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Uranium-series disequilibrium in tuff and granite: Hydrogeological implications

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1. Introduction

Uranium occurs naturally at trace levels in the major rock-forming minerals (quartz, feldspars, micas) in volcanic and plutonic rocks and is concentrated in accessory minerals (zircon, sphene, apatite). It may attain concentrations as high as 1000 ppm in the accessory minerals[1]. Radiometric age determinations on zircon and sphene have shown that uranium migration from these minerals is generally negligible over prolonged periods of geologic time. Zircon grains separated from highly weathered igneous rocks have been found to retain most of their uranium. In contrast, the uranium fixed onto mineral grain boundaries or present in less-resistant minerals such as biotite or hornblende can be readily leached by groundwater[2]. The ubiquitous presence of uranium in a rock makes it an ideal "natural analogue" for understanding the mobility of uranium at a potential site for nuclear fuel waste disposal and one that is easily overlooked in the search for suitable analogues for a disposal site.

Several of the intermediate radionuclides in the decay series of the two long-lived isotopes of uranium (^{238}U and ^{235}U) have half-lives greater than one year and are, therefore, of geological interest. In a sealed rock mass with no water-rock interactions, all intermediate radionuclides attain radioactive equilibrium with one another within a maximum 1–2 million years. Because rocks of the Yucca Mountain area and the Canadian Shield (both potential sites for nuclear waste disposal in the United States and Canadian programs, respectively) are considerably older, this condition (known as secular equilibrium) should exist in these rocks, and all daughter/parent radionuclide activity ratios should equal unity (1.000). If the ratios are found not to equal unity, then the rock has been disturbed, probably by groundwater transport of more soluble radionuclides into or away from the rock. How recently this migration has occurred can be determined from the half-life of the radionuclide involved. Depending on the analytical precision obtained, the observation of a $^{234}U/^{238}U$ activity ratio that is less than or greater than 1.000 clearly shows that an isotope of uranium has migrated within the rock in the last 1-2 million years. Other daughter/parent activity ratios can be used to detect radionuclide migration over shorter time-scales, such as $^{230}Th/^{234}U$ (300,000 years) and $^{226}Ra/^{230}Th$ (8,000 years).

Uranium-series disequilibrium is, therefore, a useful technique for application to site evaluation for nuclear fuel waste disposal because it can be used to:

1) show that so-called "intact rock" is indeed intact (i.e. radionuclides are in secular equilibrium and are immobile),

2) determine the principal flow regimes in a rock mass by analysis of rock matrix, fracture material, etc.,

3) estimate the time period of recent radionuclide migration in the rock, and

4) proxy as a natural analogue for the potential mobility of uranium at the site. Several examples of these applications have been reported[2-5].

This paper describes the use of uranium-series disequilibrium in the comparison of two North American sites: the water-saturated Lac du Bonnet granite batholith on the Canadian Shield and the unsaturated tuffs from the Exploratory Studies Facility (ESF) and Cross-Drift Tunnels at Yucca Mountain, Nevada. In particular, the fact that unfractured rock should be at secular equilibrium is applied to both sites to determine if the rock matrix is a significant flow path for groundwater.

2. Methods

Samples of granite and tuff have been analyzed at Atomic Energy of Canada Limited's (AECL) Whiteshell Laboratories, Manitoba, Canada. The samples were obtained from borehole cores that intersected both sparsely fractured, pristine rock and heavily fractured and altered rock at depths of up to 1000m (Canadian Shield) and ~300 m (Yucca Mountain). The samples from Yucca Mountain are defined as fractured or unfractured based on their location: samples from the Cross-Drift tunnel are termed "unfractured" because fracture frequency is very low in this area, whereas samples termed "fractured" are from the vicinity of the Sundance and Drill Hole Wash faults in the ESF tunnel.

Samples were trimmed to remove secondary mineral precipitates and alteration caused by drilling. They were then crushed and powdered to < 100 mesh (150 μm) and fused with lithium metaborate, in preparation for isotopic analysis. Chemical extraction of uranium and thorium isotopes, followed by alpha spectrometry, was used to determine uranium and thorium isotope activities. The analytical methods are described elsewhere[6].

