its daughters, thereby increasing the potential for radon emission.

In cities where homes are confined to small lots, hilly topography favored foundations with piers that later evolved to partial basements when coal-fired, central heating developed. These older style homes should be especially vulnerable to radon capture.

INTRODUCTION

Radon analyses in Tennessee by the Terradex Corporation showed that 123 of 430 (28.6 percent) yielded values above the Environmental Protection Agency's action level of 4.0 pCi/L. The University of Pittsburg discovered higher than acceptable radon concentrations in 48 out of 183 samples (26.2 percent) from the state, including 16 out of 48 (33 percent) from the homes tested in Nashville.

Because of the potential magnitude of the radon problem, the state of Tennessee was one of the first 10 states to enter the cooperative statewide testing program of the Environmental Protection Agency. The plan called for deployment of 3000 charcoal detectors; analyses were to be run at the EPA laboratory in Montgomery, Alabama. As of June 1, 1987, about 1865 detectors have been deployed. Results from this first group of randomly selected sites suggest that the percentage of homes with radon concentrations above 4.0 pCi/L is less than previous analyses suggested (18.0 percent), but there is a problem, especially in the Nashville area and the outer portion of the Central Basin. Figure 1 shows the physiography of central Tennessee which is dominated by the Central Basin and the surrounding Highland Rim.

The emerging pattern of high radon in central Tennessee appears to be related primarily to two low-level uranium-bearing stratigraphic units, the Chattanooga Shale and the phosphatic limestones of the Nashville Group. Figure 2 shows the phosphatic region of Smith and Whitlatch (1940) and the general boundaries between the inner and outer portions of the Central Basin. However, the actual relationship between high radon in dwellings and the activity of uranium and its daughters in the source rocks is not so straightforward. The two main modifiers to the patterns of the source units appear to be 1) the physical and chemical processes associated with weathering and mass movement of the source beds, and 2) the construction of the homes, which is partly controlled by regional geomorphology. First, let us examine the evolution of home construction and second, the uranium-rich sources and the effects of weathering.

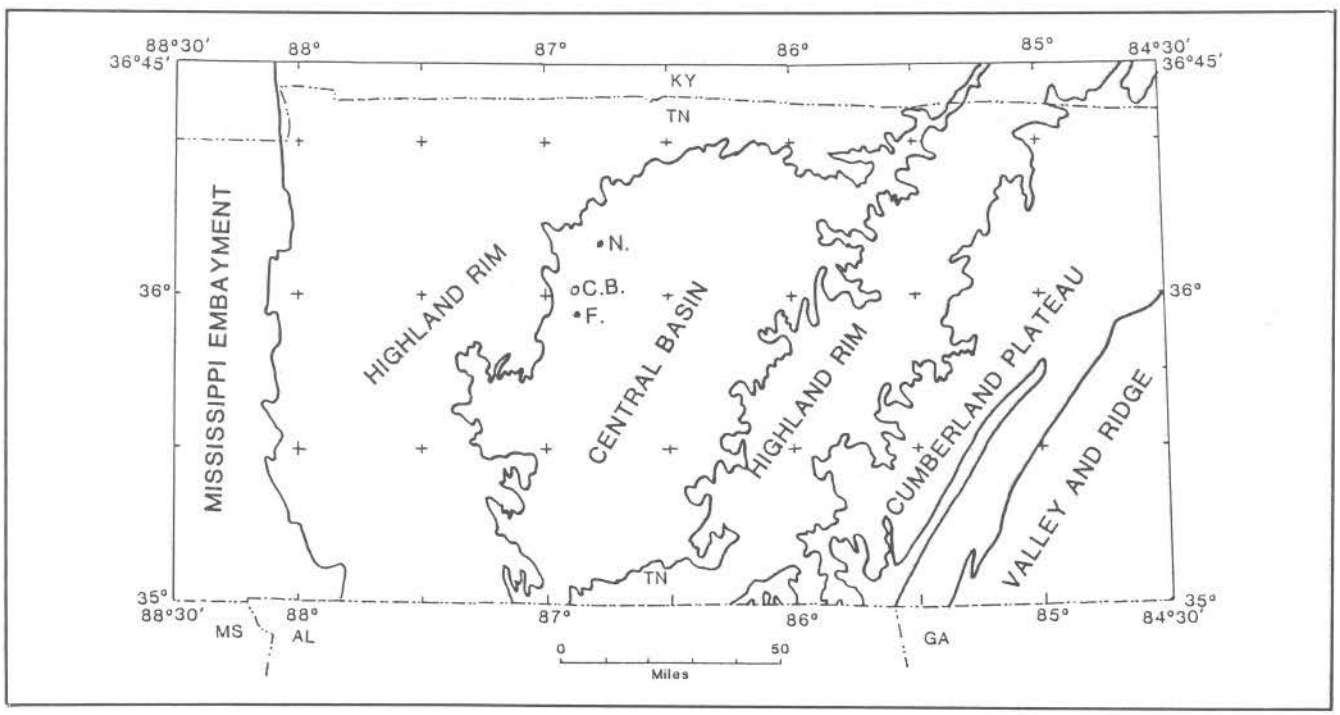


Figure 1 — Physiographic provinces of central Tennessee. The Central Basin and surrounding Highland Rim areas are generally considered to be Middle Tennessee. East Tennessee comprises the Cumberland Plateau eastward and West Tennessee is west of the Tennessee River (Mississippi Embayment). The centers of Nashville (N.) and Franklin (F.) are shown as dots. An open circle (C.B.) marks the location of Cartwright Basin, shown in detail in figure 3.

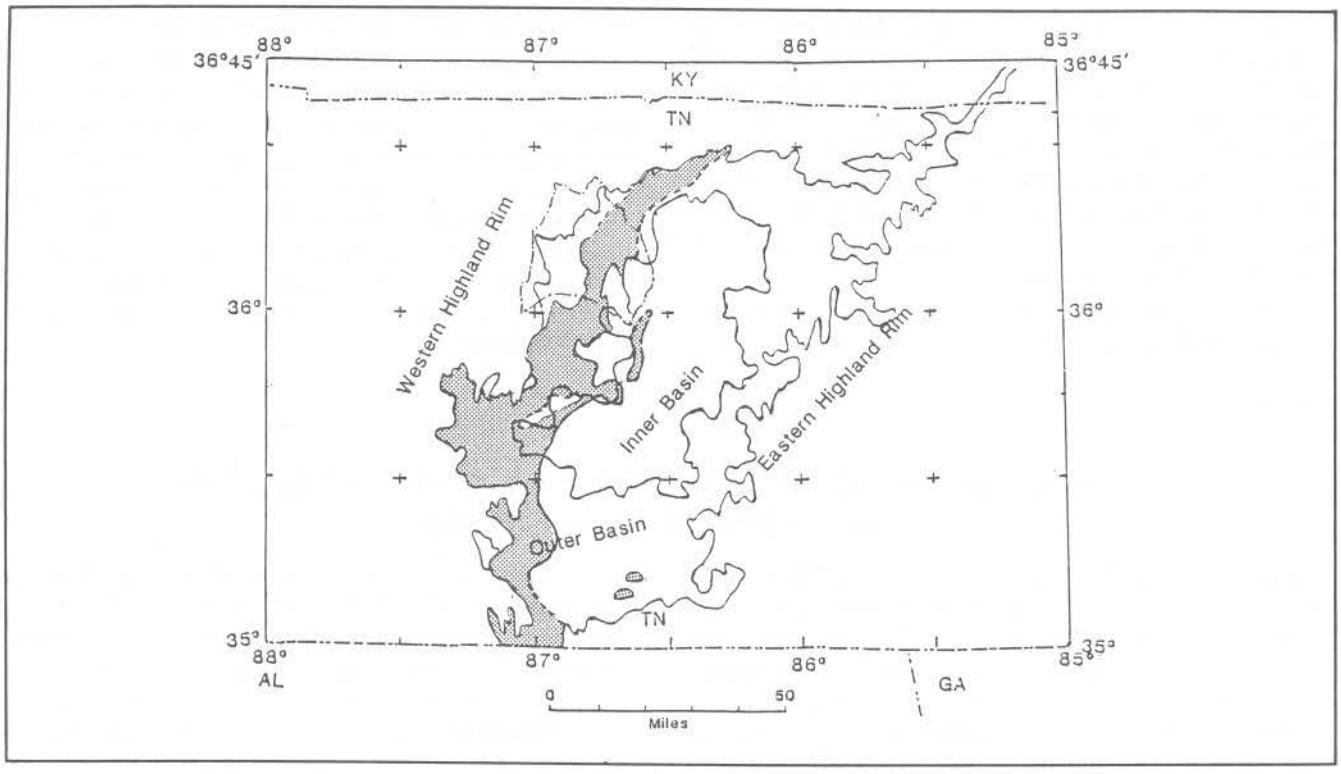


Figure 2 — The inner and outer regions of the Central Basin. Davidson County (Nashville) is bounded by the dot-dash line on the northwest side of the Central Basin. The general outcrop pattern of the Chattanooga Shale follows the escarpment between the Central Basin and Highland Rim, but outcrops are narrower than the lines used in the figure to show physiographic boundaries. The Chattanooga also crops out on numerous outliers of "Highland Rim" hills that occur in the outer basin. The total outcrop area of Chattanooga Shale is only a few square miles. The stippled pattern shows the phosphatic outcrop region, as defined by Smith and Whitlatch (1940). Its outcrop area is about 1100 mi².

HOME CONSTRUCTION AND RADON LEVELS

Because of the hilly terrain in the outer portion of the Central Basin (fig. 2) a high percentage of homes have foundations with full or partial crawl spaces. Early foundations of stacked flaggy limestone provided a quick and easy solution for leveling sills, providing ventilation to reduce rot, and protection from termites.

As houses grew larger and brick and concrete block became available, houses were set on masonry piers, which made it easier to make the houses level on sloping sites. It was also relatively easy to dig out the area on the low side of a house and enclose it in order to provide a convenient root cellar or other storage. When coal-fired, convective central heating developed, placing furnaces beneath houses was necessary, so houses built before 1940 generally had a partial basement for furnace, coal bin, and general storage. Although furnaces were fashionable in towns, stoves and fireplaces continued to provide most of the heat on the farms.

By the end of the 1940's, gas- and oil-fired, forced-air, hot-air, and electric heating systems replaced the older methods. These new systems did not need basements. However, the hilly terrain and the availability of heavy equipment to excavate the thin rocky soils made it relatively inexpensive to build a full walk-in basement.

Houses that appear to have the greatest risk for high radon concentrations are those built with partial basements, in the late 1800's through the

1930's. The original coal-fired furnaces were replaced with gas-fired units. Combustion air and some make-up air for the forced-air system are drawn from basements. Use of basement air lowers the pressure and favors outgassing of radon from the soil of unfinished crawl spaces. In addition, some of these partial basements were dry and high enough, so that their space could be cleaned and captured for use as workrooms or playrooms.

The evolution of house substructures, described above, applies to cities or larger towns. In the country, the siting of houses was not restricted to small lots, thus relatively level sites could be found, and wood or coal-fired stoves and fireplaces were used for heating until the homes were modernized with electric or oil heat. As a result, basements are not as common in the country, and the percentage of country homes effected by high radon levels should be lower. Thus, in the cities the geomorphology of the region favored house foundations providing sources and avenues for radon to enter the structures.

PHYSICAL AND CHEMICAL PROCESSES OPERATING ON RADON-BEARING SOURCES

In trying to locate the source of radon-222 we must find its parent radium-226 and ultimately look back to uranium-238. In the decay series of uranium-238 the alpha-emitting daughters uranium-234, thorium-230, and radium-226 are in the system long enough and are different enough chemically so that chemical fractionation can occur in an open weathering system. Gaseous radon, though short-lived, is the prime example of fractionation within the decay series. The degree of openness in the weathering system and the emanating power (or fraction) of the radium-bearing substances are of first importance in determining the radon flux to the hydrologic and atmospheric environments. It is only that portion of the radon that escapes to these environments that poses any environmental problem. Thus, the open conditions of chemical weathering may be extremely important in the cycling of uranium and its daughters through the near surface system, and, in the process, aid in emission of radon.

The two major sources of uranium in the Central Basin are the organic-rich Chattanooga Shale and the phosphatic limestones of the Upper Ordovician Nashville Group. The concentration of uranium in the Chattanooga is greater than that in the phosphatic limestones, but the limestones are much thicker and crop out over a much larger area (see fig. 2).

THE CHATTANOOGA SHALE AS A SOURCE OF RADON

The Chattanooga Shale averages about 15-20 ft thick and its uranium concentration ranges from about 20 to 80 $\mu g/g$ (Vine, 1969). Uranium concentrations are generally higher on the eastern than on the western side of the Central Basin. In smaller regions the distribution of uranium tends to be very uniform. Rheams and Neathery (1984) found no statistically significant positive correlation between concentrations of uranium and any other component (42 samples with 30 other variables) in the shale in northern Alabama and south-central Tennessee.

The total organic carbon in the Chattanooga ranges between 11.93 and 19.26 percent (Rheams and Neathery, 1984). This organic matter acts as a buffer to keep reducing conditions in the shale and also helps to lithify and seal it. The sealing action retards oxidation and inhibits migration of radon produced from the uranium decay. For practical purposes the "fresh" shale forms a closed system with respect to uranium and its daughters, so they should be preserved in secular equilibrium.

Even though the total uranium concentration is probably higher in the Chattanooga Shale than in the phosphatic limestone, its actual outcrop area is very small (only a few square miles) because it is relatively thin and usually crops out on relatively steep hillsides. Outcrops generally follow the boundary between the Central Basin and the Highland Rim (see fig. 2) but are narrower than the line drawn on that figure. The Chattanooga is underlain by relatively soluble limestones and capped by the relatively insoluble Fort Payne Formation. During weathering, the Fort Payne tends to protect the Chattanooga from weathering (Reesman and Godfrey, 1981). Erosion is mainly by physical breakdown of the outcrops as the more soluble under-

lying limestones are leached. The Chattanooga-Fort Payne sequence caps higher hills (as erosional remnants) in the Central Basin and the escarpments separating the basin from its surrounding Highland Rims. Rubble from the breakdown of this sequence is incorporated into colluvium that develops below the base of the Chattanooga.

WEATHERING OF THE CHATTANOOGA SHALE

The surface of the Chattanooga is usually covered by residuum and colluvium so that weathering processes at the soil-bedrock interface are not readily apparent. Most natural outcrops of the shale have already been substantially weathered.

When the Chattanooga is subaerially exposed, as in fresh roadcuts, slow, but accelerating oxidation begins. In addition to the 10 to 20 percent organic matter, the Chattanooga also averages about 10 percent pyritic sulfide, both of which are prone to oxidation. Sulfide oxidation occurs in the usually moist environment of natural outcrops. A film of moisture provides an oxygen-diffusing membrane and a medium for electron transfer. The film also allows formation of sulfuric acid, and eventually, ferric sulfate, which also aids the electron-transfer processes of oxidation. A pH between 2.0 and 3.0 is common for waters that pass through the Chattanooga (Reesman et al., 1975). The effective pH in these water films could be near 1.0, as in contact pH measurements on similar rocks (Keller et al., 1966). Such an acidic environment also helps breakdown non-sulfide minerals, especially carbonates like calcite and the alumino-silicate clay minerals. The growth of weathering products such as gypsum, alum, jarosite, and ferric hydroxide can split shaly partings and widen small fractures to expose more surface area to oxidation.

On hillslopes where the Chattanooga is capped by the siliceous, resistant Fort Payne Formation the breakdown products of the Chattanooga are incorporated with siliceous residue from weathering of the overlying Fort Payne. Downhill movement of this material forms colluvium over the underlying Ordovician limestones. Oxidation of organic and pyritic debris derived from the Chattanooga continues in this near-surface colluvial environment to produce additional acidic leachates, which percolate downward and are neutralized by the underlying limestones.

MOBILIZATION OF URANIUM AND ITS DAUGHTERS

During the formation of acids, U^{4+}, which was probably present as UO_2 would become more soluble, as would its daughters thorium and radium. The oxidizing conditions that created the acid would also promote solubility of the uranium-containing material. In an oxidizing environment U^{4+} oxidizes to U^{6+} which forms relatively stable cationic or anionic complexes, depending on the pH of the solution and the anions coordinated with it. In this oxidizing environment, anions that coordinate with U^{+6} include hydroxide, sulfate, vanadate, and phosphate (Dongarra and Langmuir, 1980). Hydroxide could be obtained from the water; sulfate, from oxidation of sulfide. The vanadium content of the shale is about 200 µg/g (Vine, 1969), and phosphate in the Chattanooga Shale averages about 0.12 percent, as P_2O_5 (Conant and Swanson, 1961). In addition, the limestones underlying the Chattanooga are generally phosphatic.

PHOSPHATIC MINERALS AS A SOURCE OF RADON

All limestones of the Ordovician Nashville and Richman Groups from the base of the Chattanooga downward through the Hermitage Formation are phosphatic on the western side of the Central Basin. The outcrop region of phosphatic limestones is shown in figure 2 (Smith and Whitlatch, 1940). The outcrop area of these phosphatic limestones (about 1100 mi²) is much greater than that of the Chattanooga Shale. Weathering of these phosphatic limestones results in concentration of the more chemically resistant phosphate minerals in residuum near the soil-limestone interface. The uranium concentration in this residual phosphate is about 10 to 30 µg/g (Cathcart, 1978).

Commercial concentrations of residual phosphate are most common in the residuum that develops from the Bigby-Cannon Formation, partly because the Bigby facies tends to be the most phosphatic of all limestones in the area, partly because of phosphate cycling within the residuum or soil, and partly because of the geomorphic setting of the Bigby-Cannon Formation. The Bigby-Cannon tends to occupy topographic lows, because it does not weather as rapidly as the overlying, slope-forming Catheys-Leipers Formation. Residuum on the Bigby-Cannon Formation is thicker because the low slope

developed in its topographic setting and the accumulation of colluvium from the adjacent hillslopes produce an "over thickened" residuum-colluvium of relatively insoluble chemically weathered products.

CHEMICAL WEATHERING ASSOCIATED WITH THE PHOSPHATE REGION

Chemical weathering dissolves the carbonate minerals in limestones and also attacks all other minerals. Those more resistant than carbonates accumulate in the residuum; however, residuum and colluvium on the carbonate-bearing bedrock have the first chance to react with rain. In the warm humid climate of Tennessee, residual soils tend to be acidic, because base-forming cations (calcium and magnesium) have been leached from the upper soil zone by carbonic acid produced by reaction of atmospheric and soil-derived carbon dioxide with water.

The whole sequence of soil (residuum-colluvium) and bedrock reacts in this open chemical system. Ideally, the most resistant minerals become concentrated at the top of the weathering sequence. Downward through the sequence, we should expect to find mineral zones or fronts that are progressively more reactive. In a relatively monominerallic limestone the soil-bedrock interface tends to be sharp and there is little calcite preserved in the residuum above the contact, which can be considered to represent the upper limit of the calcite mineral front. A similar front should exist for each mineral (including the phosphate minerals) in the residuum. Weathering fronts are not stationary, but move downward as weathering continues, e.g., the soil-bedrock contact of the Leipers Formation moves downward at about 150 ft/million years (Reesman et al., 1975). The upper portion of a mineral front is controlled by the equilibrium solubility of that mineral, its kinetic rate of dissolution, and its grain size. At the front the mineral is undergoing dissolution; some or all dissolution products are carried away from the front. As dissolved products move downward through this open chemical system, the chemical environment may change sufficiently that some of these products precipitate to form new minerals.

The distribution of phosphate-bearing species in solution is a function of its pH. In the mildly acidic upper soil zone $H_2PO_4^-$ dominates, but in and around the limestone bedrock the pH of the solution rises and HPO_4^{2-} dominates. Even though phosphate (PO_4^{3-}) is a subordinate species, the distribution of various dissolved species shifts so that the soil solutions can become supersaturated with respect to apatite or other phosphate minerals. Phosphate-bearing minerals can precipitate directly from solution, grow on grains that are already in this environment, and/or replace calcite in the limestone (phosphoritization).

