U. S. Department of the Interior
Geological Survey

U, Th, AND K CONTENTS OF SOME MAJOR PRECAMBRIAN LITHOLOGIC UNITS OF THE HARTVILLE UPLIFT, WYOMING

By

Z. E. Peterman, C. M. Bunker, G. L. Snyder, and C. A. Bush

Open-File Report 81-1028

1981

This report is preliminary and has not been
reviewed for conformity with
U.S. Geological Survey editorial standards

ABSTRACT

Late Archean and early Proterozoic granites of the Hartville uplift of eastern Wyoming are enriched in Th by 1.5 to 3 times the average for silicic igneous rocks. U is extremely variable leading to Th/U ratios that range from near the average of 4 to unsually high values of 15. If it is assumed that the granites, regardless of age, crystallized with near-average Th/U ratios, then near-surface leaching has removed substantial fractions of U from many of the samples. Alternatively, if measured U/K ratios in the range of 1-1.3 x 10^{-4} are considered to be primary, both U enrichment and depletion are indicated, and the primary Th/U ratios would have been higher than average.

INTRODUCTION

Precambrian rocks of the Hartville uplift occur in a narrow, north-northeast trending inlier surrounded by Phanerozoic rocks. This terrane is the exposed part of a broad basement high that trends northeast from the central Laramie Range towards the Black Hills of South Dakota (Fig. 1). The geology of the Hartville uplift has been studied recently by Snyder (1980), and a geochronologic investigation of the major Precambrian units is nearing completion by Z. E. Peterman, G. L. Snyder, and K. Futa. Samples collected for the geochronologic study have been analyzed for their radioelement contents (U, Th, and K) and the results constitute the basis for this report.

Granitic rocks of late Archean age (approximately 2.6 Ga) intrude a supracrustal sequence of schist, metagraywacke, dolomite, and amphibolite derived from massive and pillowed basalt. Gneisses that may be somewhat older than 2.6 Ga occur in outlying areas to the west and south of the main exposures. The Archean terrane was intruded, mainly in the southern area, by diorite and granite late in early Proterozoic time (approximately 1.7 Ga). A later thermal event of unknown geologic nature is recorded in Rb-Sr and K-Ar biotite ages of 1.3 Ga.

The granitic and gneissic units were emphasized in sampling for the geochronologic study. Because of pervasive weathering, some samples show effects of near-surface alteration such as iron staining. Several of the samples have been cataclastically deformed and the Rb-Sr systems in these are commonly disturbed. Mineralized areas were purposely avoided in the sampling so the radioelement data provide baseline concentrations for the major granitic units.