3. Results

The activity ratios $^{234}U/^{238}U$ and $^{230}Th/^{234}U$ for fractured and unfractured granite and tuff samples are shown in Figures 1 and 2, respectively. An average error ($\pm$ 1σ) for the data is shown in Figure 1 and is based on counting statistics. In Figure 1, the data for altered, fractured granite samples[2] are compared with data for pristine, unfractured granite[7]. In Figure 2, samples from both the fractured and unfractured parts of the Yucca Mountain tuff have been analyzed as part of the ^{36}Cl Validation Project coordinated by Dr. Z.E. Peterman, U.S. Geological Survey (USGS), Denver, Colorado, on behalf of the U.S. Department of Energy (USDOE).

4. Discussion and Conclusions

The unfractured, pristine granites (shown as solid circles in Figure 1) clearly cluster tightly about the secular equilibrium position shown by the intersection of lines

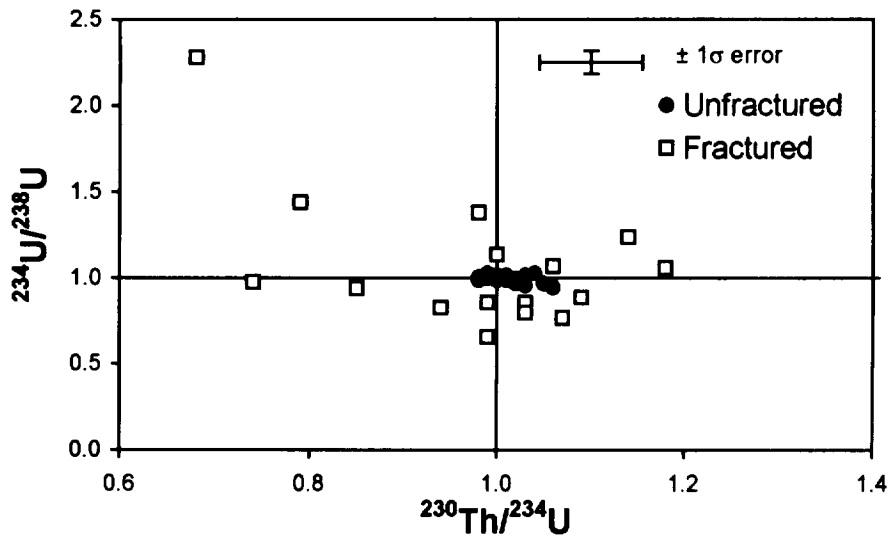

Figure 1. Uranium-series activity ratios for samples of granite from the Lac du Bonnet batholith, Manitoba, Canada.

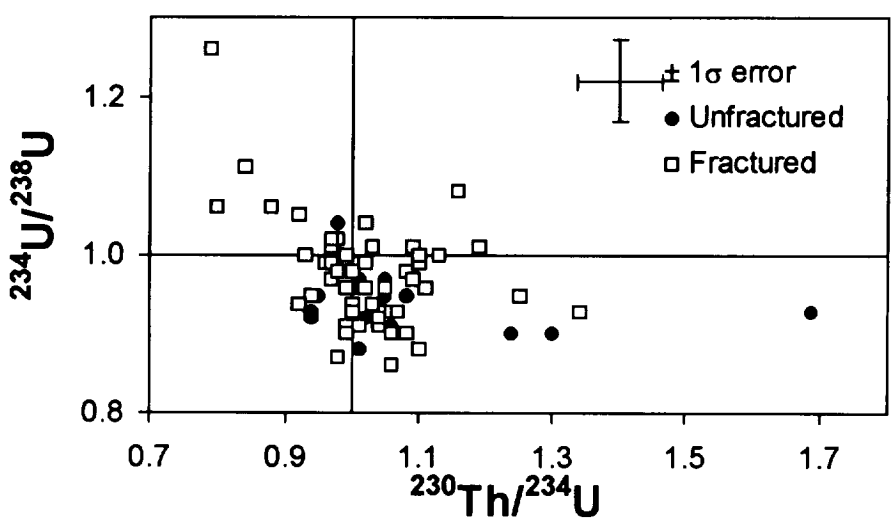

Figure 2. Uranium-series activity ratios for samples of tuff from Yucca Mountain.

describing ratios of unity. This supports the contention that these rocks are a closed system and have not significantly experienced radionuclide migration within the last million years. In contrast, activity ratio data for fractured, altered samples of granite (open squares on Figure 1) lie well away from the intersection and indicate losses and gains, principally of the more mobile ^{234}U, within the last million years and probably within the last 10,000 years[2].