PREVIOUS STUDIES IN THE CARTWRIGHT BASIN — A GUIDE TO THE STUDY OF PHOSPHATIC LIMESTONES IN THE CENTRAL BASIN

Cartwright Creek has a 5.12 mi² drainage that flows directly into the Harpeth River, about 5 mi north of Franklin, Tennessee (see fig. 3). The basin was studied by Reesman et al. (1975) to determine the linkage of hydrology, geology, and chemistry, to soils and geomorphology, and to examine the evolutionary history of this basin and the Central Basin (Reesman and Godfrey, 1981). Because conditions in this

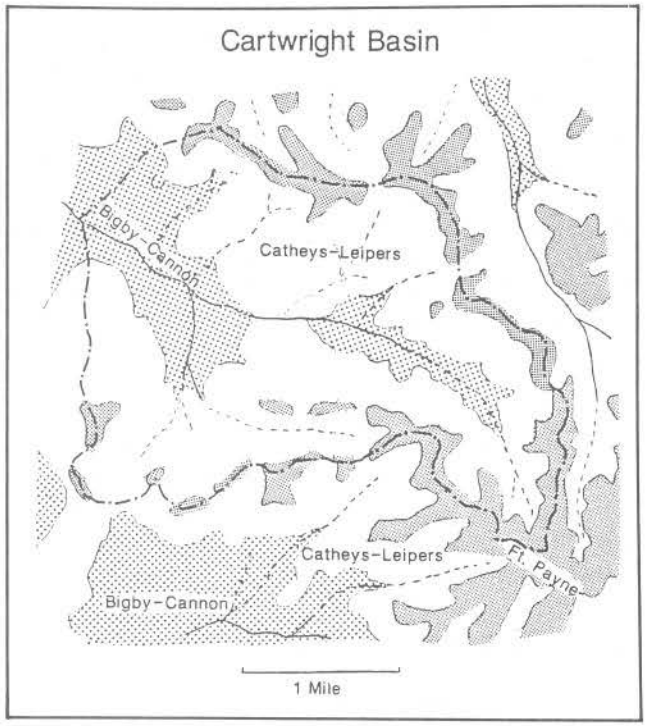


Figure 3 — The Cartwright Basin. The Cartwright Basin is a 5.12-mi² watershed of the Harpeth River. The basin is ringed by Fort Payne-Chattanooga-capped hills. The two major Ordovician mapping units (Bigby-Cannon and the Catheys-Leipers) are both phosphatic limestones. This basin was studied by Reesman et al. (1975) as a model of processes operating on the much larger Central Basin (Reesman and Godfrey, 1981).

smaller basin are essentially the same as the outer portion of the Central Basin, the Cartwright Basin can serve as a model for the study of phosphate, uranium, and uranium-daughter cycling in the Central Basin.

Relationship between Flow and Dissolved Constituents in the Cartwright Basin

The mean-annual flow from Cartwright Creek is about 6.86 $ft^3/sec.$ (1.34 cfs/mi^2), based upon long-term flow data for the Harpeth River. Streamflow recession curves from Cartwright Creek can be synthesized by considering four time-related exponential functions that are part of the peak flow after a rain. These components were termed 1) overland flow, 2) interflow, 3) rapid groundwater flow, and 4) long-term low flow. Table 1 contains the equations for each component and their estimated annual contribution in percent of total flow. The frequency of storm events and the mean-annual precipitation were estimated from U.S. Weather Bureau data and the response of Cartwright Creek to similar conditions. Figure 4 shows the generalized annual hydrologic budget for the basin, based on a mean-annual precipitation of 48.1 in., the value from the U.S. Weather Bureau for Franklin, Tennessee, and a mean streamflow of 6.86 $ft^3/sec.$, which is equivalent to 18.3 in. of runoff. By relating the recession curve at the time of sample collection to the time and flow at the crest, the relative proportion of the four flow components were estimated (Reesman et al., 1975). The general trend in total-dissolved solids ranged from 148 mg/L for overland flow to 270 mg/L for long-term groundwater flow; the overall average was 218 mg/L. Total dissolved phosphate did not follow this trend.

Phosphate-Flow Relationships in Cartwright Basin

Total dissolved phosphate was high during periods of overland flow (about 1.1 mg/L); however, it was highest during interflow periods (about 3 mg/L) and dropped to about 0.4 mg/L during long-term groundwater flow (Reesman et al., 1975).

The flow-related concentrations of dissolved phosphate are consistent with phosphate analyses from well and spring waters, soil-dissolution studies, and column studies on dissolution of Bigby-Cannon phosphates. The average phosphate analysis from 11 wells in the Cartwright Basin (most from the Bigby-Cannon) was 0.289 ± .334 mg/L. Five springs averaged 0.766 ± 0.12 mg/L (collected after rains during the rapid groundwater-flow regime).

Sprinkle (1973) collected soils, representative of the basin, from depths of 0-6 in. and 18-24 in., or just above the soil-bedrock contact. These soil samples were equilibrated with water in a 10/1 weight ratio (3 L of water and 300 g of soil) for periods of 1 to 250 days [1,2,4,8, - - - 250]. The soil-water ratio in the equilibration bottles relative to those in the actual

TABLE 1
Estimated flow components and phosphate budget for the Cartwright Basin

Flow component	Equation	Estimated inches/year	Percentage of runoff	Hours to reach 1 cfs	Average phosphate concentration
Overland	$10^{X-.XT}$	5.5	30	10	1.1 mg/L
Interflow	$10^{1.225-.0292T}$	2.0	11	42	3.0 mg/L
Rapid G.-W. Long-term	$10^{1.114-.0048T}$	9.3	51	232	0.8 mg/L
Low flow	$10^{-0.1675-.000226T}$	1.5	8	Max. flow 0.7 cfs dominates after 290 hours	0.4 mg/L

Mean annual precipitation = 48.1 inches
Runoff 1.34 cfs/mi^2 = 18.3 inches
T = time since peak flow in hours
X = $\log_{10}$ of peak flow in cfs
cfs = cubic feet/second

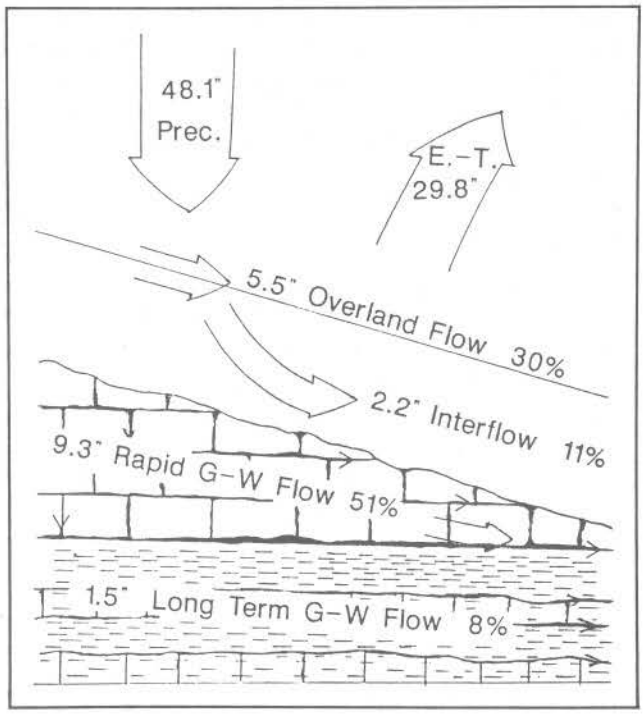


Figure 4 — The hydrologic balance in the Cartwright Basin. Long-term precipitation records for Franklin, Tennessee and long-term, streamflow data on the adjacent Harpeth River were used to determine precipitation, total runoff, and evapotranspiration (E.-T.) for the basin. The four components of total runoff are based on analyses of hydrographic records from the Cartwright Basin. This cartoon attempts to show how these four components might be related in terms of topography and geology. Table 1 contains the equations for each of these components.

soil are such that 1 hour in the soil should be equivalent to about 6 days in the equilibration bottles. Dissolved phosphate generally reached a maximum between 4 and 16 days. The surface soils yielded 8-day analyses that ranged from 0.89 to 1.5 mg/L, whereas the deeper samples ranged from 3.0 to 3.8 mg/L. Unfortunately, phosphate analyses were not run on all soils equilibrated for shorter periods.

Rapid dissolution of naturally occurring "rock phosphates" was confirmed by column dissolution studies (Reesman et al., 1975). A sample of almost pure rock phosphate from the Bigby facies of the Bigby-Cannon Formation was crushed. The 50- to 100-mesh fraction was washed several times in double deionized water to remove fine material that may have adhered to the larger grains and to dissolve as much as possible of the structurally damaged phosphatic material from the crushing process. The cleaning process took 2 days. The material was dried and 1.0 g was loaded into a ¾-in.-diameter column, above a porous polyethylene filter. About 7.5 L of water were passed through the column at various flow rates. With flow at about 1 ml/minute, the total dissolved phosphate ranged from 3.3 to 3.8 mg/L, at 10 ml/minute it was 0.43 mg/L and at 30 ml/minute it was 0.3 mg/L. The overall average for 7.5 L was 1.2 mg/L for phosphate, 1.0 mg/L calcium, and a pH of 5.4. This pH is reasonable for 1:1 soil-water ratios of soils in the basin (Edwards et al., 1974; True et al., 1964) but it is generally about 0.5 units lower than Sprinkle (1973) measured in his 8-day equilibrations.

Cycling of Phosphate Within the Cartwright Basin

Using estimates of the concentration of phosphate under various flow conditions, it is possible to approximate cycling of phosphate in the Cartwright Basin (fig. 5). About 30 percent of the runoff from the basin leaves as overland flow carrying about 1.1 mg/L total

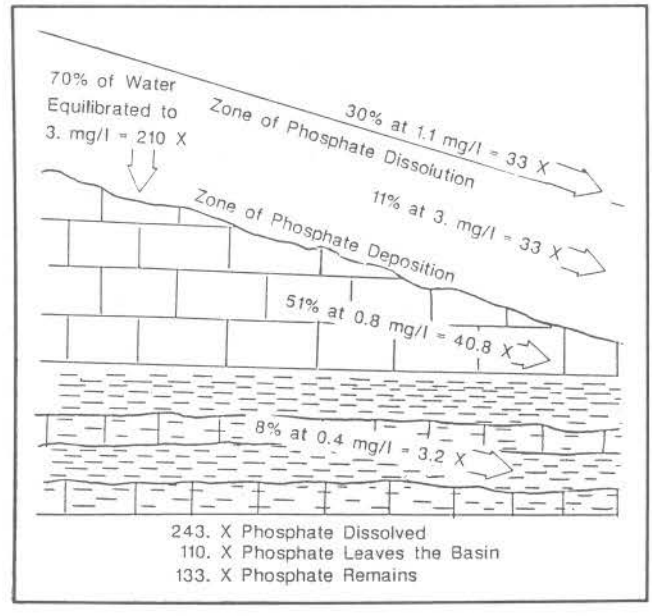


Figure 5 — Phosphate in the Cartwright Basin. This cartoon attempts to show the relationship between the four components of runoff and the estimated total dissolved phosphate concentrations related to each component and thereby approximate the relative movement of phosphate within the weathering system. For every 243 units of total phosphate dissolved, 110 units leave the basin through runoff and 133 units of phosphate reprecipitate (see fig. 6).

dissolved phosphate. The remaining 70 percent of the runoff penetrates the soil and becomes part of the interflow, rapid groundwater flow, or long-term groundwater systems. Assuming that water that recharges the rapid and long-term groundwater systems also passes through the interflow zone, then potentially, all the remaining 70 percent of the total basin flow has dissolved about 3.0 mg/L of phosphates, as estimated for the interflow component. About 11 of the 70 percent leaves the basin as interflow, carrying 3.0 mg/L of phosphate, 51 percent at 0.8 mg/L (as rapid groundwater system), and the remaining 8 percent of the total outflow at 0.4 mg/L (long-term low flow).

Figure 6 shows the estimated phosphate budget within the basin. An estimated 45 percent of the total dissolved phosphate leaves the basin through runoff; the remaining 55 percent produces secondary mineralization.

The Possible Phosphate-Uranium Relation

Because oxidized uranium forms uranyl ions (UO_2^{+2}) and complexes with phosphates, as $UO_2(HPO_4)_2^{-2}$, in the pH range from 4 to about 7.5 (Dongarra and Langmuir, 1980), it is assumed that uranium tends to follow the dissolved phosphate cycle in terms of losses from the system and

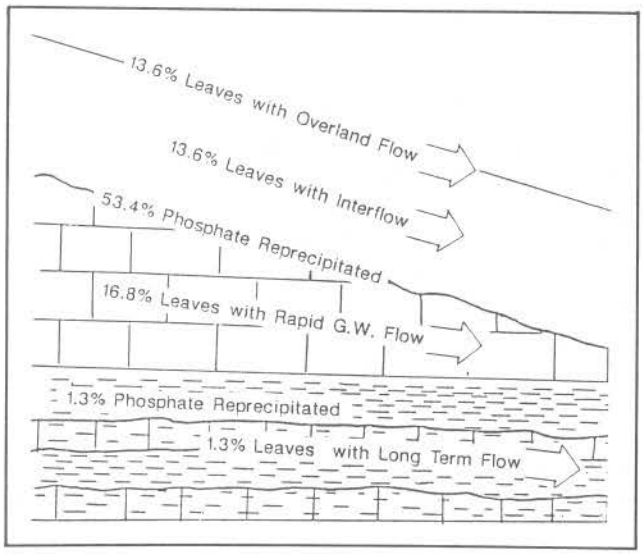


Figure 6 — Relative behavior of phosphate during weathering in the Cartwright Basin. Of the total phosphate dissolved in the Cartwright Basin, an estimated 45 percent leaves the system through stream runoff and 55 percent is assumed to reprecipitate in the basin.

also in its tendency to precipitate or coprecipitate with secondary phosphate minerals. As a result, perhaps about half the uranium mobilized in the aqueous phase during weathering is also reprecipitated as coatings on pre-existing phosphate minerals or by replacement of calcite with secondary phosphate minerals in the vicinity of the soil-bedrock interface.

During dissolution of phosphate minerals, any uranium, thorium, radium, and radon in the minerals would be liberated and some chemical fractionation would occur. Under the slightly acidic conditions in the soil zone and in the presence of about $10^{-4.5}$ m/L (or about 3 mg/L) total dissolved phosphate, some thorium (232 or 230) would be adsorbed on phosphate minerals or on amorphous and crystalline secondary iron minerals resulting from pyritic oxidation. Pyrite is a major constituent in the Chattanooga and in the shaly interbeds of the Catheys-Leipers Formation. Whether thorium-230 is incorporated on phosphate minerals or is sorbed into iron-bearing phases probably makes little difference. Its relatively short half-life helps insure that it will remain close to the surface; hence, when it decays, it is highly probable that thorium-230 is close enough to the surface that its daughter radium-226 may be active in weathering.

Chemically, divalent radium behaves differently from thorium; however, if thorium is intimately associated with a phosphate mineral, there is a high probability that radium could become reincorporated in the phosphate mineral by crystallographic substitution for calcium.

The nature of reactions involving daughter products from disintegration of uranium-238 will be affected by the immediate physical and chemical environments at the time of disintegration and afterward. If a uranium-238 atom or one of its daughters is deep within a mineral at the time of disintegration, the offspring is likely to be trapped within the structure until the mineral undergoes dissolution. In the open system of chemical weathering all minerals are transitory. In the upper and middle zones of the soil column, phosphate-bearing minerals are actively dissolved. At or near the soil-bedrock interface, chemical activity involving calcium and pH should increase, and thereby produce an environment where precipitation of phosphate minerals would be expected. In general, within the zone of active weather-

ing of any mineral the structural constituents and any trapped passive constituents are eventually dissolved. In a zone of secondary enrichment or precipitation, however, any structural or trapped constituents are buried deeper within the mineral as new growth takes place.

POSSIBLE ROLE OF PLANTS AND ORGANIC MATTER IN RELEASE OF RADON

Plants provide a means by which some of the weathered components can "short circuit" the weathering cycle. Because phosphate is a major nutrient, it is sought by plant rootlets in the soil. A zone or "atmosphere" of high hydrogen-ion activity is created around the rootlets by release of organic acids and/or through respiration of CO_2 from rootlets. In this acidic environment phosphate-bearing minerals are more soluble; thus, more phosphate (as H_2PO_4-) enters the soil solution. In plant fluids calcium is important as an electrolyte for pH control and also acts to bridge anionic sites on adjacent cell-wall proteins (Devlin, 1975). Use of calcium by plants is not all that specific, however, and is mainly a function of the general availability of calcium as a divalent cation. Other divalent cations can serve the same function and substitute for calcium. Radium is one such cation that plants should passively accept in place of calcium. Once in the plant, radium will remain until the plant dies or until defoliation and the decomposed plant materials return to the soil. In this manner radium and other chemical constituents picked up by plant roots at depth from the soil can be cycled back to the surface. Radium released through plant decay would be adsorbed on exchange sites of mineral surfaces or remain sorbed on or in humic materials. In either case the surface or near surface could become relatively enriched by radium in a form that would make its daughter, radon, much more available to enter the soil atmosphere near the surface. Phosphatic residuum-colluvium on hillside slopes is thin enough to be within easy "reach" of plant rootlets; it thereby makes soil humic-material a potentially important near-surface radium bearer in this region.

THE NEED FOR FIELD AND LABORATORY STUDIES

Field and laboratory studies are needed to locate regions of high radon emission (mainly in the field) and to define the physical and chemical processes that produce the anomalies (mainly from laboratory studies of samples collected in the field).

Field analyses for radon and its daughters should include gamma-ray surveys for bismuth-214, and alpha-track detectors similar to that of Alter and Price (1972) and "Lucas cell" scintillation detection for radon-222 (Lucas, 1957). The expected level of gamma-radiation will not be much above normal background. A ground-level survey would therefore probably not supply much information; nevertheless, such a survey is worth trying. Track detection probably offers the best method for obtaining analyses on time-integrated emission. Scintillation may be best for rapid measurements on transient soil gases and equilibrated samples (to be run in the laboratory).

Because the Chattanooga Shale generally crops out on hillsides, it would seem logical to deploy alpha-track detectors in a pattern of downhill transects. Starting at the Chattanooga outcrop, trenches in the colluvium-residuum would allow studies of the effects of mechanical and chemical breakdown during weathering. One sidewall could be misted to allow contact pH measurement of the sediment. Such pH measurements might provide a sediment-sampling guide for laboratory studies. For time-integrated measurements, alpha-track detectors could be attached to the sidewalls of a trench. Further below the Chattanooga, a sequence of pits and/or auger holes could be used to examine the sediments and determine their radon generation potential. Earth resistivity and/or shallow seismic surveys could be used to map the thickness of residuum and colluvium on hillsides.

In the laboratory, the radon generation potential of sediments collected from auger holes, trenches, and pits could be determined. Chattanooga Shale samples, equilibrated in water over several months, could be monitored for radon outgassing and changes in pH, total dissolved phosphates, sulfate, and other constituents.

Phosphatic materials, also equilibrated with water, could then be monitored for radon emanation and water chemistry changes as increments of acid are added; data on radon emanation as a function of phosphate mineral dissolution could thereby be generated.

The radon generation potential of organic matter should also be studied. Ashed leaves of several species of plants from areas of known high radon emanation could be equilibrated with water and air for monitoring of radon emanation. If the radon thus emitted is low, then this source might be considered to be relatively minor. If the radon emission is high, this source would warrant more careful study.

SUMMARY

In the Central Basin of Tennessee two uranium-rich stratigraphic intervals, the Chattanooga Shale and the phosphatic limestones of the Nashville Group, are exposed and provide major radon sources. Factors that appear to increase migration of radon from these sources into homes include the following:

1) Houses with partial basements and adjacent crawl spaces partly evolved in response to geomorphology of the area. These houses facilitate entrance of radon into them because the exposed underlying soil serves as a source and an avenue for radon migration.

2) Relatively thin soils, developed over extensive areas of phosphatic limestones, favor release of radon into the atmosphere. Even though uranium concentration in the phosphate minerals is low, this region appears to have exceptionally high radon emissions, compared to many other phosphate regions.

3) Chemical reactions associated with weathering should favor enrichment by uranium and its daughters through formation of secondary phosphate minerals in the weathering profile.