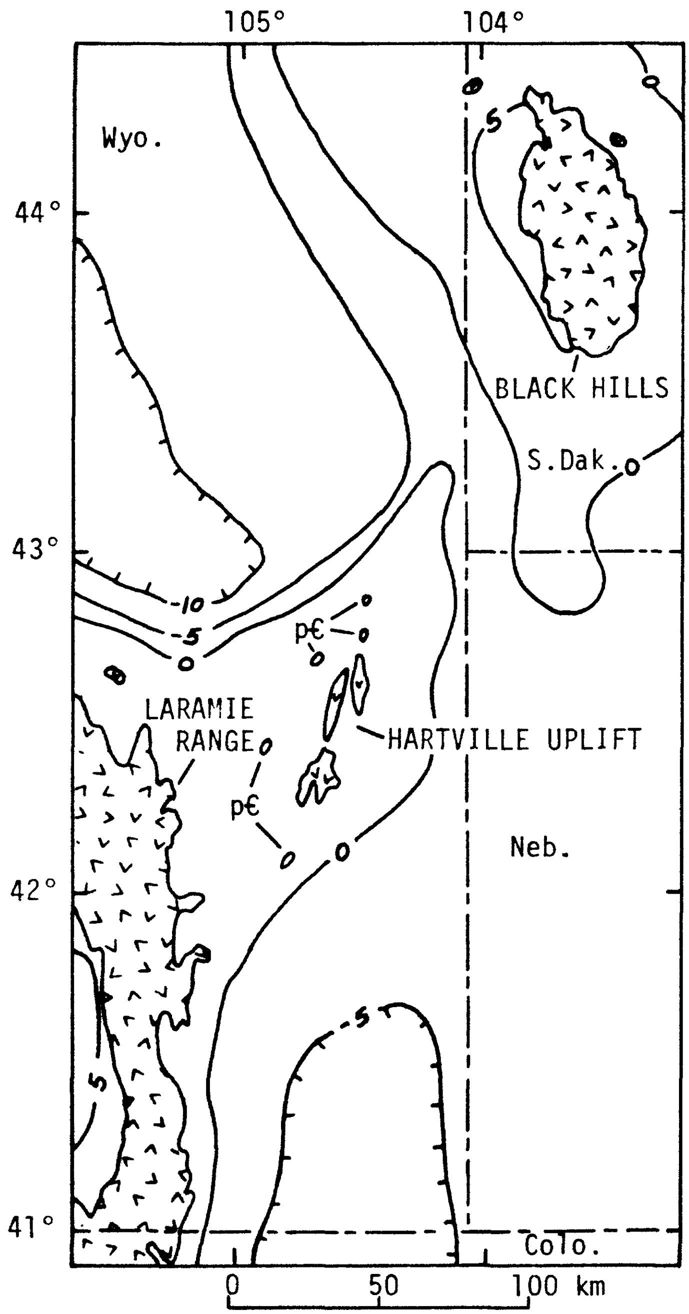

Figure 1. Sketch map showing the Hartville uplift, the Laramie Range, and the Black Hills (adapted from Bayley and Muehlberger, 1968). Patterned areas and those indicated as p€ are exposed Precambrian terranes. Contours depict the top of the Precambrian basement in thousands of feet relative to sea level.

ANALYTICAL METHODS

RaeU (radium-equivalent uranium), Th, and K contents of the samples were measured by gamma-ray spectrometry. Basic operational procedures, calibration techniques, and sample preparation were described by Bunker and Bush (1966, 1967). Approximately 600 g of sample were sealed in plastic containers 15 cm in diameter. The containers were placed on a sodium iodide crystal 12.5 cm in diameter and 10 cm thick. The gamma radiation penetrating the crystal was sorted according to energy by the associated electronic devices, and the resulting spectra were stored in a 512-channel memory of a multichannel analyzer. The spectra were interpreted with the aid of a linear least-squares computer method that matches the spectrum for a sample to a library of radioelement standards. The computer method for determining concentrations is a modification of a program written by Schonfeld (1966). Standards used to reduce the data include the USGS standard rocks, New Brunswick Laboratories standards, and several samples for which U and Th contents had been determined by isotope dilution and mass spectrometry and by alpha spectrometry.

U contents were measured indirectly by measuring the ^{226}Ra daughters (^{214}Bi and ^{214}Pb) to obtain RaeU values. Isotopic equilibrium between these daughters and ^{226}Ra was reached by allowing the sealed sample containers to sit for at least 21 days prior to analyses. RaeU is the amount of U required for secular equilibrium with ^{226}Ra and its daughters. U concentrations of the Hartville samples are RaeU values but will be simply referred to as U in the following discussions.

Although Th is also measured from daughter products (^{212}Bi, ^{212}Pb, and ^{208}Tl), isotopic disequilibrium is improbable because of the short half-lives of the daughter products of ^{232}Th. Therefore, the daughter products measured are considered to be a direct measurement of thorium. K is determined from ^{40}K, which is radioactive and in constant atomic proportion with the other K isotopes.

All of the radioelement data reported in this paper are based on replicate analyses. The coefficient of variation for the accuracy of these data, when compared to isotope-dilution and flame-photometry analyses, is about $\pm$ 2 percent of the amount reported for RaeU and Th and about $\pm$ 1 percent of the amount reported for K. These uncertainties are in addition to minimum standard deviations of about 0.06 ppm for RaeU and Th and about 0.03 weight percent for K.

RESULTS AND DISCUSSION

U in crystalline rocks is commonly mobile in the zone of weathering because a substantial fraction of the total U in many rocks can occur in loosely bound sites in metamict minerals and along grain boundaries. Consequently, measured U contents of surface samples may not be primary values and are commonly low because of leaching. This has been especially well documented for Precambrian granitoids of the Granite and Seminoe Mountains of central Wyoming (e.g. Rosholt and others, 1973; Stuckless and Nkomo, 1978) for which Pb isotope data show that large fractions of U have been removed through involvement with circulating groundwater.

