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Radium and radium-daughter nuclides in carbonates: a brief overview of strategies for determining chronologies

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ABSTRACT

Radium isotopes have been used extensively to trace the movement of groundwater as well as oceanic water masses, but these radionuclides (and their daughters) are also useful chronometers for the determination of the time scales of other Earth and environmental processes. The purpose of this overview is to present the application of Ra and Ra daughters in the dating of carbonates. We show that the choice of dating method (decay of excess radionuclide or ingrowth of daughter) depends strongly on the parent/daughter activity ratios in the water in which the carbonate was precipitated. Thus freshly precipitated carbonates uniformly show excesses of ^{226}Ra relative to its parent ^{230}Th, and ^{226}Ra decay can provide ages of carbonates over Holocene time scales. In contrast, carbonates are precipitated in waters of greatly varying ^{210}Pb/^{226}Ra. Corals, deep-sea hydrothermal vent clams and the shelled cephalopod *Nautilus* live in waters with significant dissolved ^{210}Pb and all show excesses of ^{210}Pb in their carbonate. Bivalve molluscs from nearshore and coastal waters, and carbonates deposited from groundwater environments (e.g. travertines) in which ^{210}Pb is efficiently scavenged from solution, show deficiencies of ^{210}Pb relative to ^{226}Ra. In contrast, fish otoliths strongly discriminate against ^{210}Pb regardless of the environment in which the fish lives. Deficiencies of ^{228}Th relative to ^{228}Ra are common in all carbonates. Useful time ranges for the ^{210}Pb/^{226}Ra and ^{228}Th/^{228}Ra chronometers are ~100 y and ~10 y, respectively.

1. Introduction

Disequilibrium among the nuclides of the uranium- and thorium-decay is a large subject with many possible applications (Ivanovich et al., 1992; Bourdon et al., 2003; Turekian and Bacon, 2003; van Calsteren and Thomas, 2006; Krishnaswami and Cochran, 2008). Fig. 1 shows the simplified decay series schemes for ^{238}U and ^{232}Th. The basic principle for the use of U/Th-series nuclides in dating depends on the fractionation of the different radioisotopes within a decay series due to the differences in the chemical behavior of each element in the aquatic environment (Krishnaswami and Cochran, 2008). For example, thorium and lead isotopes are readily scavenged onto particles, whereas radium and uranium isotopes tend to remain in the dissolved phase, making them available for incorporation in biological shells or tests. This separation of Th and Pb from Ra causes radioactive disequilibrium between the parent-daughter pairs (Th–Ra and Ra–Pb), creating excesses or deficiencies which may be used as chronometers. Among the U- and Th-series nuclides, the radium isotopes are of special interest as their half-lives potentially permit the dating over the 0–8 kyr BP interval (utilizing excess ^{226}Ra), overlapping with ^{14}C-dates, and also the 0–100 yr interval (utilizing ^{228}Th/^{228}Ra and ^{210}Pb/^{226}Ra disequilibria; Fig. 1). The potential for development of a Ra dating technique for carbonates arises from the different geochemical behaviors of the dissolved radium and its particle-reactive parents (^{230}Th, ^{232}Th) and daughters (^{210}Pb, ^{228}Th). Radium isotopes are incorporated into biogenic calcite and some (but not all) aragonite in proportion to their ratio to calcium in sea water. In the dating of carbonates using Ra isotopes, there are two distinct ways by which the disequilibrium method is applied: (1) the excess method in which the daughter (e.g. ^{226}Ra or ^{210}Pb) activity is much higher than its parent (e.g. ^{230}Th or ^{226}Ra, respectively) activity, and (2) the ingrowth method, in which the initial activity of the daughter (^{210}Pb or ^{228}Th) at the time of incorporation of the radium isotopes in the carbonates is negligible and only ^{226}Ra or ^{228}Ra is present. From knowledge of the half-life of the considered radionuclides, one can determine the age of the sample.