4) The topographic setting of the region (hilly terrain) and the stratigraphic relationships (uranium-bearing Chattanooga overlying the phosphatic limestones of the Nashville Group) may favor the leaching of uranium and its daughters from shale and subsequent enrichment by them in secondary phosphates in lower zones of residuum downslope from Chattanooga outcrops.

5) By uptake of radium as a nonspecific divalent cation (substituted for calcium in the plant structure) plants may actively bring phosphate-bound radium from depth to the surface. Subsequent defoliation or death of plants would leave radium-bearing organic matter at the surface. From there daughter radon could be easily released to the atmosphere.

Careful analyses of data collected from the cooperative study between the state and the Environmental Protection Agency should help focus future field and laboratory studies on the most probable sources and processes contributing to high radon activity in houses in central Tennessee.

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PROGRESS IN MEASUREMENTS OF SORPTION OF RADON ON POROUS MATERIALS AND IMPLICATIONS FOR THE RELEASE OF RADON AT THE EARTH'S SURFACE

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ABSTRACT

Migration of radon near the earth's surface and release to the atmosphere are important to a wide range of environmental and geophysical subjects, including control of radon release from radioactive tailings, uranium exploration, earthquake prediction using geochemical precursors, release of radon to the indoor air of buildings, and the budget of radioactive ions in the atmosphere. A long-debated issue is whether or not sorption of radon is an important process controlling migration and release of radon. Reports of poorly understood variations in radon release at the earth's surface are fairly common and it is possible that sorption phenomena might explain some of them. We have conducted preliminary laboratory measurements on various materials, including tailings, soil, rock, and building materials to identify more precisely the extent of radon sorption in porous materials. An adaption of the Brunauer, Emmett, and Teller (BET) procedure was carried out using radon-222 as the sorbent at temperatures between 0 and 30 degrees Celsius. Initial results indicate that the extent of sorption is quite varied, depending on such factors as the nature of pore structure, temperature, and the presence of competing polarizable gases, such as water vapor. Sorption might be more important in time-dependent (pulsed) effects and changes in the diffusion distance than in changes in the overall steady-state release of radon to air in pores. Dry materials with high clay contents or large internal surface areas are more likely candidates for sorption than wet materials or materials of low internal surface areas, such as sands.

INTRODUCTION

Migration of radon in porous materials at the earth's surface and release to the atmosphere are important to a wide range of environmental and geophysical subjects, including control of radon release from radioactive tailings, uranium exploration, earthquake prediction using geochemical precursors, entry of radon into the indoor air of buildings, and the budget of radioactive ions in the atmosphere. A long-debated issue is whether or not sorption of radon is an important process underlying migration and release of radon at temperatures characteristic of the earth's surface. There are many, often conflicting, reports of unexplained or poorly understood variations in radon release from rock and soil. For example, the recent review by King (1986) points out difficulties in studying radon release as a possible precursor for earthquakes, because of frequent unexplained background variations. Release of radon from soil and rock is a complex subject involving many variables, but it is conceivable that sorption of radon is one factor that could explain some of these poorly understood variations.

Authors tend to use the term adsorption, but since they often refer to experimental observations under environmental conditions absorption processes are probably not excluded. Tanner (1980) reviews information on adsorption of radon in porous materials. He concludes that for the dry, low-pressure lunar environment significant adsorption by rocks seems likely; however, he also concludes that the evidence for significant adsorption on porous materials at temperatures and humidities common at the earth's surface is conflicting. Several, more recent papers have also implied that sorption might influence release of radon to the air. Stranden et al. (1984) studied the effect of moisture and temperature on the release of radon from shale, soil, and concrete samples. They found striking effects, and postulated physical adsorption as a process that might explain observations. Gan et al. (1986) postulated desorption as a mechanism that could explain a number of their experimental observations, including a pulsed release of radon from tailings concurrent with a light rain.

The difficulty with much of the present experimental information is that alternate explanations to sorption are possible. For example, a common hypothesis is that increased moisture in porous samples can enhance release of radon, due to displacement of sorbed radon atoms by strongly polar water molecules. As discussed in Tanner (1980), however, increased moisture content can also enhance release of radon, by reducing embedding of recoiling radon atoms following decay of radium-226. Moisture content can change the physico-chemical form of the grains of the porous material and thereby further affect release of radon. Although increased temperature can enhance desorption of atoms, it can also cause gas expansion, and perhaps microfracturing in solids, processes leading to enhanced release of radon atoms.

Due to ambiguities in interpreting much of the existing experimental data, we decided to design laboratory experiments that would more directly measure sorption of radon on porous materials and provide less opportunity for ambiguous interpretation. We used a variant of the BET (Brunauer, Emmett, and Teller) procedure, a classic technique for studying sorption and internal surface area (Sing et al., 1985). Radon-enriched air was used as the gas phase instead of the customary argon and nitrogen, and the experiments were run at temperatures characteristic of the earth's surface rather than that of liquid nitrogen. In the remainder of this paper we will describe the initial experiments, present some preliminary results, and discuss implications concerning whether or not sorption is an important process affecting the release of radon at the earth's surface.

EXPERIMENTAL PROCEDURE

Figure 1 is a schematic diagram of the experimental arrangement used in the most recent experiments. After passage through a cooled condensation chamber and a drying agent (silicon gel), intake air passed through a radon-222 source to a series of vials containing the porous samples and controls. Flow rates of 5 to 30 ml/min were typical, resulting in radon concentration in the range of 30×10^6 to 5×10^6 Bq/m^3. Higher flow rates permitted more rapid exposure of samples; however, higher flow rates

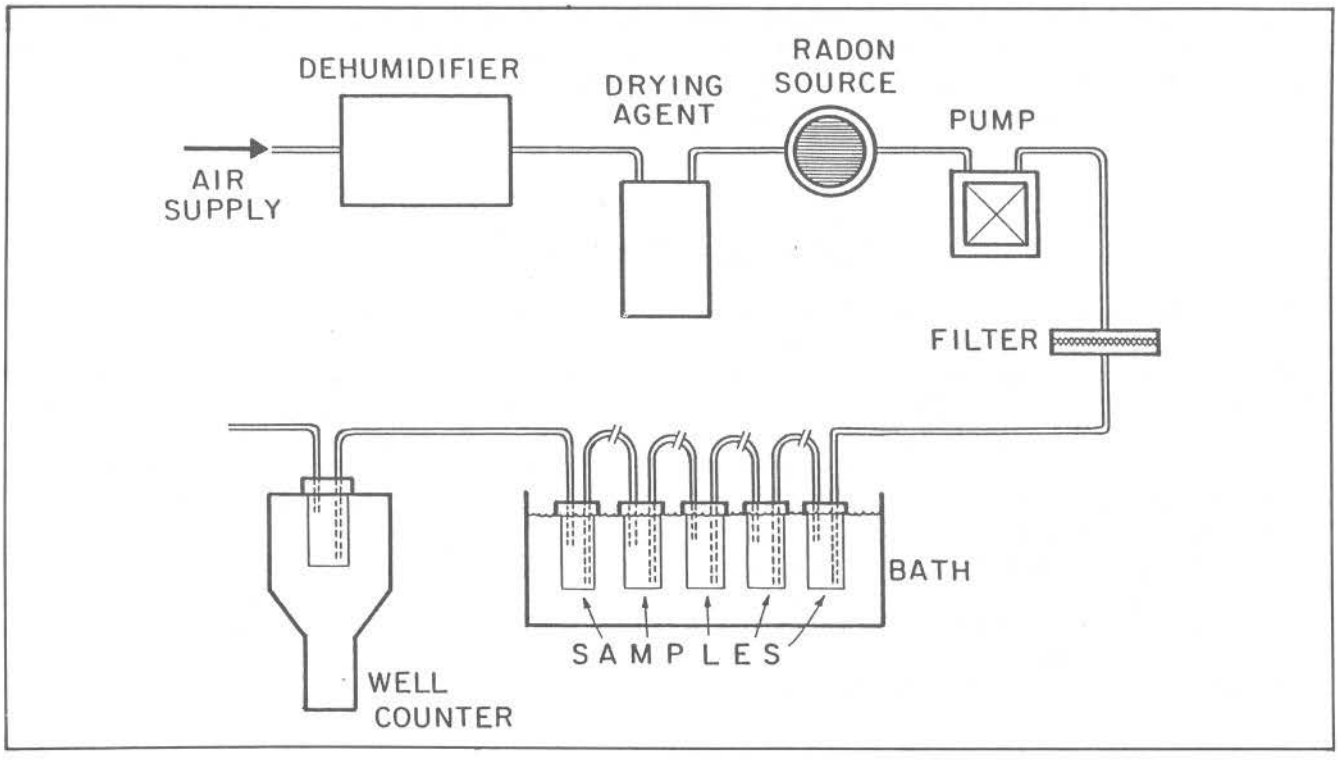


Figure 1 — Schematic diagram for the experimental arrangement to measure sorption on porous materials. About 5 cm³ of porous material were placed in each sample vial where exposure to radon took place.

result in lower radon concentrations. High radon concentrations were necessary to ensure good counting statistics and to supply a pre-gas radon concentration well above that radon released from radium in decay in the samples. Samples were exposed until steady state was reached in the gamma count rate. Exposure times of 12 to 48 hours were common.

Typically, six 7 ml vials were connected in series. One vial was a blank; another contained glass beads of known porosity as a control with negligible sorption. After steady-state conditions were reached, each vial was counted in a NaI well counter for about 5 minutes. Total counts were recorded, with the threshold energy set just below the 352 keV gamma from lead-214.

The sorption coefficient k (ml/gm, the volume of air containing the activity sorbed per unit mass of sample) was determined from

$$k=[N-N_b+C(V_m-V_e)]/(Cm), \quad (1)$$

where

- N = counts from the sample,
- N_b = a background correction,
- C = a constant, proportional to the radon concentration,
- V_m = the volume occupied by the grains of the sample (i.e., bulk volume less interconnected pore space),
- V_e = the empty volume of the container ($\sim$7 ml), and
- m = the mass of the sample.

The constants C and N_b were determined by solving the pair of equations that result from application of equation (1) to two cases: the empty vial, and the vial with glass beads, where k = 0 and the remaining terms were known.

The value of V_m was determined separately by porosity measurement using the gas expansion method (Collins, 1976). The vials were submerged in a constant temperature bath except for the short period during counting. For experiments involving moist samples and moisture-saturated air, the air was bubbled through water in an additional vial placed before the experimental string.

One difficulty with the present arrangement was significant contribution to the background N_b due to the use of plastic vials and plastic tubing between vials. Sorption of radon on the plastic

surface of vials was significant. Although the experimental procedure corrected for such sorption, it varied (increased) with time so use of low-sorption materials (glass or metal) would be preferable in future experiments. Moisture and temperature were critical parameters that could be more carefully controlled in future experiments.

EXPERIMENTAL RESULTS

Table 1 lists preliminary results for a few of the porous samples under study. In addition to the sorption coefficient k, results are quoted for r, the ratio of radon sorbed in the material to that residing in the pore space. The parameter r is important because it indicates what proportion of the mobile radon exists in the sorbed state rather than as a free gas in the pore space. Charcoal was included as a sample because k-values for it are available from the literature (generally in the range 4000 to 6000 ml/gm at room temperature). Given the estimated factor-of-two error for these preliminary results, the 3600 ml/gm result for charcoal provides confirmation of our procedure.

Accuracy of results was not limited by counting statistics but by the degree of control of temperature, humidity, and sample moisture. The values for r require accurate measurement of porosity, which can be difficult for samples of low porosity, such as concrete and certain rocks. Future refinements in the experimental technique should improve the precision of these measurements. Nevertheless, we feel the results of table 1 clearly demonstrate the presence of measurable sorption for soil, concrete, and ore samples.

DISCUSSION

UNDERSTANDING THE PHYSICAL PROCESSES INVOLVED IN SORPTION

Our preliminary experimental data, some of which are given in table 1, indicate measurable sorption in a number of porous materials of interest. However, the full picture appears quite complicated and will require much more experimental investigation. The extent of sorption is quite sensitive to temperature, moisture, and chemical and physical details of pore structure. For many materials at the earth's surface, pore structure is quite complicated and poorly understood.

One might hope that traditional fields of physical science could provide models enabling prediction of sorption. Such models exist, and in some aspects radon is an ideal candidate for such models. Radon is an inert gas, so pure physical adsorption is one indicated process. From the kinetic gas viewpoint the normal concentration of radon in pore air is so low that adsorption could be taking place in an ideal Henry's Law range with simple deposition in a monoatomic layer. Simple kinetic arguments for such ideal cases (Redhead et al., 1968) suggest

$$\sigma = \frac{3.5\times10^{22}\,p\,\tau_0\exp\left(\frac{E_p}{RT}\right)}{(MT)^{1/2}} \qquad (2)$$

where

- σ = surface density of adsorbed radon (atoms/cm^2),
- τ_0 = vibration time of an adsorbed atom (sec),
- p = the partial pressure of radon (Torr),
- T = temperature (°K),
- R = the gas constant, 8.31 J mole^{-1} K^{-1},
- M = atomic mass number, and
- E_p = the effective heat of adsorption.

Under the assumption that the internal surface area of a porous material can be characterized by the parameter s (specific surface area, cm^2/gm), from equation (2) the predicted adsorption coefficient k is (assuming $\tau_0 \sim 10^{-12}$ sec., Redhead et al. 1968)

$$k = \frac{9.9\times10^{-7}\exp\left(\frac{E_p}{RT}\right)s}{(MT)^{1/2}} \qquad (3)$$

Consider a hypothetical soil with parameters s = 10^5 cm^2/gm, porosity n = 0.35, and density ρ = 1.5 gm/cm^3 at a temperature of T = 290K. Choosing a value of E_p = 29 kJ/mole (from work with charcoal) gives a value for the sorption coefficient k of 66 ml/gm and for the ratio of the radon sorbed to that in the pore space $r = k_p/n = 280$. The predicted value for r is large and indicates significant sorption.

Unfortunately, even given that equation (3) is applicable, environmental samples are so complex that such estimates are unreliable. Surfaces are not pure, so choice of E_p for a specific soil or rock is not straightforward. Tanner (1980) discusses conflicting values of E_p from the literature, ranging from 18 to 57 kJ/mole. That range would result in a factor of about 10^7 variation in the predictions from equation (3) for the present example! Even given the relative large values of E_p for radon compared with other gases, there are still gases (such as water vapor) that have larger values of E_p and compete with radon for surface sites in a manner that makes it difficult to model. Furthermore, the sorption process need not be restricted to physical adsorption and could include other surface processes (such as implantation in multi-molecular layers) or non-surface processes such as solution (absorption). In short, estimates such as those from equation (3) indicate that significant sorption of radon may occur in common porous materials at ambient temperatures, but uncertainties are too great to make precise predictions.

Model estimates and preliminary data such as those shown in table 1 can, however, provide some qualitative insights into the sorption process. They predict that sorption strongly depends on temperature, with greater sorption occurring at lower temperatures. The data for the silt-sand-sized ore in table 1 support this prediction. It is well known from work with activated charcoal that the presence of moisture can significantly reduce the adsorption of other gases. The physical explanation is that water vapor has a very large binding energy (resulting in a larger value for E_p) and can fill up adsorption sites in charcoal and thereby prevent displacement by gases with smaller values of E_p. The data in table 1 for a sandy-silt soil support this hypothesis. Pure sand and baked brick have comparatively small internal surface areas as

TABLE 1
Measurements of the sorption of radon on porous materials

Material	Temp. (°C)	Humidity	k*	r**	Notes on material***
Charcoal	22	dry	3600	1600	Pittsburg activated carbon chip diameter ~3mm
Siliceous sand	23	dry	$\leq$0.05	$\leq$0.1	Porosity 0.41 ± 0.05
Sandy-silt soil	22	dry	0.2	1	Porosity 0.40 ± 0.05, near Ben Lomond Mine, Hg tests: median pore diameter 28 μm, pore area 2.6 m^2 gm^{-1}
	22	saturated	$\leq$0.1	$\leq$0.5	
Concrete	22	dry	0.1	3	Porosity 0.05 ± 0.03, made with ACSE Type A Cement
Brick	22	dry	$\leq$0.01	$\leq$0.1	Porosity 0.30 ± 0.05, baked brick, dry pressed
Silty-sandy ore	23	dry	0.2	0.2	Porosity 0.44 ± 0.05 Lake Way Mine, contains carnotite, Hg tests: median pore diameter 7.7 μm, pore area 12 m^2 gm^{-1}
	1	dry	1	6	

* Sorption coefficient (mg/gm), preliminary results with absolute error estimate about equal to a factor of two.
** Ratio of radon sorbed to radon in pores, preliminary results with absolute error estimate about equal to a factor of two.
***Soil and ore samples, and Hg porosimetry tests results, courtesy of K.P. Strong, Australian Atomic Energy Commission.

measured by the traditional BET procedure. Small radon sorption is predicted and is indicated in the data of table 1.

In addition to the strong dependence of radon retention on temperature and moisture, there are some less obvious consequences of the presence of significant adsorption. From basic kinetic theory, the diffusion coefficient for a trace gas in a carrier gas is expected to be proportional to the square-root of the temperature. With some modification in the power dependence, a similar relation is expected for porous materials (Tanner, 1980). However, if adsorption is significant in a porous material, diffusion may be a surface process rather than free diffusion through the pores. According to the model of Underhill (1977) the effective diffusion coefficient D_e is then proportional to the inverse of the adsorption coefficient k:

$$D_e = \frac{\gamma n D_o}{\rho k}, \qquad (4)$$

where γ is a tortuosity factor, n is porosity, ρ is the density of charcoal, and D_o is the diffusion coefficent for radon in air. Hence, the diffusion coefficient might increase much more rapidly (exponentially) with temperature than might otherwise be expected since models such as equation (3) predict an exponential dependence of k on T. One consequence is the presence of another temperature-dependent effect that may enhance release of radon with increased temperature. As an example of practical importance, diffusion barriers of non-radon-producing materials over radon-producing materials (such as soil layers over uranium tailings or concrete coverings over uranium-bearing rocks) that are quite effective at one temperature may not necessarily be effective at higher temperatures.

IMPLICATIONS FOR THE RELEASE OF RADON FROM POROUS MATERIALS AT THE EARTH'S SURFACE

Given the uncertainties described in the preceeding section, it is clear that it is currently impossible to make detailed or sweeping statements about the role of radon sorption under environmental conditions at the earth's surface. Adding to all the uncertainties of the sorption process itself are the wide range and poorly specified state of porous materials. Nevertheless, a few comments and speculations can be made.

The preliminary data and modeling suggest that sorption may be important in dry materials of high internal surface area and/or low porosity. Due to its small internal surface area, pure loose sand should therefore exhibit little sorption. Because of their higher internal surface areas, dry clays are likely candidates for significant sorption. Other things being equal, low-porosity materials, such as concrete, certain limestones, gneisses, and argillites, might have a greater *fraction* of their mobile radon sorbed than high porosity materials, such as sand, gravel, and many (moderately moist) soils.

Although porosity and surface area have interdependent influences there are some distinctions. Internal surface area affects the total sorption, whereas porosity affects the amount of mobile radon tied up in the pore space. The diffusion coefficients of lower porosity materials, other things being equal, might be more strongly temperature dependent. Under changing sorption conditions, such as increasing temperature or humidity, materials with high internal surface areas, other things being equal, would release more radon to the pore space.

At the earth's surface, increased moisture (e.g., from rain) or increased temperature could result in increased release of radon, at least transiently; however, the overall effects of rain and temperature can be complicated. It is well established that if there is enough rain to seal pores in soils and rocks, exhalation of radon will be *reduced,* due to reduction in the diffusion coefficient. In a careful study of loamy soil with 4 weight percent moisture content, Schery et al. (1984) saw little evidence of increased radon exhalation due to insolation. One interpretation is that little sorption occurs, due to the significant initial moisture content. Other possibilities are (1) that internal surface area was less than that in the case reported by Gan et al. (1986) or (2) that the temperature effect is not as strong as the moisture effect they observed.