Radioelement contents of samples from the Hartville uplift (Table 1) can be compared with average values for broad classes of igneous rocks (Table 2). Like many trace elements, the abundances of U and Th in igneous rocks follow log-normal distributions, and concentrations can range upward considerably from the average values shown (Table 2) and still be in a normal range for the particular rock classes. Ratios of

Table 1. Radioelement contents of Precambrian rocks of the Hartville uplift

Sample	Coordinates Lat.(N)	Long.(W)	Rock type and age 1/	RaeU (ppm)	Th (ppm)	K (%)	Th/RaeU	RaeU/Kx10^{-4}	Th/Kx10^{-4}
			Northern Hartville uplift						
HU-1	42°37'	104°28'	Granite LA	11.5	50.6	4.95	4.4	2.3	10.2
HU-2	42°36'	104°30'	Granite LA	2.4	33.2	5.90	14.0	0.4	5.6
HU-3	42°37'	104°34'	Granite LA	3.6	36.5	3.81	10.2	0.9	9.6
HU-20	42°40'	104°29'	Granite LA	2.2	26.8	5.69	12.1	0.4	4.7
HU-21	42°36'	104°29'	Granite LA	4.3	53.4	4.00	12.3	1.1	13.3
HU-23	42°38'	104°29'	Granite EP	2.8	21.5	2.47	7.6	1.1	8.7
HU-26	42°37'	104°30'	Granite LA	6.4	49.7	4.85	7.8	1.3	10.2
HU-27A	42°37'	104°30'	Granite LA	2.7	48.0	4.75	17.7	0.6	10.1
HU-27B	42°37'	104°30'	Aplite LA	1.0	7.7	4.85	7.7	0.2	1.6
			Southern Hartville uplift						
HU-5	42°16'	104°42'	Granite LA	12.0	37.2	4.05	3.1	3.0	9.2
HU-6	42°19'	104°39'	Granite EP	5.1	44.7	4.07	8.8	1.2	11.0
HU-7	42°20'	104°39'	Granite EP	5.4	45.3	4.05	8.4	1.3	11.2
MP-7A	42°22'	104°39'	Granite EP	13.9	60.7	4.10	4.4	3.4	14.8
MP-7B	42°22'	104°39'	Granite EP	30.7	89.2	4.58	2.9	6.7	19.5
HU-32	42°24'	104°38'	Granite LA(?)	6.7	68.6	4.85	10.3	1.4	14.1
HU-30	42°28'	104°37'	Argillite LA	<1	2.6	6.45	>2.6	<0.2	0.4
HU-33	42°24'	104°30'	Argillite LA	3.7	40.0	5.86	10.9	0.6	6.8
			Outlying areas						
HU-14	42°26'	104°55'	Granite LA	9.9	27.4	4.23	2.8	2.3	6.5
HU-15	42°26'	104°55'	Granite LA	5.2	51.8	4.19	10.0	1.2	12.4
HU-16	42°26'	104°55'	Gneiss LA	3.7	51.6	2.85	14.1	1.3	18.1
HU-17	42°39'	104°42'	Gneiss LA	1.9	4.0	1.17	2.1	1.6	3.4
HU-18	42°41'	104°40'	Gneiss LA	3.5	85.9	5.09	24.5	0.7	16.9
HU-19	42°52'	104°28'	Granite EP	1.6	0.4	4.10	0.3	0.4	0.1
HU-34	42°07'	104°47'	Gneiss LA	3.8	56.5	2.64	15.0	1.4	21.4

1/ Age assignment is based on geochronologic study. LA is late Archean and EP is early Proterozoic.

Table 2. Estimates of average radioelement contents of sialic crust and major classes of igneous rocks.

	Crust	Mafic	Intermediate	Silicic
U, ppm	2.8	0.9	2.0-2.6	3.5-4.8
Th, ppm	6-10	2.7	8.5-9.3	17-20
K, percent	1.6-2.6	0.6-0.8	2.7-3.4	3.4-3.8
Th/U	3.5-4.0	3.0-4.8	4.1	4.0-4.7
$(U/K) \times 10^4$	1	0.6	--	1.0-1.3
$(Th/K) \times 10^4$	3.3	2.8	--	4.9-5.0

Average values are compiled from Clark and others (1966), Heier and Rogers (1963), Heier and Billings (1970), Z. E. Peterman (unpubl. data, 1963), Rogers and Adams (1969a and 1969b), and Stuckless and others (1981). Ranges encompass the maximum and minimum average values given by the various estimates.

