5 U-SERIES NUCLIDES AS TRACERS IN GROUNDWATER HYDROLOGY
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5.1 Introduction

5.1.1 Importance

The occurrence of the heavy radionuclides in the hydrosphere has become increasingly important in the context of today's emphasis on the measurement of quality and quantity of water resources. The study of the natural aqueous behaviour of uranium, radium, and the shorter-lived daughters serves both as a background for radioactivity pollution studies, and also as a widely applicable method of tracing movements of the groundwater itself.

Sensitive new measurement techniques have enabled this approach to become more applicable to diverse hydrologic environments, and a better understanding of the mechanisms of isotopic fractionation has been the result. This is an appropriate time to review the current state of progress of the study of U-series radionuclides in hydrologic tracing.

5.1.2 Early history of the use of U-series disequilibria in the hydrosphere

It was not so surprising to find that the radioactivity of $^{226}\text{Ra}$ and $^{222}\text{Rn}$ in groundwaters far exceeded, at times, that of the ultimate parent $^{238}\text{U}$ (Kuroda et al., 1954; Cherdantsev et al., 1955; Scott and Barker, 1962). The chemistry of Ra is quite different from that of U, and the mobility of the gaseous elemental Rn was only to be expected. However, discovery of the widespread disequilibrium of $^{234}\text{U}$ relative to $^{238}\text{U}$ in groundwaters and related soils and sediments by Cherdantsev et al. (1955, 1971), in sea water by Thurber (1962), and groundwaters by Rosholt et al. (1963) came as a surprise. It was at that time that the role of decay-related mobilisation of the alphagenic daughters in the aqueous environment became apparent. It is our view that even today the importance of alpha recoil in causing U-series disequilibrium in groundwaters is generally underestimated. The use of $^{234}\text{U}/^{238}\text{U}$ disequilibrium as a tracer for groundwater was demonstrated by Osmond et al. (1968), and soon became an established technique (Osmond and Cowart,
A favourable aspect has been the relatively simple yet accurate measurements that could be made by alpha spectrometry.

The use of the $^{234}\text{U}/^{238}\text{U}$ pair in tracing water has been reviewed by Osmond (1980), and Osmond and Cowart (1976, 1982, 1992).

5.1.3 New developments

In recent years, the development of mass spectrometric methods has permitted the analysis of much smaller water samples and with greater accuracy. As a consequence, aquifers of lower porosity can be studied, and the movement of water through semi-permeable aquicludes as well.

Given the new techniques that permit the study of an expanded number of environments, together with the need for a better understanding of water-rock interactions, and in particular the role of recoil in causing the mobilisation of U-series daughters in groundwaters, this review of the subject is, we think, timely.

5.1.4 Organisation of this review

After a discussion of the pertinent chemical behaviour of uranium, radium, and short-lived daughters, and the principles governing their isotopic fractionation in nature, we will study how these principles are manifested in one type of aquifer, the sandstone roll-front uranium deposits. We then will show how the basic pattern of U-series fractionation in these roll-fronts can be applied to understand and classify aquifers of various types.

The most diagnostic parameter and distinguishing character of groundwaters is the variation in the activity of the daughter $^{234}\text{U}$ relative to its parent $^{238}\text{U}$. This is usually expressed as an activity ratio, $^{234}\text{U}/^{238}\text{U}$ (AR), and constitutes a 'fingerprint' that can be used to trace water masses under a wide variety of circumstances.

Large excesses of $^{226}\text{Ra}$ and $^{222}\text{Rn}$ are found in many groundwaters, often associated with uraniferous host rocks and so these nuclides have also at times been useful as water tracers (Kuroda et al., 1954; Scott and Barker, 1962). However, the unique redox geochemistry and longer lifetimes of the uranium isotopic pair result in a more stable and consistent fingerprint system for groundwaters, and will be the principal focus of this review.