Effects of temperature and moisture would vary depending on the nature of the sorption process. For pure physical adsorption, residence times of radon on surfaces can be as small as picoseconds. Under steady-state conditions the surfaces would reach equilibrium with residence times much shorter than the radon half-life. The *steady-state* emanation coefficient, for example, measured by an experiment sweeping out pore air, would not change. On the other hand, transient effects could result in *pulsed* release of radon, upon heating, due to the temperature-dependence of the sorption coefficient. A similar pulse might be observed with increased humidity.

Actual release of radon at the earth's surface could be complicated by the previously hypothesized shift from surface diffusion to free diffusion in the pore spaces. Such a shift may result in a larger steady-state diffusion coefficient. As radon atoms could diffuse farther before decaying, deeper radon sources could contribute to release of radon at the surface, and thereby cause an overall increase in the steady-state radon emanation.

A major objection to the importance of ideal physical adsorption near the earth's surface is the common presence of moisture-saturated air in the soil and rock pores. Other sorption processes, such as solution, deserve serious consideration, and warrant further laboratory studies to determine details of the sorption process. The solution process should also be temperature-dependent (decreased solution with increased temperature) but the timing factors would be more complicated (Holub, R., private communication, 1987). Clearly much work remains to be done.

CONCLUSIONS

Given the limited extent of previous studies of sorption under environmental conditions and the preliminary nature of current data and modeling, only modest conclusions can be drawn:

1) Laboratory studies clearly demonstrated the presence of measurable sorption in some common porous materials at the earth's surface, at naturally occurring temperatures under dry conditions. Materials such as dry clay, soils, and tailings exhibited measurable sorption, whereas sorption in pure sand was not detectable.

2) Sorption might significantly affect the temperature dependence of the effective diffusion coefficient for radon. A larger diffusion coefficient will enhance release of radon at the earth's surface.

3) It is feasible that increased temperature and moisture could enhance release of radon from initially dry materials. Ideal physical adsorption might result in a transient "pulsed" effect, whereas more complicated sorption processes would be needed to explain steady-state or more complicated time-dependent effects.

4) Sorption might explain some of the poorly understood variations in radon release detected at the earth's surface; however, the experimental evidence is conflicting and inconsistent. Given the pervasiveness of moisture in soil, rock, and other materials, it is difficult to understand how simple sorption processes such as physical adsorption could account for many of the anomalies. Non-sorption explanations can also account for many variations due to temperature or rain. It may even be necessary to postulate more complicated sorption mechanisms.

5) Improved laboratory studies of radon sorption on environmental materials are feasible and should provide valuable insight into the unanswered questions. Sorption time-dependency studies would be particularly valuable.

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MEASUREMENT OF RADON AVAILABILITY FROM SOIL

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ABSTRACT

A method is under development to evaluate the intrinsic ability of the ground at a specific site to be a source of indoor radon. Radon availability, a quantity that indicates a practical upper limit to the amount of radon that can be drawn into a structure from the soil, is here defined as the radon concentration in the soil pores multiplied by the mean one-dimensional migration distance of radon in a homogeneous soil. This distance is calculated from the effective diffusion coefficient and a steady-state convection velocity calculated from the gas permeability of the soil in question, by using an arbitrary standard driving-pressure difference. From estimated extreme ranges of radon concentration, effective diffusion coefficient, and gas permeability, radon availability values should range from 10 Bq/m^2 (3 x 10^2 pCi/m^2) to 10^8 Bq/m^2 (3 x 10^9 pCi/m^2), although it is unlikely that the higher end of the range would be realized. A practical method of determining radon availability is based on analyzing the radon concentration in air drawn from a small augered hole in the ground, simultaneously measuring permeability in situ, and estimating the effective diffusion coefficient by means of soil type and moisture content. Measurements are being made in places where indoor radon concentrations are known, in order to test the utility of the method and the spatial and temporal variations of radon availability.

INTRODUCTION

The world literature on indoor radon has clearly indicated that where indoor radon levels are high enough to be of unusual concern to health, radon entry from the ground is usually the principal source. Considerations of surface radioactivity and geologic characteristics of near-surface materials show some promise for the evaluation of radon hazard potential on a regional basis, but airborne and ground radiometric surveys and geologic maps are not usually adequate to indicate the degree of radon hazard potential at a given site. Airborne and surface radiometric surveys measure radiations from only the uppermost 20 to 30 cm of soil and do not necessarily indicate the degree of uranium-series radioactivity at the depth of a basement slab. Maps of permeability, degree of water saturation, and drainage, which are relevant to radon movement in the soil, are not usually available at a scale adequate for evaluation of specific sites. Developers, consultants, mortgage insurers, and health authorities have expressed need for a site-specific procedure. This paper addresses the need for a protocol to measure the ability of soil to supply radon to a structure. It should be understood that the method is not designed to predict the radon concentration in a structure, because the concentration also depends on characteristics of the structure, door- and window-opening habits of its occupants, and many other factors unrelated to the intrinsic capability of the ground to supply radon. Eaton and Scott (1984) defined a "radon index number" that involves both soil and house characteristics; however, it has not become a matter of practice (R.S. Eaton, oral communication, 1986).

THEORETICAL BASIS

The mechanisms of radon movement through the ground to the subsurface shell of a structure are primarily molecular diffusion and convective or advective transport. Although convective transport does not apparently always dominate where significant radon entry occurs (Holub et al., 1985), it is believed to be more important, in general, than diffusion (see, for example, Åkerblom et al., 1984; Nazaroff and Doyle, 1985; Nazaroff et al., 1985; Nero, 1985; Nero and Nazaroff, 1984; and Sextro et al., 1987).

A RADON AVAILABILITY PARAMETER

A parameter that is to be used to describe the availability of radon from the ground must take into account not only the concentration of radon in the soil pores but also the ease of movement by both diffusion and convective-advective transport. The formulation of the parameter and its measurement are somewhat arbitrary; no optimum choice for either is obvious. A widely applicable parameter is developed here for a structure emplaced in homogeneous ground at some depth below grade. A mathematically equivalent, simpler method that is applicable to sites for crawl-space and slab-on-grade structures is given briefly in the section on procedures.

Radon entry may occur through the horizontal slab, the vertical subgrade foundation walls, and any cracks or other openings between them. Subslab aggregate and backfill tend to enhance permeability immediately adjacent to the foundation; therefore, the entire subgrade shell must be considered as an entry surface, and the adjacent ground, both below and beside the foundation, as the source. Consider a model (fig. 1) in which the subgrade foundation walls are unfolded outward to lie in the plane of the slab. Edge and corner effects, the near-surface depletion of radon in the soil, vertical variation of diffusivity and permeability of the soil, and variations of radon concentration with depth may be ignored, because the method is to be calibrated empirically. A porous solid whose horizontal shape is defined by the unfolded foundation area and whose height is equal to the mean migration distance for radon (the distance of migration during one mean life, 5.52 days) contains an amount of radon that represents the maximum that could be sustained in the structure if it were perfectly efficient at drawing in and retaining soil gas having that radon concentration. The volume of the porous solid is proportional to the subgrade foundation area. To the extent that the volumes of structures are roughly proportional to the subgrade area of their foundations, the amount of radon available to them is independent of the sizes of the stuctures, and depends only on the radon concentration, porosity, diffusivity, and permeability of the ground. A logical parameter

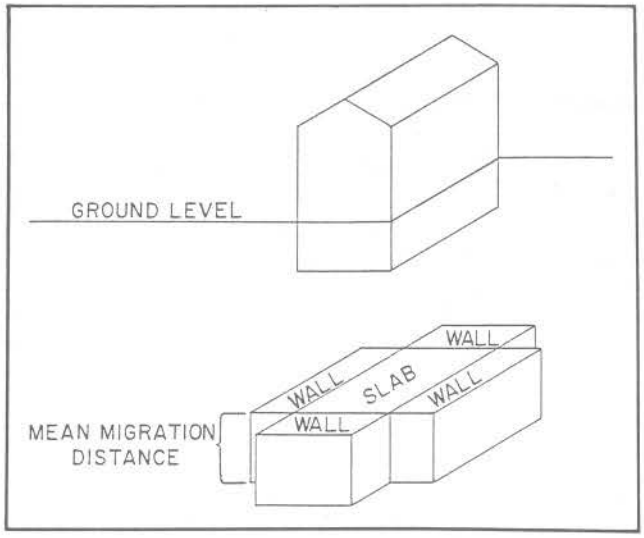


Figure 1 — Scheme of the model used to define the radon availability parameter. The subgrade foundation walls are unfolded outward to lie in the plane of the projection of the building slab. A solid of the same porosity as the investigated soil has a height equal to the maximum mean migration distance of radon averaged over the geometrical volume of the solid (that is, multiplied by the porosity). The amount of radon contained in the pores of the solid is assumed to be the worst-case amount that could enter and be retained by the building.

for radon availability is then the amount of radon contained in the solid per unit horizontal surface area, equal to the product of radon concentration in the pores of the solid times the height of the solid, which is the mean migration distance. For example:

$$\frac{\text{pCi (Rn)}}{\text{m}^2\text{ (horizontal surface area)}} = \frac{\text{pCi (Rn)}}{\text{m}^3\text{ (solid)}} \times \text{m (mean migration distance}$$

The mean migration distance is an extension of the well-known diffusion length parameter (equal to the square root of the ratio of effective diffusion coefficient to the product of the porosity and the radon decay constant) to movement by a combination of diffusion and convection-advection. If one measured the mean migration distance (the distance over which a radon stream was reduced by decay to 1/e of its original concentration) in the interstitial space, the height of the porous solid model would be too great. The radon stream from the solid issues only from the pores. The radon flux density through the horizontal surface of the solid is equal to the flux density through the porous part of the horizontal surface times the porous fraction, which may reasonably be assumed to be equal to the porosity of the solid. Hence, the interstitial mean migration distance must be multiplied by the porosity in order to be used for the calculation of the radon availability number.

Because the convective component of migration depends on the driving pressure gradient, I have adopted an arbitrary pressure difference of 5 Pa, based on the experience of the Lawrence Berkeley Laboratory Indoor Air Environment Program (R.G. Sextro, 1987, oral communication).

ANTICIPATED VALUES OF RADON AVAILABILITY NUMBER

The radon availability number (RAN) is defined above to be

$$RAN = [Rn] M_i \epsilon$$

where [Rn] is the interstitial radon concentration, M_i is the interstitial mean migration distance, and ϵ is the porosity of the ground. In SI units, [Rn] is in becquerels per cubic meter (Bq/m^3); 1 pCi/L equals 37 Bq/m^3. M_i is in meters, and ϵ is dimensionless; the RAN is consequently in units of Bq/m^2, or more conveniently, in kBq/m^2.

A minimum value of the RAN may be estimated by considering that basalts (among the least radioactive of common rocks) contain about 1 ppm uranium, or 0.33 pCi of radium-226 per gram, that a basaltic soil might emanate into the pores as little as 5 percent of the total amount of radon generated and have a porosity as great as 40 percent, and that with nearly water-saturated conditions the mean migration distance would be as little as 0.01 m (under which conditions practically none of the radon in soil gas would be lost to the atmosphere). The pore concentration of radon may be calculated to be 75 pCi/L, and the RAN is then

$$75\ (\text{pCi/L}) \times 37 \times 0.4\ (\text{porosity}) \times 0.01\ (\text{m}) = 10\ \text{Bq/m}^2.$$

A maximum value may be estimated by considering that soil-gas radon concentrations of nearly 10^5 pCi/L and radon concentrations of about 0.6 μCi/L of groundwater have been found, and that a coarse sand could have a porosity as low as 30 percent and a mean migration distance of about 17 m. Although such conditions substantially overesti-

TABLE 1
Some calculated radon availability numbers

Location	Soil type	RAN (kBq/m^2)	Indoor Rn (pCi/L)
Montgomery County, Maryland	sandy loam	9, 4	2
Fairfax County, Virginia	clayey silt	32, 25, 11, 4	21
Socorro, New Mexico	gravelly sandy loam*	20	No structure
Spokane, Washington	well-sorted sand**	20	100-200
Lehigh County, Pennsylvania	sandy clay loam	4-150	43
Berks County, Pennsylvania	coarse sand	10^3	$>10^3$

* Schery et al. (1984)
**R. G. Sextro, oral communication, 1986

mate any likely circumstances, the maximum RAN would be

$$0.6\ (\mu Ci/L) \times 10^6\ pCi/\mu Ci \times 37 \times 0.30\ (porosity) \times 17\ (m) = 10^8\ Bq/m^2.$$

Some RANs calculated to date are given in table 1. They suggest that a RAN of less than 2 kBq/m^2 implies that indoor radon problems are unlikely, and that a RAN of more than 20 kBq/m^2 implies that problems are likely.

APPARATUS FOR DETERMINING RADON AVAILABILITY

The determination of radon availability entails boring a small-diameter hole in the ground to be tested, inserting a testing probe, sucking soil gas from the ground through the probe under carefully monitored conditions, measuring the alpha radioactivity of the soil gas, determining the permeability of the ground at the sampling point, from the monitored pressure and flow, estimating the diffusion coefficient, computing the mean migration distance, and calculating the RAN.

In practice, the most difficult parts of the procedure can be selecting the depth at which the sample is taken and boring the hole. The depth selected should, if possible, meet several criteria: (1) it should be deep enough that the radon concentration measured will approach the value undepleted by exhalation to the atmosphere; (2) it should be at the approximate depth of the slab of the structure anticipated to be built at the site; (3) it should bottom in the most permeable layer of soil within about 1 m of the slab depth; and (4) it should bottom in the layer of greatest radium concentration. Obviously a single depth may not satisfy all criteria, and at many sites it is not possible to drill to such depth because of interfering rocks or bedrock. The holes drilled in this research are 3.5-cm in diameter and are bored by means of a conventional soil auger or an electric drill driving a rod with an attached wood auger bit reinforced with a hard alloy on the cutting edges.

Figure 2 is a diagram of the apparatus currently used. The probe contains four conduits of small-diameter copper tubing, each of which passes into and out of the main pipe but does not communicate with the air space within the pipe. A bicycle pump applies air pressure to the air space in order to inflate the two rubber packers to seal the augered hole. Inflation of the packers creates a space, the "waste" space, in the hole between the packers and another space, the "sample" space, below the lower packer. In operation, the waste pump draws a slightly greater suction on the waste space than the sample pump draws on the sample space. The waste space acts as a guard to intercept atmospheric air, even that passing through the ground near the hole, from entering the sample space or cavity, and also limits intake of soil gas into the sample tube, to that from the lower hemisphere of ground centered at the lower packer. This design was invented by Gerald L. Hassler (1940).

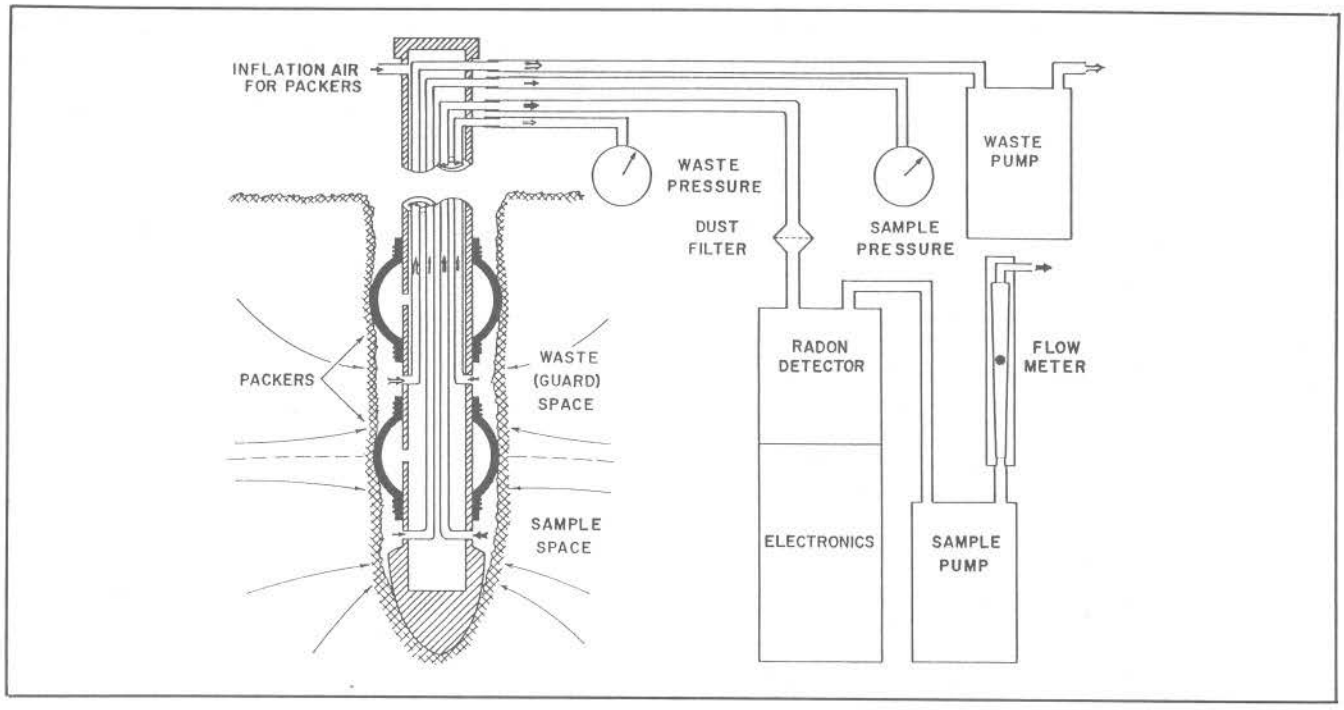


Figure 2 — Schematic diagram of apparatus for extracting and measuring radon concentration of soil gas and measuring flow rate and driving pressure for permeability calculation. The sampling probe (at left) is of 3.15-cm maximum diameter; 1.4- and 2.7-m-long probes have been made. The packers are rubber sleeves of 3.2-mm thickness and are bound to the probe pipe by several wraps of 1.0-mm galvanized steel wire. The pumps are small battery-operated personal air samplers. If the sample pump has any bypass or relief paths whereby the intake and exhaust flow rates are not identical, it is necessary to put the flow meter (a rotameter) in the sample line between the radon detector and the sample pump.

PROCEDURES

SOIL-GAS EXTRACTION METHOD

In order to determine the RAN, the following steps are performed:

1) The sampling hole is augered. A sample of the final auger cuttings may be taken for determination of the water content, radium concentration, and other characteristics.

2) A background count is started with the radon detector, an alpha scintillation flow counter. One-minute counts are used.

3) The sampling probe is inserted and the packers are inflated.

4) Hoses from the four tubes in the sampling probe are attached to the respective connectors on an instrument box on which the pumps and gauges are mounted.

5) The absolute atmospheric pressure is recorded.

6) Suction is applied to the waste space by means of the waste pump.

7) Flow is started from the sample space through the dust filter, the radon detector, the sample pump, and the flow meter.

8) When the flow rate and the pressure have been steady for a minute, the flow meter reading and the pressure difference between the sample space and the atmosphere are recorded.