the radioelements are useful in detecting the effects of post-crystallization mobility of U and in identifying units that may be enriched or depleted, from average values, as primary features. For example, Stuckless (1980) has suggested, on the basis of Th/U ratios deduced from Pb isotope compositions, that high measured Th/U ratios may be good indicators of loss of U from whole-rock samples. Commonly measured radioelement ratios for silicic igneous rocks (Table 2) are Th/U = 4-5; U/K = $1.0\text{-}1.3 \times 10^{-4}$; and Th/K = 5×10^{-4}. In granites K rarely exceeds 5 percent because of their mineralogic composition. U and Th contents, however, are not controlled by the proportions of the major rock-forming minerals and can be much more variable as primary features or as the result of low-temperature modification.

Samples from the Hartville uplift range widely in their radioelement contents (Table 1). Th and U are plotted on Fig. 2 and Th/U and Th/K ratios on Fig. 3. Only two samples of metasedimentary rocks were analyzed (Table 1). Both samples are exceptionally high in K, indicating their argillaceous compositions, but are greatly different in Th and U contents suggesting that more extensive sampling and analyses would show very large variations in these elements in the metasedimentary units. Four samples of gneisses range in composition from tonalitic (HU-17 with 1.17 percent K) to granitic (HU-18 with 5.09 percent K), and Th and U vary accordingly.

The remaining samples represent various felsic intrusive units. In the ensuing discussion, we will consider only those samples of granitic composition that represent major intrusive units. Accordingly, samples HU-23 (granodiorite), HU-27B (aplite dike), and HU-19 (a granite from an outlying area with anomalously low Th) are excluded for