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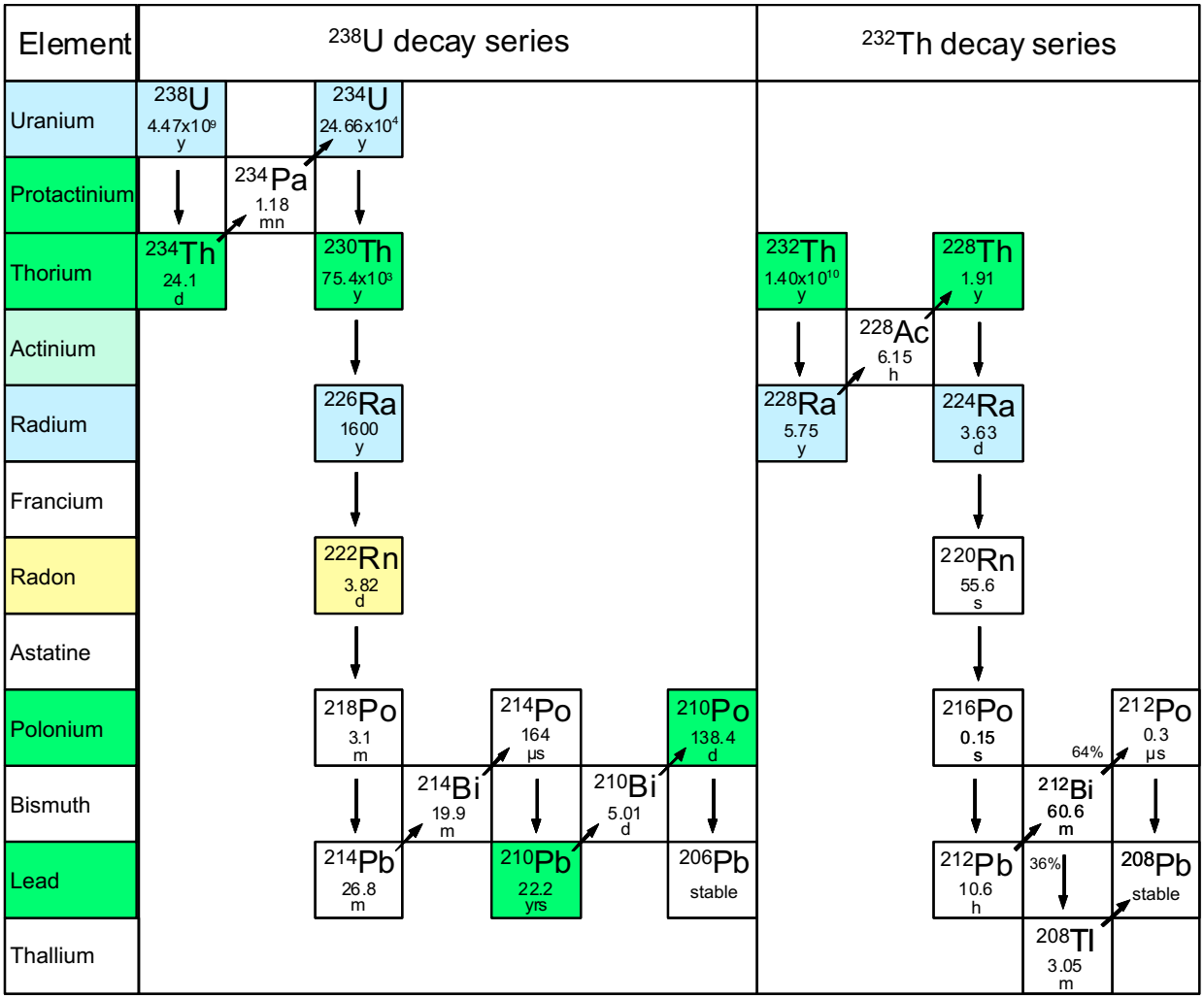

Fig. 1. Simplified chart of the ^{238}U- and ^{232}Th-decay series, colored according to the behavior of the element in aquatic environments (blue, soluble; green, reactive toward particles; yellow, noble gas/unreactive). Some of the radioisotopes within the decay series (not colored) do not have direct interest for environmental studies due to their very short half-lives, but could be used to determine a parent nuclide (see Section 3).

Carbonates suitable for dating by radium include biogenic carbonates, such as those deposited by molluscs and corals, and inorganic carbonate deposits, including low-temperature speleothems or travertines and high-temperature hydrothermal carbonates. The latter form when hydrothermal mineral springs enriched in dissolved CO_2 emerge and calcium carbonate precipitates (Rihs et al., 2000). Pedogenic carbonates or calcretes generally form on times scales long compared with the half-life of ^{226}Ra, and their dating is accomplished by U/Th disequilibria (e.g. ^{238}U–^{234}U–^{230}Th; Candy et al., 2004; Chgabaux et al., 2008; Cornu et al., 2009); thus they are not discussed further in this review. The present overview focuses on two main environmental applications of Ra and daughter isotopes for dating carbonates: the dating of carbonate deposits for the reconstruction of geological or climatic history, and the dating of shellfish, fish, or crustaceans for determination of growth rates and development of fisheries management strategies.

2. Principles

2.1. The excess method

Holocene carbonates can be dated using the U–Th ingrowth method, but this approach is less useful for carbonates younger than ~10 ka because of the low ingrowth of ^{230}Th. As with U–Th methods, it is assumed that only U and Ra isotopes are co-precipitated during the formation of carbonates at the time of deposition, and not ^{230}Th, because Th is not present in solution. This initial Ra (Ra_0) represents the excess or unsupported radium, which is used for dating. The temporal evolution of ^{226}Ra activity may be expressed as (Eikenberg et al., 2001; Soligo and Tuccimei, 2008):

$$(^{226}\mathrm{Ra}) = (^{226}\mathrm{Ra}_0)e^{-\lambda^{226}t} + (^{234}\mathrm{U})\frac{\left[\lambda^{226}\left(1-e^{-\lambda^{230}t}\right)-\lambda^{230}\left(1-e^{-\lambda^{226}t}\right)\right]}{\left(\lambda^{226}-\lambda^{230}\right)} \quad (1)$$

Eq. (1) includes terms for the decay of Ra initially co-precipitated into the carbonate and the production of ^{226}Ra from ingrowth of ^{230}Th from the decay of ^{234}U. The terms: λ^{226}, λ^{230} are the decay constants of ^{226}Ra and of ^{230}Th, respectively; (^{226}Ra) and ($^{226}Ra_0$) are the activities of ^{226}Ra at time t and at the time of incorporation of Ra; (^{234}U) is the activity of ^{234}U. (We use parentheses to denote activities and activity ratios in this paper). For carbonate material <10 ky, the measured ^{234}U activity can be considered equal to the initial ^{234}U activity because the ^{234}U half-life is sufficiently long that minimal decay has occurred. The excess Ra activity is generally