9) When the counting rate shows no further ingrowth of polonium-218, the sample pump is stopped and flow through the radon detector ceases. The counting rate during the last minute of flow indicates the combined activity of radon and its decay products, of thoron (radon-220) and its decay products, and of background. Another count between the third and fourth minutes after

flow ends is made to obtain the activity less that of thoron and its decay products.
10) The waste pump is stopped, the packers are deflated, the sampling probe is removed from the hole, and the hole is backfilled and covered.
11) Four minutes after sample flow is stopped, atmospheric air is pumped through the radon detector for a 10-minute flush and background reading. The field procedure is now completed.
12) The flow rate is determined from the flow meter calibration chart or function and the permeability is calculated. For the small pressure differences used in the soil-gas extraction (less than 2 kPa, or less than 2 percent of atmospheric pressure), the calculation may be made from the formula (A.B. Tanner, manuscript in preparation),

$$k\,(m^2) = \frac{4.8 \times 10^{-9}\, Q_V(L/min)}{r_W(cm)\; p(Pa)},$$

where k is the permeability, Q_V is the volumetric flow rate, r_W is the radius of a hemisphere having the same surface area as that of the borehole below the lower packer, and p is the difference between the atmospheric pressure and the pressure in the sample space.
13) The effective diffusion coefficient, D_e (the coefficient of concentration gradient in Fick's first law), must be estimated by some means. The interstitial effective diffusion coefficient, D, is equal to D_e/ϵ, where ϵ is the porosity of the medium. In quite dry porous media over a wide range of grain size, D is about 7×10^{-6} m^2/s. Nielson et al. (1984) have shown from modeling and experimental data that D is reduced to about 2×10^{-6} m^2/s at 40 percent water saturation, to about 2×10^{-7} m^2/s at 80 percent saturation, and to about 2×10^{-8} m^2/s at 90 percent saturation. Rogers et al. (1984) have fitted experimental values of D to the value of pore water saturation, m, and the porosity, ϵ, by the relation,

$$D = 0.07 \exp\left[-4(m - m\epsilon^2 + m^5)\right].$$

An estimate of the water saturation and porosity of the soil can therefore yield an estimate of the diffusion coefficient; note below that the diffusion coefficient appears under the square root sign, so that errors of improper estimation are not great.
14) The mean migration distance on a geometric volume basis is computed by the following steps:
a. Pressure in the porous solid of figure 1 is assumed to increase with depth at steady state at a gradient of dp/dz = -5 Pa/m. (The vertical axis, z, is positive upward.)
b. The resulting upward steady-state velocity component of migration is calculated by the Darcy relation (neglecting gravitational effects),

$$v = -(k/\mu)(dp/dz),$$

where k is the permeability (m^2) and u is the dynamic or absolute viscosity of air (1.82×10^{-5} Pa·s at 290 K and 1.01 kPa pressure).
c. A trial mean migration distance M, is obtained from a formula due to Clements (1974):

$$M = \left(\frac{v}{2\sqrt{\epsilon \lambda D_e}} + \sqrt{\frac{v^2}{4\epsilon \lambda D_e} + 1} \right) \sqrt{\epsilon D_e / \lambda},$$

where ϵ is the porosity, λ is the decay constant of radon, and D_e is the effective diffusion coefficient.
d. It is assumed that the pressure difference is distributed linearly over a depth equal to the distance over which a one-dimensional flux of radon diminishes one hundredfold by decay, equal to 4.6 times M. The arbitrary pressure difference of -5 Pa is divided by 4.6 M, and compared with the trial value of -5 Pa/m from step a. A new value of dp/dz is chosen to yield a value of M that will cause [(dp/dz)4.6M] to approach -5 by an iterative process until the error is less than an arbitrary 1 percent. The computation is easily performed in a small computer.
15) The radon concentration is obtained by the appropriate conversion of the net radon-plus-polonium-decay-product count to pCi/L or Bq/m^3. If the counter has been calibrated for radon in equilibrium with its decay products, the result should be multiplied by 1.5. The value obtained may also need to be increased to compensate for depletion due to exhalation to the atmosphere. The most satisfactory way to determine the needed compensation is to make radon measurements at several depths, until progressive increases in depth yield little further increase of radon concentration. In moist soils, measurements at depths of 1 m or more should yield near infinite-depth concentrations.
16) The result of step 14 is multiplied by the result of step 15 to give the RAN. Note that the concentration in pCi/L should be multiplied by 37 to obtain Bq/m^3. The final RAN should be given with no more than two significant figures if the first digit is less

than four or one significant figure if the first digit is greater than three.

FLUX MEASUREMENT METHOD

An alternative procedure, applicable to crawl-space or slab-on-grade housing sites, is to measure the radon flux density from the ground surface to the atmosphere at the same driving suction (5 Pa) as is used for the computation of the RAN, and to multiply the flux density by the mean life of radon ($1/\lambda$ in the appropriate time units). The result is equal to the RAN for isotropic ground. Instrumentation for flux density measurements has been reviewed by Collé et al. (1981).

UNCERTAINTIES AND PROBLEMS

The radon availability procedure has several associated uncertainties that must be evaluated by research and experience.

As suggested above, it appears that a RAN between 2 and 20 kBq/m^2, a range subject to change as experience accumulates, is equivocal. There is no indication at present whether the percentage of RANs falling in the equivocal range is desirably small or so great as to make the procedure worth little.

Real soil in the zone of interest often has significant vertical and lateral variations in radium concentration, permeability, and diffusion coefficient. A valid RAN requires data from enough sampling points to provide typical values for the RAN calculation. At some sites the sampling density might need to be unreasonably great. Supplementary measurements such as density, moisture, and gamma-ray logging might facilitate characterization of a site.

In addition to point-to-point changes, the relevant soil characteristics can be expected to vary with time and season under the influence of precipitation, barometric pressure changes, and sealing of the ground by freezing. The variation is great at depths less than 1 m below the surface. There are practically no data on temporal variation of radon concentration below 1 m, excluding data from passive detectors, which do not measure a constant fraction of the radon concentration in soil gas. It is to be hoped that making the measurements at greater depth results in more consistent data.

Preliminary experiments have shown that stopping suction on the waste space does not nearly double the flow rate at the sampling point as expected; therefore, assumption of hemispherical or spherical flow is not entirely correct. Because of the typically greater horizontal than vertical permeability of soils, most of the flow may be cylindrical and little affected by flow from the waste space and above. Experiments are needed to quantify errors in permeability determinations associated with the radon availability procedure.

In many soils, particularly in moist climatic zones, the soil permeability can be confidently assessed as less than 10^{-11} m^2. Sextro et al. (1987) have shown that in soils of permeability significantly lower than 10^{-11} m^2, diffusion is so dominant as to make the permeability (and perhaps the permeability measurement) unimportant. For such soils it should be possible to reduce the field measurements to determination of the radon concentration and some estimator of the diffusion coefficient.

The radon availabilty procedure is conceived primarily for use in characterizing undeveloped sites. Subsequent site preparation and construction may so modify the land that the RAN is no longer accurate. This effect must be evaluated at actual construction sites throughout the course of development.

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GROUNDWATER GEOCHEMISTRY AND RADON-222 DISTRIBUTION IN TWO SITES ON THE READING PRONG, EASTERN PENNSYLVANIA

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ABSTRACT

High levels of indoor radon-222 (Rn) have been found in houses built on the Reading Prong, a continuous exposure of Proterozoic metamorphic rocks trending northeastward from Reading, Pennsylvania. The radon-222 is derived from radioactive decay of uranium-238, with which these rocks are enriched. Radon-222 is present also in the groundwater in these fractured crystalline aquifers. Groundwater samples were taken from 31 domestic supply wells in two areas and were analyzed for total uranium, radon-222, and radium-226 (Ra). The highest radon-222 and uranium concentrations were in water from mylonitized quartz-feldspar gneiss. Radon-222 concentrations as high as 100,000 picocuries per liter (pCi/L), and total uranium concentrations as high as 200 pCi/L were measured. Radium-226 concentrations ranged from 0.1 to 10.1 pCi/L, but seldom exceeded 1 pCi/L.

Secular equilibrium between radon-222 and uranium-238 is not attained in any of the samples. In every case, radon-222 activity greatly exceeds that of uranium-238; thus, the source of the dissolved radon-222 lies ultimately in solid-phase uranium-238. Likewise, radium-226 activity is lower than that of radon-222 in every sample. Data suggest that uranium concentrations in oxidized groundwater are independent of major chemical parameters such as pH and carbonate concentration, but depend strongly on aquifer rock type. Reduced groundwater, restricted to two narrow zones of mafic gneiss, contains uniformly lower uranium concentrations (<1 pCi/L); therefore, aquifer rock type appears to be the dominant factor in determining the radon-222 potential of groundwater in the two studied sites in the Reading Prong.

INTRODUCTION

Although the issue of indoor radon and its sources has received considerable attention, there is still little information concerning the source(s) of radon-222 dissolved in groundwater. Most studies of radon-222 in groundwater have been aimed at characterizing radon-222 values for statistical or geochemical exploration purposes (cf. Dyck and Tan, 1978; Prichard and Gesell, 1983; Loomis, 1987) or at understanding the hydrologic processes governing radon-222 availability (cf. Brutsaert et al., 1981; Rumbaugh, 1983; Wathen, 1986). Few studies examined the role that specific chemical processes may play in controlling radon-222 availability. This paper presents results of a field study designed to understand the source(s) of the radionuclides uranium, radium-226, and radon-222 in domestic groundwater-supply wells from two areas in the Reading Prong physiographic province of eastern Pennsylvania.

In addition to radionuclide concentrations, other groundwater geochemical parameters were measured, including pH, dissolved oxygen, and major and trace cation and anion concentrations. This paper describes the chemical behavior of the radionuclides.

GEOLOGY AND GROUNDWATER CHEMISTRY OF THE STUDY AREAS

The study was performed in two areas in the Reading Prong (figs. 1 and 2), near Boyertown and Easton, Pennsylvania. The geology of both is dominated by a complex sequence of metamorphic rocks of varying grade and composition. Structural features such as folding, faulting, and foliation further complicate geologic interpretation. Specific geologic characteristics of the two areas are briefly summarized below; for a more detailed description of the geology, the reader is referred to Gundersen et al. (1988) and Drake (1967).

Rocks in the Boyertown study area (fig. 1) constitute a metasedimentary sequence that includes interlayered biotite and quartz-feldspar gneisses, and hornblende-pyroxene gneisses. The more mafic gneisses contain relatively low amounts of uranium, and may contain sulfide minerals such as pyrite. Groundwater in the mafic gneisses typically has low or below-detection dissolved oxygen concentrations, high iron concentrations (up to several parts per million), variable pH, low uranium concentrations, and variable radon-222 concentrations. The quartz-feldspar gneiss (QFG) contains abundant uranium, sometimes in discrete grains of uraninite, or in uraniferous minerals such as allanite, monazite, or sphene. The QFG has been severely mylonitized, and groundwater flow through this rock unit is probably controlled by the structural anisotropy of the rock. Groundwater in the QFG has generally low pH (5.2-6.2), high dissolved oxygen contents, and high concentrations of dissolved uranium and radon-222. Weathered surfaces of the quartz-feldspar gneiss typically are iron-stained, a fact that is discussed later in some detail.

The Easton study area (fig. 2) contains gneisses of variable composition, which represent a metasedimentary sequence. The rock units in the area include interlayered quartz-feldspar and biotite gneisses, sillimanite gneiss, and marble. The quartz-feldspar gneisses are enriched in uranium from uraninite or other exotic uraniferous minerals. Limestones of the Lower and Middle Cambrian Leithsville Formation underlie and crop out to the north of the quartz-feldspar gneisses. Groundwater in the quartz-feldspar gneiss generally has low pH and high dissolved oxygen, uranium, and radon-222 contents. In one of the wells sampled, the water had relatively higher pH (6.7), alkalinity (100 ppm HCO_3), and total dissolved solids (nearly twice the average of the other samples); these factors indicate that the water was a mixture of limestone- and quartz-feldspar-derived groundwaters.

METHODS OF SAMPLING, ANALYSIS, AND DATA TREATMENT

Samples were collected from private domestic-supply wells. Before sampling, each well was pumped until temperature and specific conductivity stabilized (usually 10-20 minutes). Field analyses were conducted for concentrations of dissolved oxygen and radon-222, as well as pH, temperature, specific conductivity, and alkalinity. Table 1 lists a summary of the methods used and detailed references for each.

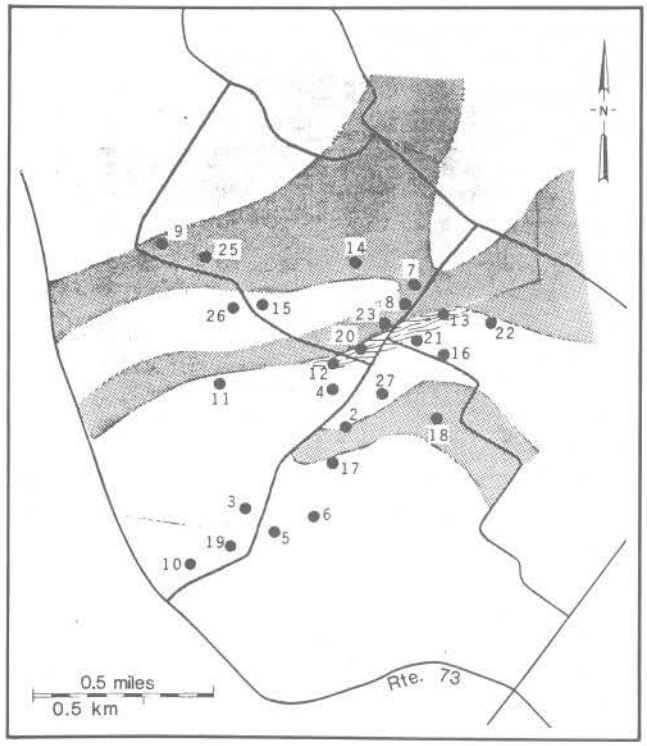


Figure 1 — Geologic sketch of the Boyertown study area. Dots show the sample locations. Numbers correspond to table 2. The light and intermediate stippled patterns represent various mafic gneisses. The hachured pattern near the center is the quartz-feldspar gneiss unit. For a detailed description of the geology of the Boyertown area, see Gundersen et al. (1988).

In addition to field analyses, samples were collected for later laboratory analysis. They were filtered through a 0.45 micrometer filter, collected in polyethylene bottles, acidified to pH < 1 with concentrated HNO_3, and returned to the laboratory for major and trace cation and major anion analyses. The cations were analyzed by inductively coupled argon plasma atomic-emission spectroscopy; the anions, by ion chromatography.

The chemical data were entered into a geochemical model to determine the saturation state of the groundwaters with respect to certain solids. The program used was PHREEQE (Parkhurst et al., 1980), a geochemical computer program for modeling natural processes. In the simplest model runs, PHREEQE was used to calculate the equilibrium distribution of aqueous species, and to determine the saturation state of various phases in the groundwater. The saturation state of the water is quantitatively expressed as the saturation index (SI), defined as the logarithm of the ratio of the ion-activity product of a solid to its solubility-product constant. Positive values of SI indicate supersaturation of water with respect to the solid; negative values indicate undersaturation, and an SI of zero indicates equilibrium. For further details about the method of calculation and theoretical fundamentals, see Truesdell and Jones (1974) and Parkhurst et al. (1980).

CHEMISTRY OF THE RADIONUCLIDES

It is important that a distinction be made between secular and chemical equilibrium. Secular equilibrium refers to the condition in which the radioactivity of all elements in a decay series is equal within the chosen system. Attainment of secular equilibrium in that system is time dependent. Chemical equilibrium is a broad term that includes mass-action processes such as precipitation, dissolution, complex-ion formation, adsorption, desorption, etc. Attainment of chemical equilibrium is governed by the laws of thermodynamics. Secular and chemical equilibrium are in no way related. As shown in this paper, the tendency of groundwater to approach chemical equilibrium with aquifer minerals may cause it to deviate further from secular equilibrium.

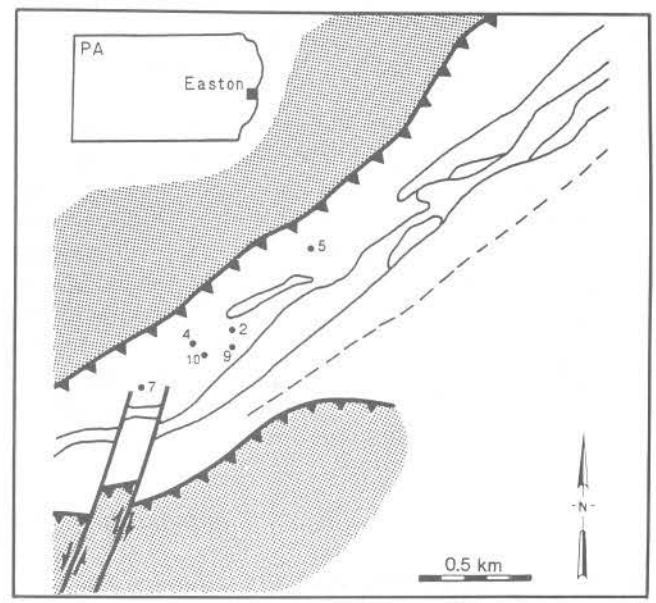


Figure 2 — Geologic sketch of the Easton study area. Dots show the sample locations. Numbers correspond to table 3. All samples studied are from a quartz-feldspar gneiss unit. The outcrop of the Leithsville Formation is stippled. For details of the geology, see Drake (1967) and Gundersen et al. (1988).

TABLE 1
Field methods

Property	Method	Reference
pH	Electrode	Wood, 1981
Conductivity	Conductivity bridge	Wood, 1981
Alkalinity	Titrimetric	Skougstad et al., 1979
Dissolved O_2	Electrode	Wood, 1981
Dissolved H_2S	Precipitation with zinc acetate, gravimetric determination	Skougstad et al., 1979; Tuttle et al., 1986
Dissolved radon-222	Degassing followed by scintillometry	Reimer (1986, pers. comm.)

A key feature of this study is the examination of geochemical processes governing the mobility of uranium-238, radium-226, and radon-222. Study of these geochemical processes may give insight into groundwater radon-222 availability. This paper is concerned primarily with the elements uranium and radium. Actually, radium-226 is derived from thorium-230, but because thorium is highly insoluble (Langmuir and Herman, 1980), it does not move far from its point of generation. Uranium-238 and radium-226 are the two most mobile parents of radon-222. Because radon-222 is a short-lived radionuclide, it does not migrate far from its point of generation before it decays (cf. Tanner, 1964).

The aqueous chemistry of radium, as we know it, is dominated by the species of radium(II), including, under some conditions, its complexes with sulfate, carbonate, or chloride (Riese, 1982; Langmuir and Riese, 1985). The solubility of radium in natural waters is seldom, if ever, limited by the solubility of phases such as $RaSO_4$ or $RaCO_3$. More likely Ra^{2+} is incorporated as a coprecipitation or cocrystallization product in phases such as barite or celestite (Doerner and Hoskins, 1925; Langmuir and Riese, 1985). In addition to the precipitation/dissolution processes, dissolved radium may also be limited by adsorption/desorption reactions.

Substrates that may adsorb Ra^{2+} under various conditions include quartz, kaolinite (Riese 1982), and iron oxides (Ames et al., 1983a, b, and c). In general, adsorption onto these substrates will increase as pH increases. A common misconception of radium geochemistry is that radium is soluble in reduced waters and insoluble in oxidized waters. Radium solubility is independent of oxidation potential; the source of this misstatement appears to lie in the similarly mistaken generalization that oxidized waters contain sulfate while reduced waters contain sulfide. It is true that regardless of oxidation potential, radium solubility may be limited in high sulfate waters, provided that the solubility of $RaSO_4$ or some similar solid (barite, celestite) is exceeded. However, a much more likely control of dissolved radium concentrations in natural groundwaters is adsorption onto aquifer grain surfaces.

The chemistry of uranium is considerably more complicated and involves several oxidation states (IV, V, and VI), and strong complexes with many ligand species (cf. Hostetler and Garrels, 1962; Langmuir, 1979). In oxidized systems, uranium is dissolved as the uranyl ion, UO_2^{2+}, or in complexes with anions such as fluoride, sulfate, phosphate, or carbonate. The uranyl ion is quite soluble but may be adsorbed by substrates including iron oxides (Hsi, 1981; Ames et al., 1983a, b, and c; Hsi and Langmuir, 1985), silica (Stanton and Maatman, 1963), or organic material (cf. Van der Sloot et al., 1975). In reduced systems, uranium is present as UO_2 (uranium(V)), or as uranium(IV), which is strongly hydrolyzed and quite insoluble. Therefore, uranium concentrations are likely to be higher in oxidizing waters, provided the aquifer minerals have leachable uranium.

RESULTS AND DISCUSSION

BOYERTOWN STUDY AREA

Twenty-seven wells (approximately eight per square kilometer), representing the aquifer units described above, were sampled in the Boyertown area. Analytical results are presented in table 2. Although the water samples were of generally good quality (all meet EPA drinking water standards for total dissolved solids), many of the wells contain high levels of various radionuclides. The highest radon-222 activities occur in waters sampled from the quartz-feldspar gneiss (fig. 3).