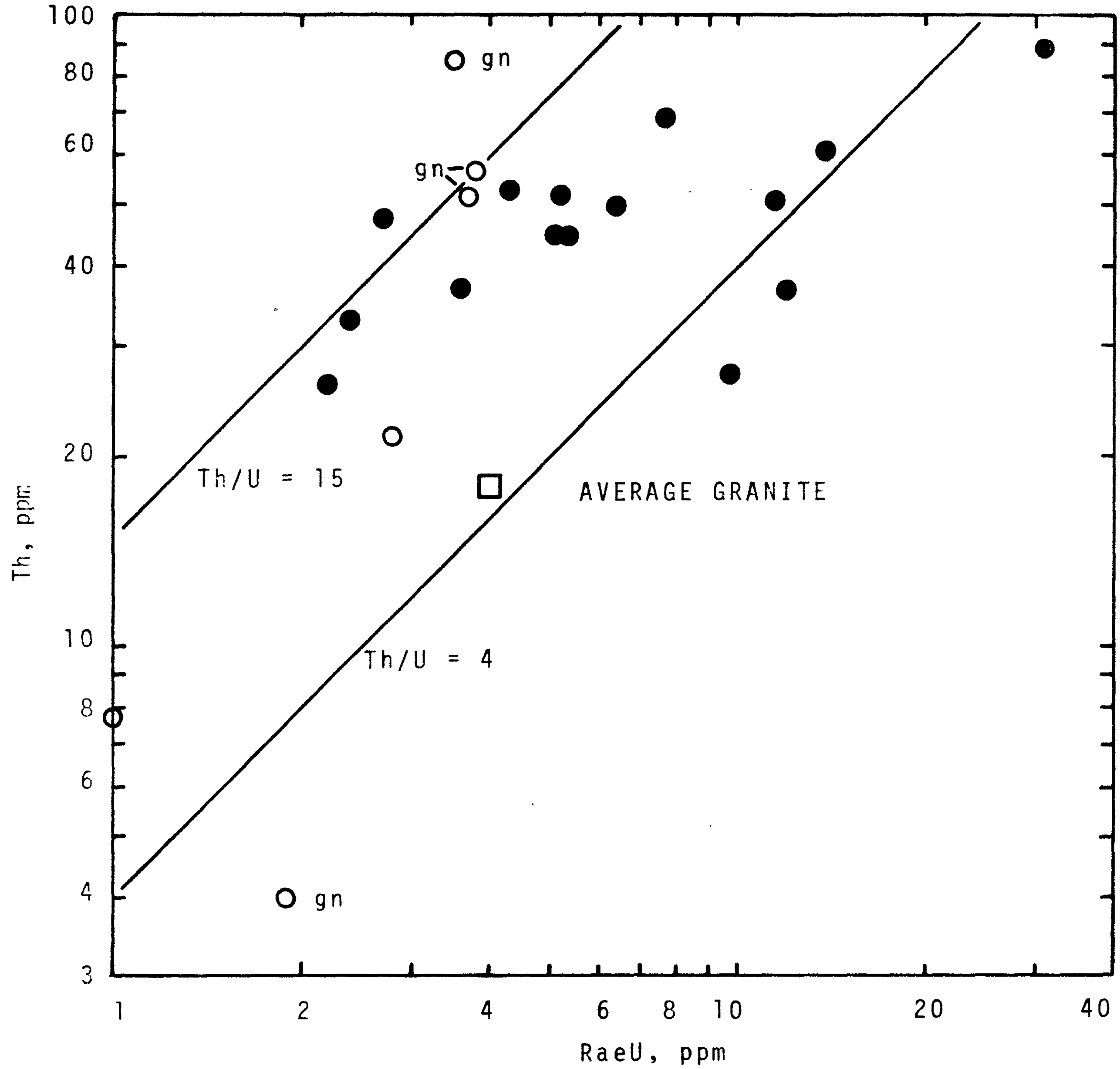

Figure 2. Th and RaeU contents of granites and gneisses. Values for the average granite are from Table 1. The granite samples discussed in the text as a group are indicated by the closed circles. Open circles labeled gn are gneisses; others are the igneous rocks excluded from the group of granites. HU-19 is not plotted because of the unusually low Th content.