A different situation is indicated in the data for the tuff (Figure 2). Here, there is little difference in the isotopic distribution patterns of the fractured and unfractured samples and both show that many of the points lie slightly below the $^{234}U/^{238}U$ equilibrium line. Although much of this displacement from the equilibrium value comes within the range of the ± 1σ error of the data, the general tendency for samples to show a $^{234}U/^{238}U$ ratio < 1.00 suggests that there is a small but measurable (~ 5%) loss of ^{234}U for many of the samples from both the Cross-Drift and ESF faulted areas. This has been confirmed by regular analysis of a standard uraninite known to be in secular radioactive equilibrium and by analysis of six randomly selected samples from the ESF tunnel for $^{234}U/^{238}U$ ratio using Thermal Ionisation Mass Spectrometry, a technique that gives an order of magnitude better precision in uranium-series measurements. Results of this work showed that all six samples were from 3.3 to 6.8 % (± 0.4%) deficient in ^{234}U (L. Neymark, written communication).

Loss of ^{234}U from the Yucca Mountain samples is probably caused by alpha recoil of ^{234}U from the solid phase into the surrounding pore fluid during decay of parent ^{238}U. This is a well-known process that can account for disequilibrium between these two isotopes of uranium[5]. The deficiency is measurable because ^{234}U is removed from the rock matrix by fluid transport through the relatively permeable tuff matrix. Alpha recoil of ^{234}U is also occurring in the unfractured granite of the Canadian Shield, but, in this case, the permeability of the rock is orders of magnitude lower than the tuff, so the daughter isotope is not significantly removed from its source. The transport of ^{234}U into the tuff at Yucca Mountain is supported by the observation of high $^{234}U/^{238}U$ ratios in pore fluids in the unsaturated zone[8].

Because the amount of the ^{234}U deficiency is dependent on factors such as pore fluid flow rate, water-rock volume and surface area ratios, and the half-life of ^{234}U, it is possible to model this process to determine pore fluid velocity and hence provide an independent estimate of recharge rate for the Yucca Mountain site. This work is in progress. The principal finding of the results presented here, however, is that uranium-series disequilibrium occurs in the unfractured rock matrix of the Yucca Mountain tuff to the same extent as in heavily fractured rock, and there is no indication, as found in the Canadian Shield granite, to suggest that fractures are the preferred flow-paths.

5. Acknowledgments

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6. References

1. Gascoyne, M. 1992. Geochemistry of the actinides and their daughters. In Uranium-series Disequilibrium: Applications to Earth, Marine and Environmental Sciences, 2nd ed., (eds. M. Ivanovich and R.S. Harmon), Clarendon Press, Oxford, 34-61.

2. Gascoyne, M. and J.J. Cramer. 1987. History of actinide and minor element mobility in an Archean granitic batholith in Manitoba. Appl. Geochem. 2 (1) 37-53.

3. Schwarcz, H.P., M. Gascoyne and D.C. Ford. 1982. Uranium series disequilibrium studies of granitic rocks. Chem. Geol. 36 (1/2), 87-102.

4. Griffault, L.Y., M. Gascoyne, D.C. Kamineni, R. Kerrich and T.T. Vandergraaf. 1993. Actinide and rare earth element characteristics of deep fracture zones in the Lac du Bonnet granitic Batholith, Manitoba, Canada. Geochim. Cosmochim. Acta, 57, 1181-1202.

5. Ivanovich M. I. and R.S. Harmon. 1992. Uranium-series Disequilibrium: Applications to Earth, Marine and Environmental Sciences, 2nd ed., Clarendon Press, Oxford.

6. Gascoyne, M. and J.P.A. Larocque. 1984. A rapid method of extraction of uranium and thorium from granite for alpha spectrometry. Nucl. Instr. Methods in Phys. Res. 223, 250-252.

7. Shewchuk,T. and M.Gascoyne. 1997. Uranium-series disequilibrium studies of unaltered rocks from the Lac du Bonnet Batholith. Atomic Energy of Canada Limited Tech. Record TR-788/COG-97-320-I.

8. Paces, J.B., K.R. Ludwig, Z.E.Peterman and L.A. Neymark. 2000. Uranium isotopic composition of water in the Death Valley groundwater basin emphasizing flow patterns at Yucca Mountain, Nevada, USA, in prep.