As stated earlier, the QFG contains anomalously high uranium, either as discrete uranium mineral grains, or as impurities in other minerals such as

sphene. Groundwater samples from the QFG contained the highest concentrations of dissolved oxygen (fig. 4). As uranium is most soluble in oxidized waters, high dissolved uranium concentrations would be expected in water from the QFG; this is exactly what is observed (fig. 5). Furthermore, the saturation indices for uraninite, a reduced uranium solid (UO_2), are lowest in water samples from this rock unit (fig. 6). Some water samples from outside the QFG also had low uraninite SI values, but the rocks hosting those groundwaters contained much lower concentrations of leachable uranium. Waters in the QFG also had the lowest pH values observed in the Boyertown study area. Hsi (1981) showed that low pH impedes uranium adsorption onto iron oxides. Qualitatively, other adsorption substrates should behave in the same way. The combination of relatively low pH and high dissolved oxygen in the QFG groundwater, and leachable uranium in that rock results in high concentrations of dissolved uranium in the groundwater.

Radium-226 activities in Boyertown groundwater samples were variable, but all samples tested below the EPA recommended maximum contaminant level of 5 pCi/L. The highest values were found in the QFG, the maximum activity being 4.1 pCi/L. Weathered surfaces of the QFG contain abundant iron oxides, known to be effective adsorbents for radium (Ames et al., 1983a, b, and c). Therefore, adsorption probably limits the radium-226 content of QFG groundwaters.

The highest activities of uranium, radium-226, and radon-222 occur in waters from the QFG. These nuclides, however, are not in secular equilibrium. Dissolved radon-222 concentrations are several orders of magnitude higher than would be expected if secular equilibrium were established in the groundwater alone (table 2); therefore, virtually all the dis-

TABLE 2
Chemical analyses from the Boyertown, Pennsylvania study area.
Units are as follows: pH and uraninite SI, dimensionless; dissolved oxygen (DO), ppm; uranium, ppb; radium-226 and radon-222, pCi/L; and ionic strength, molal

Sample	pH	DO	U	Radium-226	Radon-222	Ionic Str.	Uraninite SI
2	6.05	9.20	0.18	0.2	4300	0.0021	−12
3	6.75	0.30	0.36	0.2	100	0.0042	−0.39
4	6.30	5.50	6.0	0.2	16600	0.0031	−16
5	6.65	0.30	0.0	0.2	1200	0.0038	n.a.
6	6.45	0.22	0.18	0.2	670	0.0031	+1.8
7	7.90	0.30	0.14	0.1	120	0.0040	−1.3
8	8.95	0.10	0.18	0.1	1400	0.0023	−3.7
9	6.05	2.90	0.0	0.1	1200	0.0023	n.a.
10	6.65	4.80	0.33	0.1	3700	0.0040	−18
11	6.15	8.10	0.33	0.2	5500	0.0019	−25
12	6.05	8.40	6.6	0.3	41000	0.0023	−24
13	5.95	9.30	4.6	0.5	34000	0.0029	−23
14	6.65	3.60	2.1	0.2	11100	0.0041	−7.6
15	5.95	7.60	0.14	0.1	8200	0.0029	−25
16	5.85	8.70	0.48	0.2	6300	0.0038	−25
17	7.65	0.69	3.48	0.3	28800	0.0038	+0.74
18	8.55	0.79	1.8	0.1	13400	0.0025	−1.3
19	6.65	6.80	0.67	0.3	26300	0.0024	−18
20	6.10	11.10	1.18	0.2	12000	0.0020	−24
21	6.65	3.60	58	0.6	99000	0.0039	−5.9
22	7.65	0.08	590	4.1	71900	0.0040	−1.7
23	5.95	7.80	3.6	0.4	39600	0.0025	−16
25	6.35	3.50	0.21	0.1	100	0.0044	−7.8
26	6.65	2.30	0.33	0.2	1400	0.0038	−8.1
27	6.05	9.80	0.05	0.1	11300	0.0020	−26



Figure 3 — Radon-222 activities in groundwater of the Boyertown study area. All values are in pCi/L; actual values are listed in table 2. Patterns depict lithologies as in figure 1.

solved radon-222 is derived from solid-phase radium-226 and uranium-238. It is logical to assume that the dominant control on radium (and, to some extent, uranium) solubility is adsorption onto mineral surfaces. Thus, radon-222 activities in groundwater are unsupported by parent nuclides in the water, although they are concentrated in the solid phase. The implications of this observation are extremely important: rocks with the highest leachable uranium concentrations generally cause the highest groundwater radon-222 activities. In the past, groundwater and soil-gas radon-222 have been used as an exploration guide for uranium deposits (cf. Dyck and Tan, 1978; Chatham et al., 1981; Wanty et al., 1987).

Although uranium-238 chain nuclides in the water itself are not in secular equilibrium, they may be in the total water-rock system. Soil and rock chemistry in the Boyertown area suggests this to be the case. Analyses of rock samples collected in Boyertown indicate that uranium-238 and radium-226 activities are in the correct order of magnitude to support the observed groundwater radon-222 activities (Gundersen et al., 1988). In support of this argument, Rumbaugh (1983, 1987) successfully modelled radon-222 activities in groundwater, assuming secular equilibrium in the local water-rock system.

EASTON STUDY AREA

Sampling from the Easton study area was limited by the small number of houses with wells; most Easton residents are connected to municipal water supplies. Of ten wells sampled, only six provided reliable chemical data. Of the remaining four, it was not possible to sample water before it entered a pressure tank or a pretreatment device. All six wells sampled were in the same geologic unit (QFG) (fig. 2). Indeed, the overall water chemistry of these wells is similar, with the exception of site 5. It is apparent from the ionic strength, pH, radon-222 activity, and

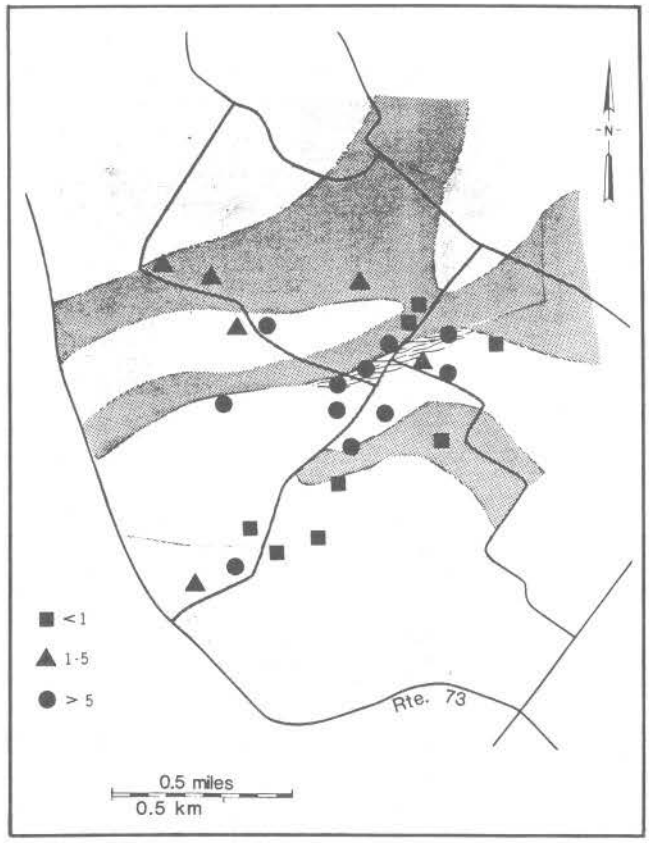


Figure 4 — Dissolved oxygen concentration in the Boyertown groundwater. All values are in parts per million (ppm); actual values are listed in table 2. Patterns depict lithologies as in figure 1.

bicarbonate concentration (table 3) that well 5 is drawing some of its water from the Leithsville Formation limestones, which underlie the main quartz-feldspar gneiss body.

Except for site 5, the Easton samples closely resemble the samples drawn from the QFG in Boyertown, and many of the observations and conclusions derived from the Boyertown QFG samples also apply to Easton. The Easton groundwater generally is of good quality, except for high radionuclide concentrations. It is characterized by high concentrations of dissolved oxygen, low pH, low total dissolved solids, and high dissolved radon-222. As in Boyertown, dissolved radon-222 is almost completely unsupported by dissolved uranium-238 and radium-226. Nevertheless, uranium-238 chain nuclides in the rock-water system, taken as a whole, may be in secular equilibrium. As in the Boyertown study area, solid-phase radium-226 and uranium-238 activities in the aquifer are in the right order of magnitude to support observed dissolved radon-222 activities (Gundersen et al., 1988).

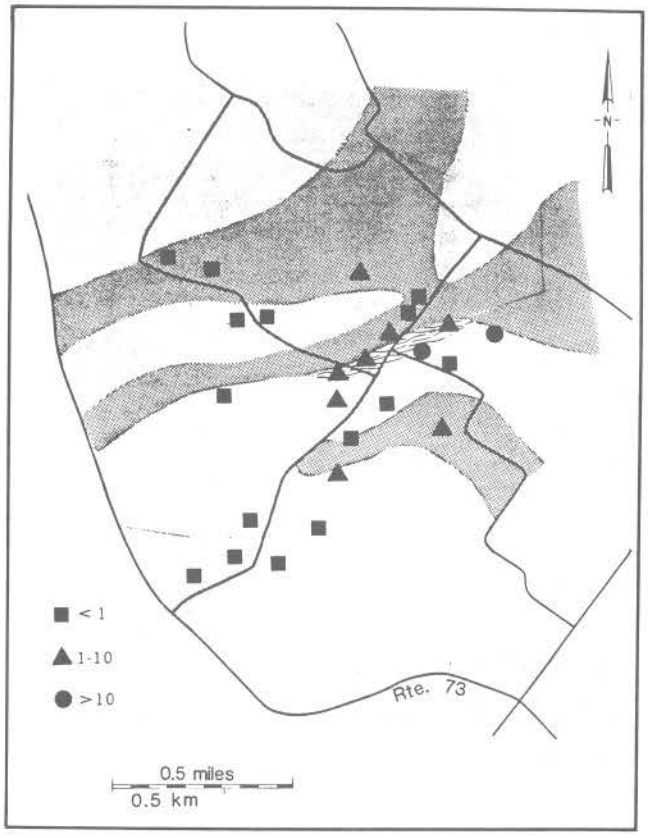


Figure 5 — Dissolved uranium concentration in the Boyertown groundwater. All values are in parts per billion (ppb); actual values are listed in table 2. Patterns depict lithologies as in figure 1.

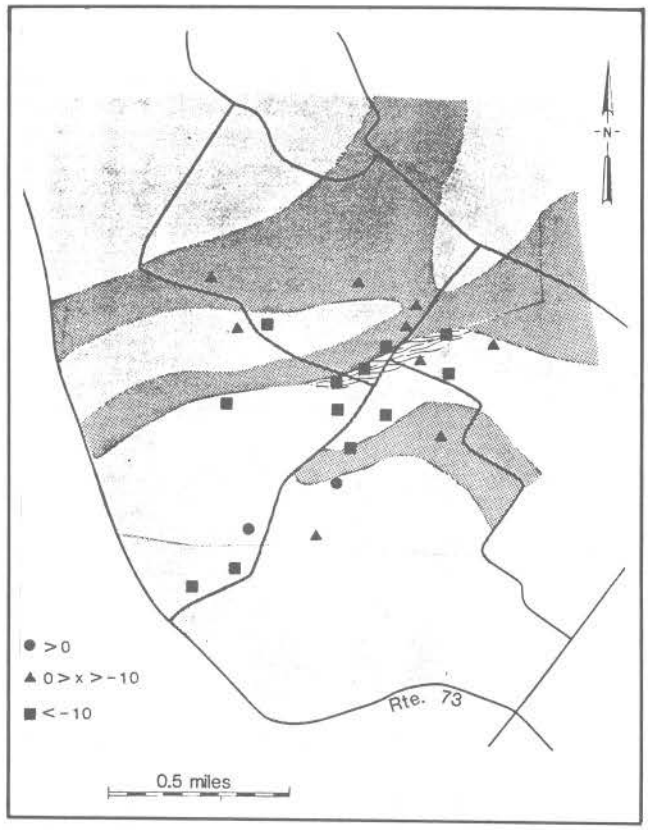


Figure 6 — Uraninite saturation indices for the Boyertown groundwater samples. Positive values indicate supersaturation with respect to uraninite; negative values represent undersaturation. The values are listed in table 2. Patterns depict lithologies as in figure 1.

Total uranium concentrations in the Easton groundwaters ranged from 0.5 to 14 ppb (table 3). Radium-226 activities ranged from 0.2 to 10.1 pCi/L. Uranium-238 and radium-226 approach secular equilibrium in some cases, although this is probably fortuitous. Every sample from the Easton area is extremely undersaturated with respect to uraninite (maximum uraninite SI value is -7.1, most are less than -23); therefore, reduced uranium solids do not control the mobility of uranium in this groundwater. Similarly, no radium solids approach saturation in these waters. Two processes may limit uranium-238 and radium-226 concentrations in these waters: slow dissolution kinetics of uranium and radium minerals, or, more likely, strong adsorption of both elements on various aquifer materials, most likely iron oxides and quartz. Iron oxides are less abundant,

TABLE 3
Chemical analyses from the Easton, Pennsylvania study area.
Units are as follows: pH and uraninite SI, dimensionless; dissolved oxygen (DO) and HCO_3, ppm; uranium, ppb; radium-226 and radon-222, pCi/L; and ionic strength, molal

Sample	pH	DO	U	Radium-226	Radon-222	Ionic Str.	Uraninite SI	HCO_3
2	5.55	8.6	4.4	1.6	80300	0.0034	−23	32
4	5.60	8.9	0.5	1.2	34700	0.0035	−24	16
5	6.70	3.6	6.5	0.2	10600	0.0055	−7.1	100
7	5.80	9.0	12.0	10.1	23400	0.0028	−23	27
9	5.90	9.5	14.0	5.1	43900	0.0033	−23	36
10	5.75	11.0	6.3	5.2	26300	0.0024	−23	18

but are more effective adsorbents (Ames et al., 1983a, b, and c; Hsi, 1981). Quartz, although a weak adsorbent, is much more abundant in the rock. On the other hand, radon is weakly, if at all, adsorbed on mineral surfaces. Radon is therefore partitioned into the aqueous phase, and its concentration is higher than would be expected for secular equilibrium in the water itself.

CONCLUSIONS

Radionuclide concentrations in groundwaters from crystalline aquifers in two sites in eastern Pennsylvania are controlled primarily by aquifer lithology. In the geologic framework, specific chemical processes, including adsorption/desorption and mineral dissolution, act to control concentrations of the individual elements. Uranium concentrations are highest in oxidizing groundwater, but only in rocks that contain leachable uranium. In the Boyertown and Easton study areas, the highest dissolved uranium concentrations occur in uraniferous quartz-feldspar gneisses. Radium-226 concentrations are highest in low-pH groundwaters, where adsorption on minerals such as iron oxides and quartz is weakest. Groundwater concentrations of radon-222 are much higher than expected, given the relatively low dissolved uranium-238 and radium-226 concentrations. Uranium-238 and radium-226 activities of the aquifer rocks are sufficient to support the observed dissolved radon-222 activities; therefore, although uranium-238 chain nuclides in the waters are never in secular equilibrium, they may be in the overall water-rock system.

Specific chemical processes active in every aquifer at the rock-water interface, cause each phase to affect the others chemically. Detailed study of these processes, predictable from thermodynamics and kinetics, should lead to a better understanding of radionuclide systematics in the overall water/rock system.

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REGIONAL AERIAL GAMMA-RAY MAPS FOR ILLINOIS AND PARTS OF WISCONSIN, IOWA, MICHIGAN, INDIANA, MISSOURI, AND KENTUCKY

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ABSTRACT

The U.S. Department of Energy conducted a National Uranium Resource Evaluation (NURE) Program during the period from 1975 to 1983. As part of that program, aerial gamma-ray surveys were flown over most of the United States, with flight-line spacings of 1, 2, 3, and 6 miles. The 1- and 2-mile-spaced data are limited to a few areas. The 3-mile-spaced data are common in the west and 6-mile data are common east of the Rocky Mountains. Although the 3-mile and wider flight-line densities are not suitable for detailed studies, the data can be used to produce regional maps at scales of 1:1,000,000 or smaller. The data for an area of 6 degrees of longitude by 6 degrees of latitude, covering parts of Missouri, Iowa, Illinois, Wisconsin, Indiana, and Kentucky, have been processed to produce regional maps at a scale of 1:1,000,000. These maps include contour maps of the apparent surface concentrations of uranium (ppm eU), potassium (percent K), and thorium (ppm eTh). Various composite-color maps have also been made, which can be used to establish the regional radioactivity of geologic materials exposed at the surface. The uranium map in particular can be used to define a first-order estimate of the relative indoor radon hazard that could be used to prioritize areas for more detailed studies.

INTRODUCTION

Aerial gamma-ray maps for Illinois and parts of the surrounding states were prepared with digital data acquired by the U.S. Department of Energy, as part of the National Uranium Resource Evaluation (NURE) Program (U.S. Department of Energy, 1980a-d, 1981a-k, 1982a-c). The NURE Program conducted aerial gamma-ray surveys from 1975 to 1983 for most of the conterminous United States and Alaska. The surveys were flown by a number of different contractors using detector volumes of 2000-3000 $in.^3$ of sodium iodide. Nominal survey altitudes were 400 ft, and flight-line spacings were 0.25 mi (rare), 1 mi (rare), 2 mi (rare), 3 mi (common in the western United States), and 6 mi (common east of Colorado and in Alaska). The contractors processed the data to correct for cosmic-ray background, aircraft contamination, Compton scattering, altitude variations, and airborne bismuth-214. Aerial gamma-ray systems used were calibrated by use of facilities at Grand Junction, Colorado (Ward, 1978) and Lake Mead, Nevada (Geodata, 1977). Most of the data are reported in concentration values of percent potassium, parts per million equivalent uranium (ppm eU), and parts per million equivalent thorium (ppm eTh). The term *equivalent* is used because of possible secular disequilibrium in the uranium and thorium decay series. Because the calibration facilities were not ready at the beginning of the NURE Program, some of the initial survey data were reported in counts per second.

DATA PROCESSING

To prepare the maps, the data were further processed. (1) A 5-point Median filter was applied to the flight-line data, as a noise-rejection technique. (2) The flight-line data were filtered by a Gaussian filter (with the standard deviation equal to three data points along the flight line) to reduce noise and other high-frequency variations. (3) Detector sensitivity corrections were then made by multiplying all or part of a data set by a constant factor, because the different systems sometimes did not give the same values over similar material. (4) The data were then gridded at a 2-mi grid interval using a minimum curvature algorithm (Briggs, 1974; Webring, 1981). (5) The gridded data were additionally filtered by a fast Fourier technique to reduce the amplitude of short-wavelength features (less than 25 km) that trend parallel to the flight-line direction.

Because of the wide flight-line spacing, the 2-mi grid interval, and the applied filters, the resulting maps are regional and should only be used in a regional context. Concentration-value accuracies are estimated to be better than 20 percent in a relative sense and from 50 to 100 percent in an absolute sense. By "relative sense," we mean the comparison of data from different parts of the map area. By "absolute sense," we mean the comparison of these concentration values to values from other sources, such as ground or laboratory measurements.

DATA PRESENTATION

Figure 1 shows the area for which the NURE aerial gamma-ray data were compiled. Figure 2 shows the distribution of potassium with values ranging from 0 to 2.8 percent. Figure 3 shows the distribution of uranium with values ranging from 0 to 6 ppm eU. Figure 4 shows the distribution of thorium with values ranging from 0 to 22 ppm eTh.

These maps can aid geologic mapping and mineral exploration. Bates (1962), Gregory (1960), Maxham (1960), and Pitkin (1968) discussed the use of aerial gamma-ray data to aid geologic mapping. Force et al. (1982) and Yeates et al. (1982) gave examples of applications to mineral exploration. Clark et al. (1972), Darnley (1970), Duval et al. (1971), and Grasty et al. (1978; 1979) described various aspects of aerial gamma-ray spectroscopy and its limitations.