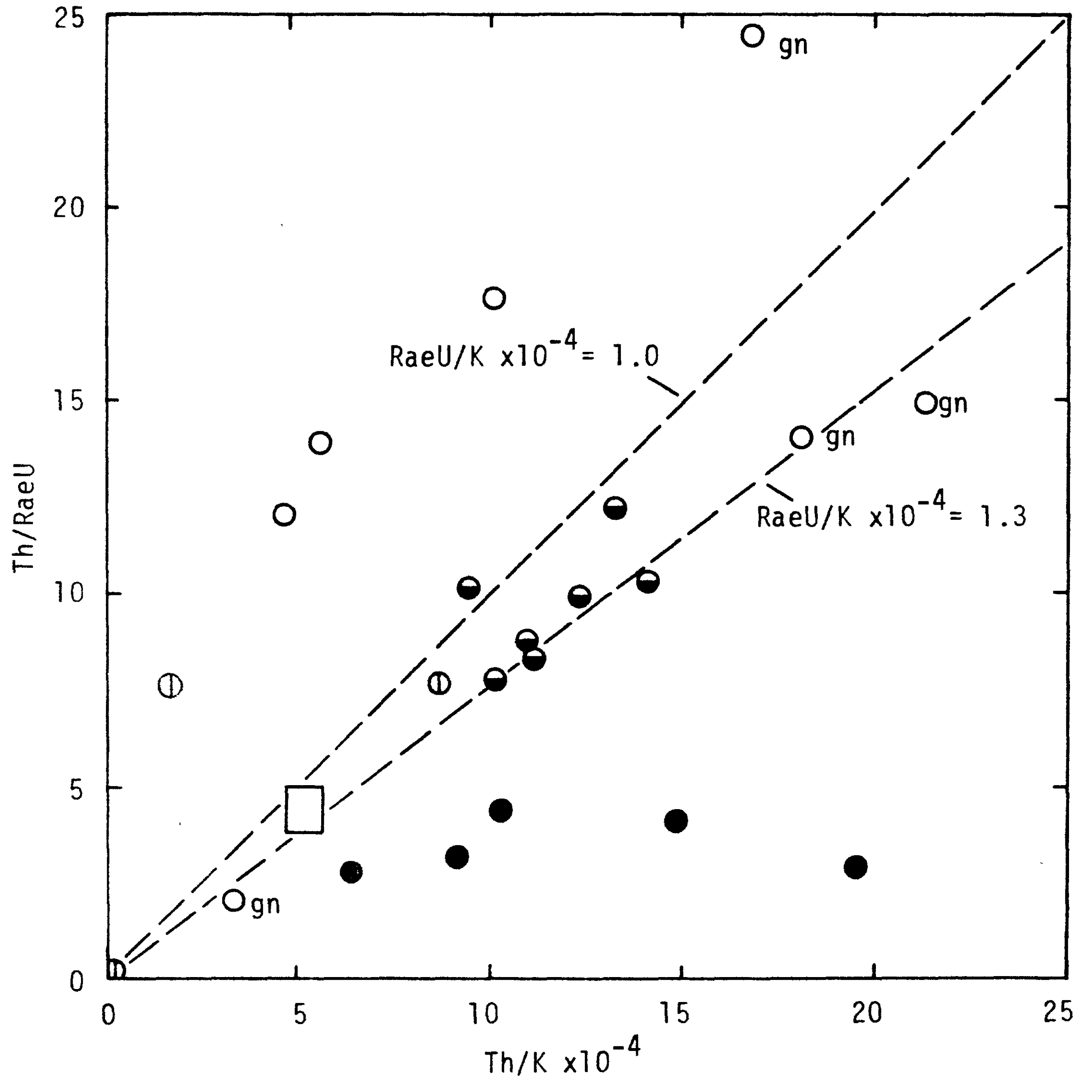

Figure 3. Relation between Th/RaeU and Th/K ratios for granites and gneisses. Gneisses are identified by gn. U contents of the granites discussed as a group in the text are indicated by the following symbols: open circles, less than 3 ppm U; half-closed circles, 3 to 8 ppm U; and closed circles, greater than 8 ppm U. Symbols with vertical lines are samples excluded from this group as discussed in the text.

purposes of discussing the radioelement variations. The remaining 15 granite samples show no relation between Th and U contents and age. The variability of radioelements within this group can be expressed as means and standard deviations (coefficients of variation, in percent, are given in brackets): K, 4.54 $\pm$ 0.63 (14) percent; Th, 48.2 $\pm$ 16.2 (34) ppm; and U, 8.1 $\pm$ 7.2 (89) ppm. By far the greatest variance is shown by the U contents, and it would be valuable to know if this is a primary feature of the units or due to post-crystallization mobility of U.

All of the granite samples are higher in Th than the average for silicic igneous rocks, and many samples have unusually high Th/U values (Fig. 2). Within this group, samples with higher U contents tend to have Th/U ratios closer to the average value of 4 (Fig. 3). Most of the samples have high Th/K ratios, which are probably close to the primary values as Th is generally less mobile than U in granitic rocks that have been weathered. Only those samples containing between 3.6 and 6.7 ppm U have nearly normal U/K ratios.

If it is assumed that all of the samples had primary Th/U ratios near 4, the relations shown in Figs. 2 and 3 suggest that many of the samples have lost considerable fractions of their original U. For example, an interval of 48 $\pm$ 16 ppm Th (the average value) would require that many of the samples with less than 8 ppm U would have to have had primary values of 8 to 16 ppm U (two to four times the average granite) for Th/U ratios of 4. Alternatively, if the U/K ratios in the normal range (Fig. 3) are considered to be primary, then those samples with higher and lower U/K ratios would have had to have gained and lost U, respectively. In either case, some degree of U mobility is indicated.

Samples MP-7A and MP-7B (Table 1), drill cores from approximately 200m below the surface, are unweathered and otherwise mineralogically fresh. These samples are among the highest in U and Th and have Th/U ratios close to the average value of 4. The data support the idea that loss of U from surface samples was an important process in causing the variations in U, Th/U, and U/K. However, it must be noted that the holes were drilled in the vicinity of a massive sulfide occurrence. Although this type of mineralization would not commonly involve U, the presence of iron sulfides, if oxidized, could trap U from circulating ground waters. The near normal Th/U ratios of these samples, however, does not support this speculation.

Presently exposed Precambrian rocks of the Hartville uplift were near the surface during the Cambrian and were re-exposed during the Laramide orogeny. Leaching of U could have occurred at either or both of these times. The history during the middle and late Proterozoic is poorly known. Biotite ages of about 1.3 Ga indicate a thermal event but this could have been one of regional uplift and cooling below the blocking temperature of biotite. Thus, the present surface would have been at considerable depth at about 1.3 Ga and probably prior to that time. The history between 1.3 and 0.5 Ga is not known.