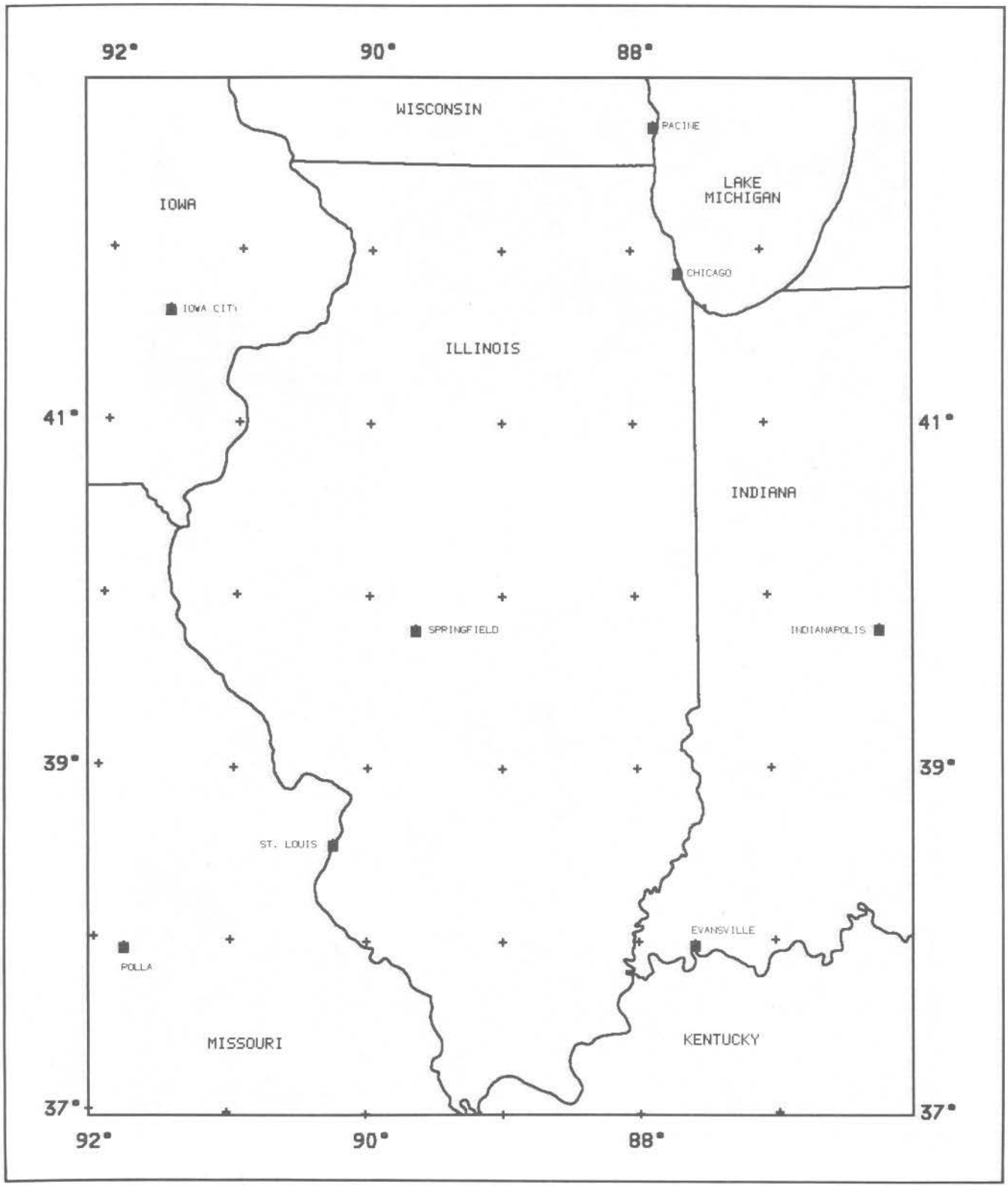


Figure 1 — Index map.

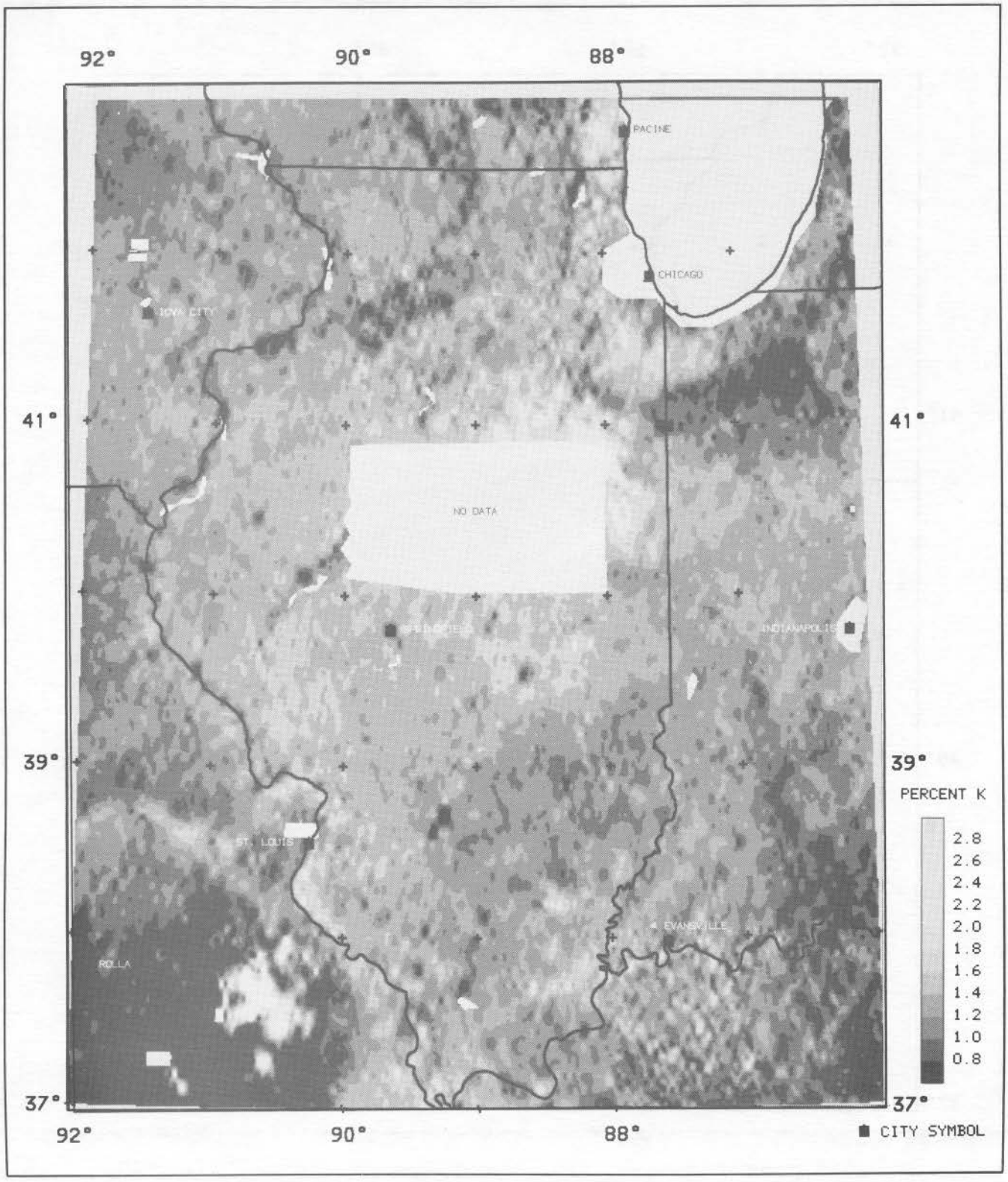


Figure 2 — Potassium contour map (percent K).

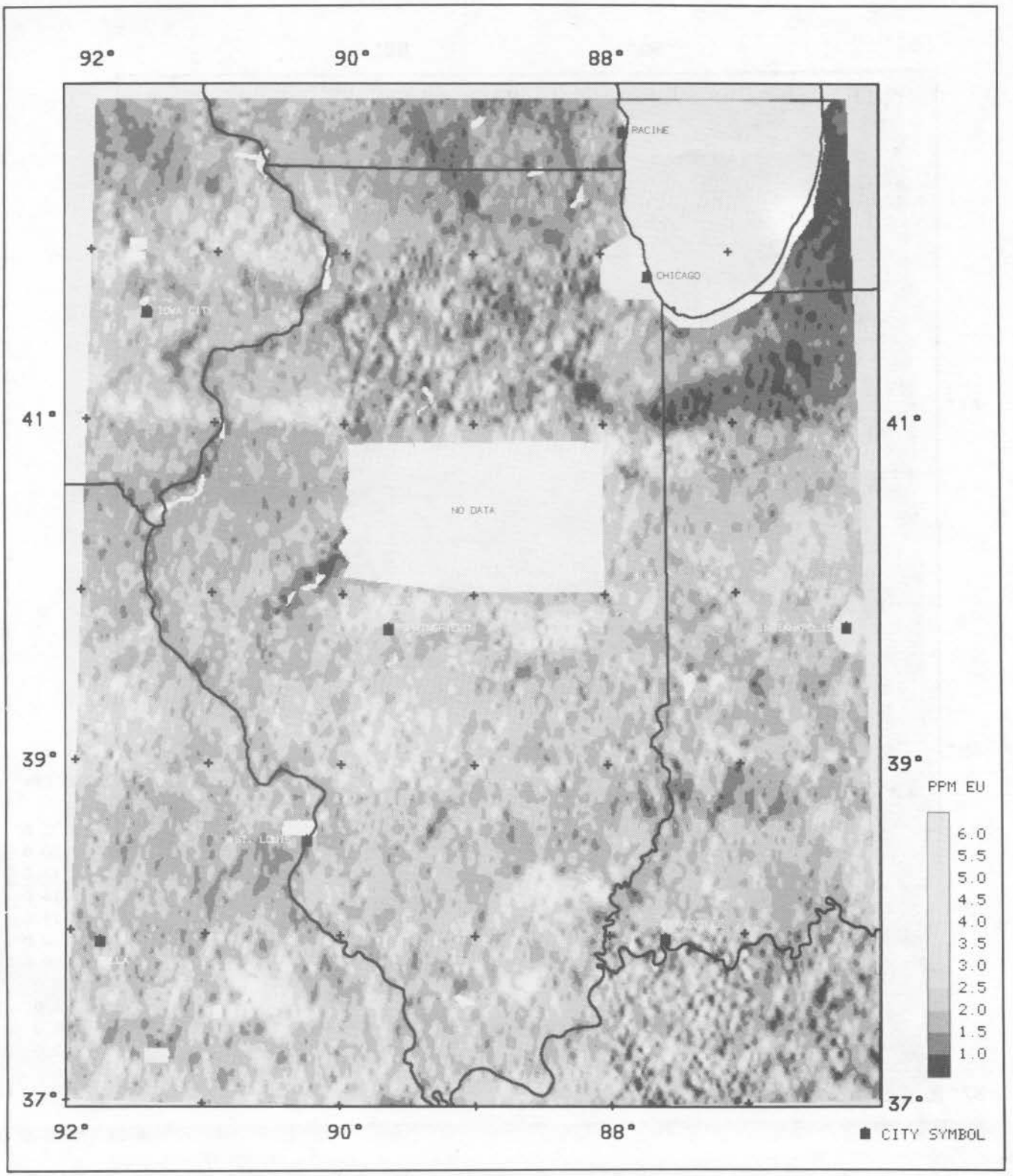


Figure 3 — Uranium contour map (ppm eU).

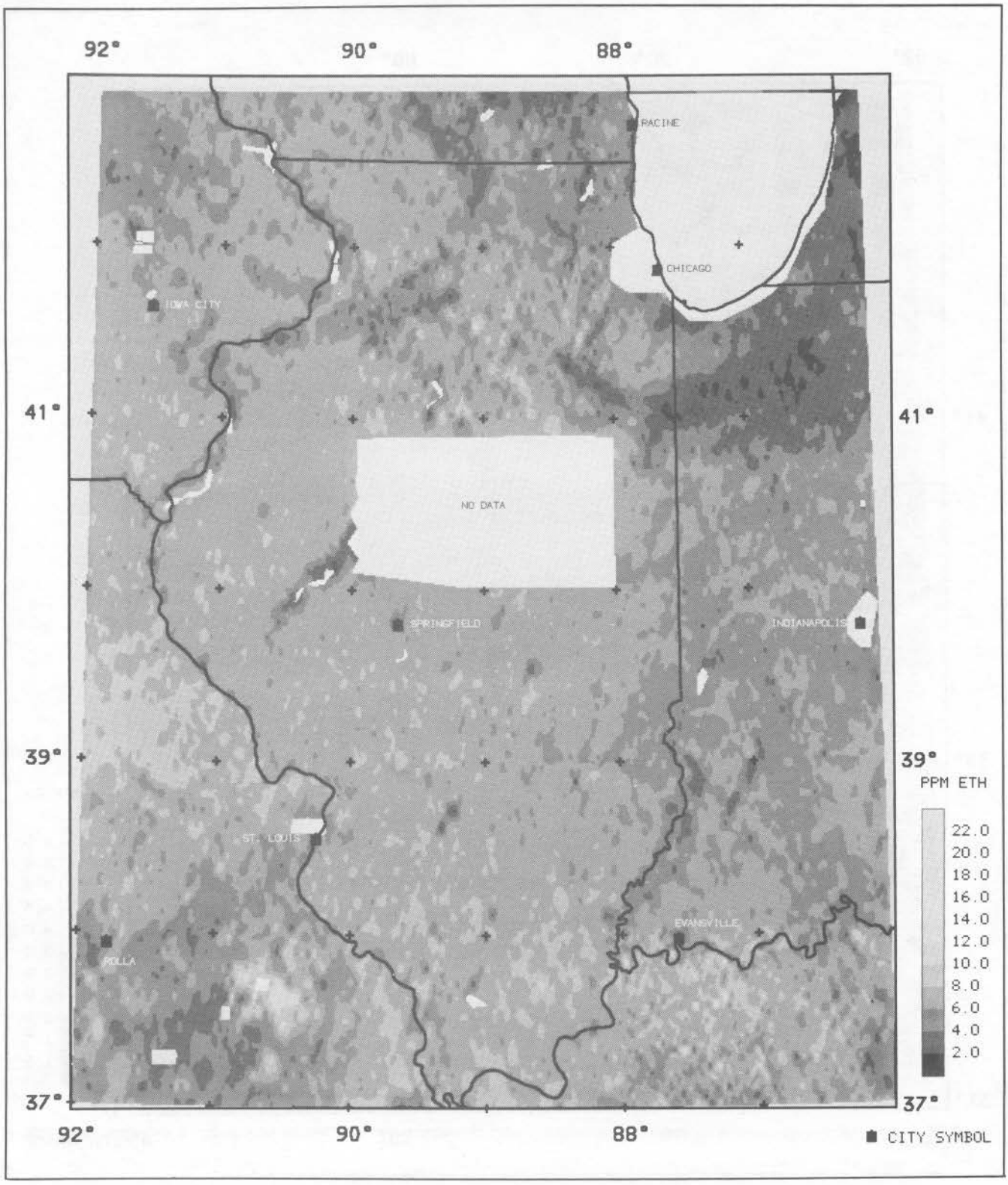


Figure 4 — Thorium contour map (ppm eTh).

DISCUSSION

Most of the higher potassium concentrations (fig. 2) are in Illinois but the highest, in an area east of Rolla, Missouri, range from 1.4 to 2.8 percent. Precambrian and Cambrian rocks of the St. Francois Mountains are associated with the high concentrations in Missouri. The large area of low potassium concentrations, (less than 1.0 percent) surrounding the St. Francois Mountains correlates with Ordovician rocks: the Smithville, Powell, Cotter, and Jefferson City Formations, which are fine grained, silty, and cherty dolomites, and the Roubidoux Formation, comprising sandstone, chert, and interbedded fine-grained dolomites (Saville and Davis, 1962). Another area of distinctive low concentrations, south and east of Lake Michigan, correlates with glacial outwash and eolian sheet sands that are facies of the Atherton Formation in Indiana and part of the Parkland Sand in Illinois (Lineback et al., 1983).

The thorium map (fig. 4) shows that most of the study area has concentrations of 6 to 8 ppm eTh. Most of the higher thorium concentrations are in Missouri and Kentucky; the highest concentrations, up to 14 ppm eTh, are east of Rolla, in the St. Francois Mountains. The lowest thorium concentration, (0-4 ppm eTh) are in a broad belt south and east of Lake Michigan and coincide with potassium lows associated with glacial and eolian sands. The uranium map (fig. 3) shows similar low concentration (0-1.5 ppm eU) in the area of the sands. The highest uranium concentrations, exceeding 3.5 ppm eU, are also in the St. Francois Mountains.

CONCLUSIONS

Although the above discussion is only a minimal interpretation of the maps presented here, the maps themselves prove that regional compilations of the NURE aerial gamma-ray data are possible and the resulting maps, useful. Because the NURE flight-line spacings are generally greater than 3 mi, the compiled maps are suitable for scales of 1:1,000,000 or smaller.

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GEOLOGIC ASSESSMENTS OF RADON HAZARDS: A COLORADO CASE HISTORY

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ABSTRACT

A preliminary geologic assessment of radon hazards must often rely on existing data to characterize those geologic features that are likely to influence indoor radon levels directly. The features believed to be most important are the radium content and permeability of the soil and substrate (surficial materials, weathered and unweathered bedrock) at or near the ground surface. Because no databases exist that can provide direct information on the distribution of these features, interpretations of geological, geochemical, and geophysical data form the basis for assessment. These principles are illustrated in a recently completed preliminary assessment of radon hazards in the state of Colorado. Key databases used include the NURE aeroradiometric flight-line data (most of the state was flown at a 3-mi flight-line spacing; several areas were flown at a 1-mi spacing), uranium occurrence compilations (Colorado has been intensively explored for uranium), and soil permeability estimates from Soil Conservation Service mapping (less than half the state is covered but more than 90 percent of the state's population lives in the covered areas).

Colorado has long been known to have high natural-background radioactivity. Uranium concentrations in soils across the state probably average just below 3 ppm, as estimated from examination of NURE flight-line data, so most soils across the state are expected to have several hundred pCi/L of radon in the soil gas. Thus, in virtually all areas of the state a significant percentage of homes (10-30 percent) are expected to have elevated (>4 pCi/L) indoor radon levels. The area considered to have the highest risk includes all the Front Range of Colorado, from Pueblo north to the Colorado-Wyoming state line. This area is underlain by granitic, metamorphic, volcanic, and sedimentary rocks, including several moderately (3-6 ppm uranium) to highly (> 6 ppm uranium) uraniferous granites and many smaller uranium occurrences and deposits. Soils over the granites, many metamorphic rocks, and alluvium are typically highly permeable, and the rocks are, in many areas, highly fractured.

HYDROCARBON DISTRIBUTION PATTERNS OVER URANIUM DEPOSITS — IMPLICATIONS FOR SURFACE-PETROLEUM GEOCHEMICAL PROSPECTING TECHNIQUES

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ABSTRACT

Recent surface-petroleum-hydrocarbon geochemical work on uranium deposits in the Powder River basin, Wyoming illustrates some factors that can significantly affect results of surface-hydrocarbon geochemical surveys. Hydrocarbons are consumed by bacteria in a specific environment. Conditions conducive to bacterial growth on hydrocarbons depend on availability of oxygen, nutrients, temperature, groundwater salinity, and moisture. The well-defined chemical environment in a uranium roll-front deposit can be used to explain the petroleum hydrocarbon signature above the ore body, in terms of environmental constraints upon microbiologic growth. Application of this knowledge to surface geochemical prospecting for petroleum can be of significant value.

RADIONUCLIDE ANOMALIES IN GEOLOGIC EXPLORATION

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ABSTRACT

Radon is an ubiquitous component in the geologic environment. From an environmental point of view, it represents a health hazard to be recognized, understood in geologic context, and circumvented. From an exploration point of view, radon represents an exploration tool to be understood in geologic context and employed for targeting potential geologic resources. Both viewpoints are complementary. Recognized high radon-risk areas may be associated with potential resources. Conversely, certain resource areas may reveal a potential radon-risk.

Radon geochemistry has been used successfully in uranium exploration programs, and more recently in subsurface fault/fracture delineation, and geothermal and hydrocarbon exploration. The technique is currently being evaluated as a precious-metals exploration tool, and for hydrologic fracture mapping.

Radon geochemistry has proven potential in hydrocarbon exploration. Surveys over known and suspected fields reveal that equilibrium soil radon values correlate with deep reservoirs. Soil-reduced radon data have effectively delineated reservoir boundaries at depths of 1-2 km. In addition, radon flux attenuation vs. time may be correlatable with reservoir depletion. Used alone, or in conjunction with other geologic and geophysical information, the technique is a viable exploration tool. Preliminary surveys over epithermal gold deposits indicate that radon may be an effective method of delineating permissive structural controls and "seeing" epithermal activity through sediment gravel cover.

Modeling based on known geologic and geochemical mechanisms allows interpretation of observed radon data, although specific models may require invocation of "not-so-obvious" geologic mechanisms to resolve half-life vs migration-rate engimas (e.g., "deep-source" radon).

AN INITIAL IDENTIFICATION OF AREAS WITH A POTENTIAL FOR HIGH INDOOR RADON LEVELS

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ABSTRACT

To help assess the distribution of areas in the United States that might have elevated indoor radon levels, the Environmental Protection Agency (EPA) has prepared national maps delineating areas that appear to have the greatest potential to cause indoor radon problems. These maps are based on uranium concentrations in rock or soil in lieu of actual data on indoor radon levels, which are available for only certain areas of the country.

Swedish researchers have shown rough correlations of indoor radon concentrations with the uranium content of soils and rock around Swedish houses. In the United States, it appears that extremely elevated indoor radon levels are also associated with elevated uranium concentrations in the rock and soil near affected houses; therefore, a map based on rock and soil uranium content might approximate those areas that may have radon problems. Such a map would not be conclusive, however, because other factors such as soil permeability and building characteristics also influence radon concentrations in structures.

In general, the rock types most likely to contain above average concentrations of uranium, and which may suggest potential radon problems, include some granitic rocks, black shales, phosphatic rocks, and some sedimentary rocks adjacent to or derived from uraniferous source rocks. The EPA's composite map includes most of these rock types; it also includes uranium-resource information from the National Uranium Resource Evaluation (NURE) database and adapted to be more applicable to indoor radon concerns.

The EPA maps, however, cannot be used as the soil source for predicting elevation radon levels. Instead, it is necessary to use the information from these maps in conjunction with data on other factors (e.g., soil type, soil permeability, and housing characteristics) to predict local radon levels. Furthermore, the predictions on these maps have not yet been confirmed by actual measurements. The EPA plans to continue to develop and refine the maps as additional information becomes available.

BANQUET SPEECH

A CHALLENGE FOR GEOSCIENTISTS: CAN WE LEARN TO MAKE THE ELEPHANT MOVE?

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ABSTRACT

Our nation's geochemical environment pervasively affects our quality of life. This geochemical impact has become one of our highest priority national concerns. In recent months, major hazards to environment and health, associated with radon gas leakage into houses and selenium concentrations in irrigation waters, have raised both local and national alarm. These newly recognized dangers must be dealt with urgently. The proposed program does that, but also addresses other potential hazards and especially brings to bear research of underlying broader, longer-range aims: In order to protect the quality of our environment we need information on present environmental quality and an understanding of the natural conditions and human activities that affect that quality. We propose a program to collect descriptive and process-oriented information on the solid earth components that will complement the USGS National Water Quality Assessment program, which will be coordinated with other Federal and State agencies. Priorities for topic and site selection will be based on present knowledge of potential natural contamination hazards and on the perceived need for a rapid response. This program will result in relatively rapid scientific surveys, reports, and assessment maps of immediate hazards like radon, but also will bring together a national environmental geochemistry data base and new understanding of the weathering processes that affect toxic elements. The research from this program will result in optimum mitigation strategies to solve present environmental problems effectively, to prevent many future problems, and to reveal when mitigation is unfeasible, given the geologic constraints.

INTRODUCTION

Most of you have heard the tale of the blind men and the elephant. Each man touched a different part of the elephant and had a very different perception of what the elephant looked like. One felt its trunk and said, "Ah, the elephant is like a snake!" Another bumped into a leg and said, "No. The elephant is like a tree." The third felt the tail and said, "You're both wrong. The elephant is like a rope." None saw the whole elephant.

We can see better than the blind men. I believe that all of us interested in attending GEORAD can see the whole elephant (fig. 1). We see how various geologic disciplines fit into the environmental geoscience picture. Now the next step is to make the elephant move, to make it function, to keep it alive, and well. To accomplish this goal, we need to develop an integrated, rational, balanced approach to environmental problems. We need to make sure our knowledge is both useful and used by policymakers.

We've gotten our elephant to take some first steps. One step has been our work on the relationship between geology and indoor radon levels. We were lucky in this area. Geologists were already investigating uranium occurrences because uranium was once thought to be the cure for the world's energy problems. The U.S. Geological Survey (USGS) was particularly lucky.

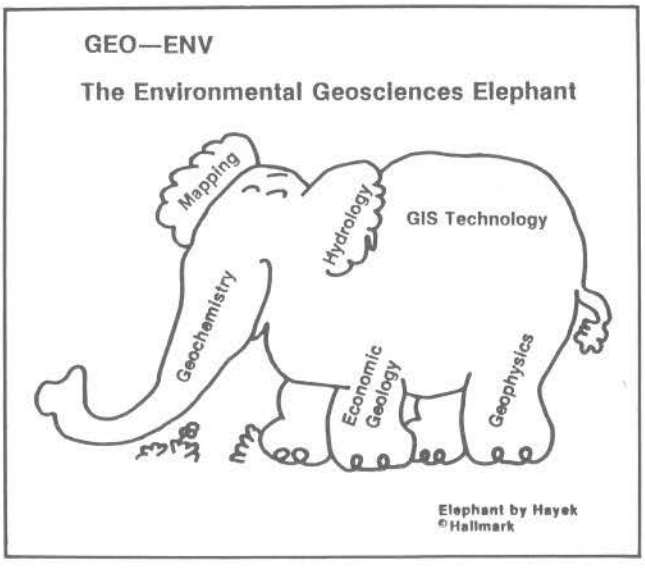


Figure 1 — The Environmental geosciences elephant. (Elephant shape by Hayek, copyrighted to Hallmark Cards.)

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The indoor radon crisis began in the Reading Prong, and fortunately, Linda Gundersen, of the USGS, had developed a model for the origin of magnetite and uranium occurrences in Precambrian rocks of the Prong for her doctoral dissertation. She was able to apply her information to study the geologic cause of high radon levels in Boyertown, Pennsylvania. She showed the excellent correlations of a mylonite zone with high radon levels in soil gas and high indoor radon levels (Gundersen et al., this volume).

An isolated early step occurred several years ago, this time involving the chemists in the USGS Branch of Exploration Geochemistry laboratory near Denver. When I joined the Survey about 8 years ago, my office was in a building that had previously been a garage. An unusual feature of the building was the presence of water coolers containing bottled water, even though the building had running water. I found out the reason.

A few years previously, one of our chemists had been developing a new method of measuring uranium in geological materials. He used the tap water as a blank. However, he couldn't get his readings for the "blank" to go below 100 μg/L. Two methods later, the tap water was discovered to have a uranium concentration of about 300 μg/L. The source of the tap water was a reservoir that was receiving drainage from a uranium mine. No standards existed then for uranium in drinking water. However, the tap-water concentration was generally considered to be much higher than "normal." The press picked up the issue. Finally, the water district imported water from Denver and from then on supplied a mixture of nine parts Denver water to one part reservoir water. Even so, people at the lab never would drink the water again!

Discovery of the uraniferous water was accidental. The establishment of ongoing research in the Reading Prong was a lucky coincidence. Next I'd like to discuss another crisis in which the availability of data was part luck and part foresight. (This crisis involved selenium, not a radionuclide. However, since we all see the whole elephant, I feel the example is appropriate.) The foresight was due to Jim McNeal of the USGS, who had done a broad-scale geochemical survey (one sample per 100 km^2) to test the data's applicability

to both exploration and environmental problems. The luck was that the study had been done in the southern two-thirds of California, which included the San Joaquin Valley and the Kesterson Reservoir. The San Joaquin Valley provides a large percentage of the United States food supply. Because of the dry climate, however, the land must be irrigated. In addition, the southern part of the valley has poor drainage, so runoff resulting from irrigation must be channeled away to prevent salt buildup. To that end, the U.S. Bureau of Reclamation (USBR) began to build a drainage canal that was originally planned to empty into San Francisco Bay. The drain was never completed. Instead, the USBR built evaporating ponds for storage of the drainage waters, near the town of Kesterson. Because the ponds attracted migrating waterfowl, the ponds, collectively called Kesterson Reservoir, became a national wildlife refuge. In 1982, near the reservoir, waterfowl mutations and deaths were attributed to high levels of selenium.

The USGS, a sister agency to the USBR, was called in to locate the source of the selenium. The previously completed broad-scale geochemical survey proved invaluable to this effort. Most of the samples from the survey were taken from stream sediments, but, because there are few streams in the San Joaquin Valley, soil samples were collected instead. The original budget for the survey had been very low, so elements such as selenium, arsenic, and mercury, which are expensive to determine, had not been measured. (If they had been, perhaps the selenium problem would have been anticipated!)

The archived samples were retrieved and analyzed for these elements and other potentially toxic elements. The results (fig. 2) showed generally higher concentrations of selenium, arsenic, and mercury on the western side of the valley, where soils had been derived from the southern Coast Range Mountains, and lower concentrations on the eastern side in soils derived from the Sierra Nevada Mountains. The highest concentrations of all three elements occurred in the area of the Panoche Fan, which also was the area of highest dissolved selenium in the groundwater.

A more detailed soil survey (one sample per square mile) was conducted in the Panoche Fan area as part of the Kesterson investigation. The results revealed different sources of selenium and mercury. The selenium in the soils comes from a rise known as Monocline Ridge, which is composed of ancient mud flows. The highest mercury levels were found in drainage from the New Idria Mercury Mining District.

The Kesterson problem showed the utility of geochemical surveys in predicting areas of potential environmental problems. The selenium problem is also very relevant to researchers looking at radionuclide distributions, because the pattern of uranium solubility is similar to that of selenium, arsenic, molybdenum, and other anionic species. All are most soluble at the higher pH oxidizing conditions typical of the alkaline desert environment and least soluble in reducing conditions.

In these cases, we were able to respond to environmental problems because we have a broad research base. However, we would be much more effective if we actually *set out* with the goal of understanding and sustaining our environment. The United States has no *national* geochemical data base to provide background information to help solve new environmental problems when they arise. More importantly, we lack the means to predict and prevent problems.

The Europeans are much farther along. The Government of West Germany, for example, has conducted a geochemical survey throughout the entire country for use in both exploration and environmental studies. Included in the data are background levels of soil or ground radiation. After the Chernobyl accident, the West Germans remeasured ground radiation in Lower Saxony. Because they had the background data, they were able to determine the amount of ground radiation that was actually due to the Chernobyl accident.

This example points out that many environmental problems are of regional or international concern because of atmospheric or water transport or similar climatic conditions. In another example, the atmospheric transport of lead from car exhaust has been linked to learning defects in children. On this front, good news has recently been reported. Evidently, the use of unleaded gas has significantly reduced lead levels in U.S. cities. The Washington Post (Weisskopf, 1987b) reported a 32 percent decrease in airborne lead in 1985 alone.

Now, just as we think we have the lead problem licked, the Environmental Protection Agency (EPA) tells us that we have too much lead in some of our drinking water, resulting from the lead solder in our

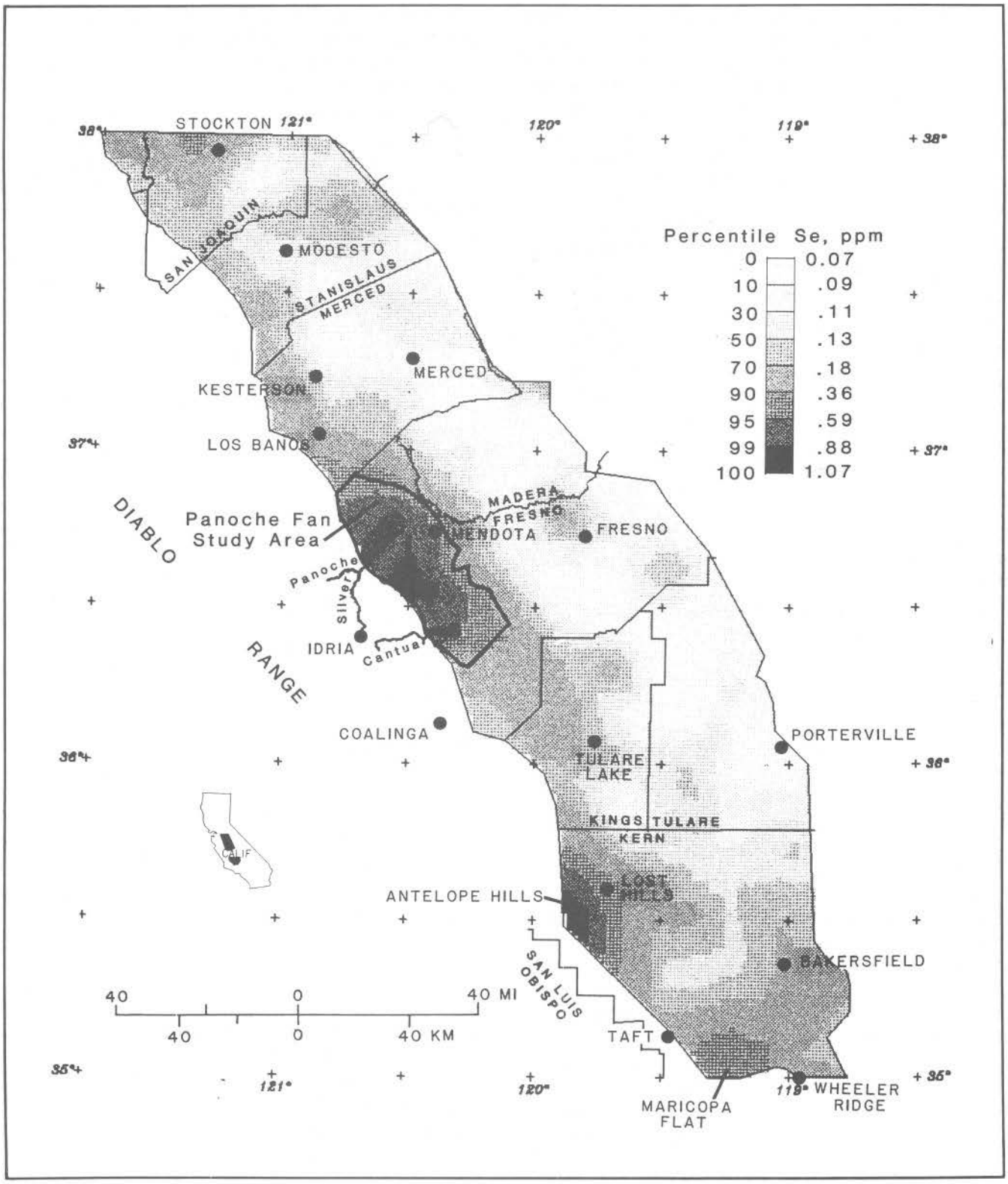


Figure 2 — Map of the San Joaquin Valley, California, showing the distribution of selenium in soils (from Tidball et al., 1986).

pipes (Weisskopf, 1986). Lead occurs as a cation similar to iron, cadmium, and radium. The behavior of cations is somewhat opposite to that of anions such as selenium and uranium. Cations tend to be most soluble in acidic soft water.

The lead problem may extend beyond gasoline and lead solder, and the problem may include other toxic elements. Municipal incinerators, which burn household trash, are now under scrutiny because of the toxic-element content of their ash, especially lead and cadmium (Weisskopf, 1987a). The first municipal incinerators were used by forward-thinking municipalities because landfills were considered a pollution source and were getting too full. The use of incinerators was considered to be a holistic approach to the garbage problem, because the burning could create usable energy. Few people considered household trash as potentially toxic. Even a holistic attitude does not guarantee the absence of environmental problems.

The Swiss have a holistic attitude. They have been recycling waste for years, using sewage and compost on crops, and incinerating some of their garbage. Unfortunately, they have developed at least two problems in spite of their good intentions, First, the incineration ash must be disposed of somehow. The Swiss have put the ash in their remaining landfills. Now cadmium from the ash is being leached from the landfills. The second problem is more insidious: The continued use of sewage, compost, and fertilizer on soil over a long period has produced a near-toxic buildup of cadmium (Haggin, 1986).

A close connection exists between the cadmium problem and radionuclides, especially in fertilizers. Phosphates often contain high concentrations of uranium and radium, so recycling could be concentrating these elements, too. Apparently, finding *really* holistic solutions to the dilemma of maintaining both a high standard of living and a clean environment requires planning far beyond the obvious. The problems are multidimensional, and facts must be combined from many seemingly unrelated disciplines.

How do we as geoscientists fit into the picture? How do we most effectively make our contribution to effective holistic solutions? There is a fine line between creating enough interest to win support for a problem or a program and causing all-out public panic. To ensure its survival, the elephant has to know how to get along with all the other animals of the jungle — the environmental managers, the toxicologists, the policymakers, the press, and the special interest groups. Environmental issues affect each of us, not only in our paychecks but also in our entire lives. They hit very close to home, literally.

Jim Otton, who coordinates our radon projects at the USGS, can personally attest to this fact. He recently moved from Denver to Washington, D.C. to carry out his new assignment. Because the housing market in Denver is poor, Jim decided to sell his house there through the relocation service provided by the Government. The relocation company hired a consultant to do radon testing on Jim's home. The tests were conducted during a weekend, on the coldest night of the winter, when thick snow covered the ground — conditions conducive to producing unusually high indoor radon levels. The results showed levels of approximately 6 pCi/L. The consultant recommended remedial measures at a cost of almost $2,400. (The EPA has set no standards for radon levels but has suggested that, for initial results between 4 and 20 pCi/L, further tests should be conducted for an entire year to determine if the average concentration is greater than 4 pCi/L. The EPA has also stated that reduction of indoor radon levels below 4 pCi/L is difficult to achieve.) On the basis of the consultant's recommendations, the relocation company reduced the offer for Jim's house by $2,450.

The relocation company and the consultant seemed to be unaware of all the factors controlling indoor radon levels and how to use published guidelines properly. As Jim pointed out in a letter he wrote to EPA, "The relocation industry needs to be listening to radon researchers and not just the radon measurement and mitigation industry."

I agree. I believe Jim's statement holds true for all environmental issues. The public and the policymakers need to hear the facts and be given scientific solutions. Otherwise, the results are hysteria, panic, and laws based on emotion that not only do not solve the problem but also sometimes cause more problems. Lester Lave (Lave, 1986) pointed out in a recent Wall Street Journal article that, "The failure to develop a program on toxic chemicals in the environment has led to wasting billions of dollars and given rise to Superfund. Not taking timely action shifts the debate to motives and trust, away from how to accomplish near-term goals effectively."

In order for people to hear the facts, we must tell them, in words they understand. We must make the

policymakers and the public aware of the information we have, and we must make that information useful to them.

Our information will not be very useful if we present it in isolated bits and pieces culled from individual disciplines and leave nonscientists to put those pieces together. We need to work together and use our scientific reasoning to develop an integrated approach to solving environmental problems.

My personal goals are (1) to get professionals — geoscientists, environmental managers and engineers, toxicologists, public policy analysts — to talk to one another and to understand the need for and utility of one another's information, and (2) to develop an effective multidisciplinary environmental program within the USGS that cuts across Office and Division boundaries. To help make the elephant move, I need to move another animal — my boss, the Department of Interior buffalo.

We each have other animals to move, as well as ourselves. As Lester Lave's Wall Street Journal article continues, "Even if the White House doesn't act, business and the agencies can work cooperatively to shore up the scientific foundation, learn about the basis of public fears and desires, and learn how to initiate a dialogue with the public."

To develop effective environmental solutions, all need to work together — with one another, with EPA, with industry, with the press, and the public — in a positive, nonadversarial, cooperative way. Our own health and money are at stake! If we can achieve this cooperation, the environmental elephant will be well on its way. If we can't, the future looks bleak for all of us.

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