CONCLUSIONS

Late Archean and early Proterozoic granitoids of the Hartville uplift are characterized by Th contents that are appreciably higher than the average for silicic igneous rocks. U contents and Th/U ratios are extremely variable. The high Th/K ratios are considered to be primary features. These relations lead to two possibilities:

(1) The unusually high Th/U ratios of many samples of the granites may have resulted from leaching of U under surface or near-surface

conditions. Based on the average Th content of 48 $\pm$ 16 ppm, original U contents of many of the samples may have been between 8 and 16 ppm if the original Th/U ratios were near the average value of 4.

(2) Samples with present-day and near average U contents have U/K ratios in the normal range of 1-1.3 x 10^{-4}. If these are primary values, many of the samples crystallized with unusually high Th/U ratios. U mobility is also suggested with some samples being depleted and others enriched in U.

In either situation, the extremely variable U contents and Th/U ratios indicate some degree of U mobility. The timing of this is not known but exposure of the Precambrian granites in the Cambrian and again during the Laramide orogeny would have offered ample opportunity for leaching of U to occur. The possibility that these units may have been near the surface in middle and late Proterozoic time cannot be evaluated from the existing geologic record.

REFERENCES CITED

Bayley, R. W., and Muehlberger, W. R., 1968, Basement rock map of the United States: U.S. Geological Survey, Scale 1:2,500,000.

Bunker, C. M., and Bush, C. A., 1966, Uranium, thorium, and radium analyses by gamma-ray spectrometry (0.184-0.352 million electron volts), in Geological Survey Research 1966: U.S. Geological Survey Professional Paper 550-B, p. B176-B181.

Bunker, C. M., and Bush, C. A., 1967, A comparison of potassium analyses by gamma-ray spectrometry and other techniques, in Geological Survey Research 1967: U.S. Geological Survey Professional Paper 575-B, p. B164-B169.

Clark, S. P., Jr., Peterman, Z. E., and Heier, K. S., 1966, Abundances of uranium, thorium, and potassium, in Clark, S. P., Jr., ed., Handbook of Physical Constants: Geological Survey of America Memoir 97, Sect. 24, p. 521-541.

Heier, K. S., and Billings, G. K., 1970, Potassium, in Wedepohl, K. H., ed., Handbook of Geochemistry: Springer-Verlag, New York, p. 19E1-19E14.

Heier, K. S., and Rogers, J.J.W., 1963, Radiometric determination of thorium, uranium, and potassium in basalts in two magmatic differentiation series: Geochimica et Cosmochimica Acta, v. 27, p. 137-154.

Rogers, J.J.W., and Adams, J.A.S., 1969a, Thorium, in, Wedepohl, K. H., ed., Handbook of Geochemistry: Springer-Verlag, New York, p. 90E1-90E14.

Rogers, J.J.W., and Adams, J.A.S., 1969b, Uranium, in Wedepohl, K.H., ed., Handbook of Geochemistry: Springer-Verlag, New York, p.92B1-92B3 and 92E1-92E8.

Rosholt, J. N., Zartman, R. E., and Nkomo, I. T., 1973, Lead isotope systematics and uranium depletion in the Granite Mountains, Wyoming: Geological Society of America Bulletin, v. 84, p. 989-1002.

Schonfeld, G. L., 1966, Alpha M--an improved computer program for determining radioisotopes by least squares resolution of the gamma-ray spectra: U.S. National Laboratories, Oak Ridge, ORNL-3975, 43 p.

Snyder, G. L., 1980, Map of Precambrian and adjacent Phanerozoic rocks of the Hartville uplift, Goshen, Niobrara,and Platte Counties, Wyoming: U.S. Geological Survey Open-File Report 80-779, 11 p.

Stuckless, J. S., 1980, Interpretation of thorium to uranium ratios in granitic rocks and implications for uranium exploration [abs.]: Book of Abstracts, America Association of Petroleum Geologists, Denver, p. 125-126.

Stuckless, J.S., and Nkomo, I. T., 1978, Uranium-lead isotope systematics in uraniferous alkali-rich granites from the Granite Mountains, Wyoming: Implications for uranium source rocks: Economic Geology, v. 73, p. 427-441.

Stuckless, J. S., Bunker, C. M., Bush, C. A., and Van Trump, George, Jr., 1981, Radioelement concentrations in Archean granites of central Wyoming: U.S. Geological Survey Open-File Report 81-948, 40 p.