

Investigation of $^{226}\text{Ra}/\text{Ba}$ Dating of Marine Carbonate by TIMS

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Age-dating of Holocene marine carbonate (e.g. molluscs, foraminifera, etc.) is generally done by measuring cosmic-ray produced radiocarbon, and subsequent conversion to absolute age using the atmospheric tree-ring radiocarbon master-record. This conversion includes a correction for the apparent radiocarbon age of ambient ocean water, usually 400 years at sea surface. However, in many oceanic regions this reservoir age is up to three times higher due to upwelling of aged subsurface water, and may also be variable in time. A potential alternative for age-dating, and for assessing surface water ^{14}C values in the past, is to use ^{226}Ra ($t_{1/2} = 1600$ years) in marine carbonate. Radium does not have a stable isotope, but due to similar geochemical cycling $^{226}\text{Ra}/\text{Ba}$ ratios are constant within analytical uncertainty with a molar ratio of 5×10^{-9} throughout the world ocean apart from the deep Pacific (Östlund et al. 1987). A pilot study using an alpha-counting technique on two recent mollusc samples from the Antarctic, each of > 25 g reproduced the global seawater $^{226}\text{Ra}/\text{Ba}$ ratio (Berkman and Ku 1998). We have adopted existing methods of ion-exchange to separate Ra from marine carbonates (Chabeaux et al. 1994) and used thermal ionization mass spectrometry with a ^{228}Ra spike to analyze the ^{226}Ra concentrations (Cohen and O'Nions 1991). Yields of Ra through the chemistry are currently 60%. We have measured the ^{226}Ra concentration in molluscs from the North Atlantic, the Antarctic, and the Arabian Sea, and also in bulk marine carbonate and foraminifera samples from the Arabian Sea. The molluscs range from 15 to 30 fg $^{226}\text{Ra}/\text{g}$ carbonate (fg = 10^{-15} g). Internal precision is 1% (2s) and we observe no significant mass fractionation. Analysis have been made down to 1 fg Ra - equivalent to less than 100 mg of typical marine carbonate. This allows measurement of individual shells or subsamples of shells. Three replicates of one mollusc shell gave an external reproducibility within 4% (2s). One 0.5 g sample planktonic foraminifera (mixed species) and five bulk marine carbonate samples were also measured (the latter consisted of 0.5 - 1.0 g dominated by foraminifera and fish debris). These samples were taken from core tops from the upper continental margin off Pakistan at water depths between 100 and 1800 m, where sulfate reducing conditions at the sedi-

ment surface are common. They were cleaned with an oxidative-reductive procedure (Lea and Boyle 1991), but without the final complexing step to remove adhesive particulate barite. Although adhesive barite is thought to increase Ba and Ra concentrations in foraminifera significantly, $^{226}\text{Ra}/\text{Ba}$ ratios in bulk marine particles at shallow depths are equal to seawater (Moore and Dymond 1991) so this increase does not impact the ratio. ^{226}Ra concentrations are 118 fg/g carbonate in the planktonic sample and between 80 and 200 fg/g in the bulk carbonate samples. Using the Ba partition coefficient of Lea and Boyle (1991), and seawater ^{226}Ra and Ba concentrations, expected ^{226}Ra values for foraminifera are between 10 and 15 fg/g carbonate. The very high measured values indicate a contamination by a non-carbonate phase. The $^{226}\text{Ra}/\text{Ba}$ ratios for three mollusc samples range from 1.7×10^{-9} to 6.0×10^{-9} . These values are close to the seawater ratio but show unexpected scatter, perhaps due to differences in the $^{226}\text{Ra}/\text{Ba}$ ratio close to shore. A similar scatter is observed in the bulk carbonate samples from the Arabian Sea. This cannot be attributed to a near-shore effect but may be due to an upward ^{226}Ra flux out of the sediments. Most promisingly, the planktonic foraminifera sample yielded a $^{226}\text{Ra}/\text{Ba}$ of 4.9×10^{-9} and was within error of the seawater $^{226}\text{Ra}/\text{Ba}$ ratio despite the high concentrations. This demonstrates the potential usefulness of $^{226}\text{Ra}/\text{Ba}$ ratios for age-dating at least open-marine carbonates. We are continuing work on improving the cleaning procedure and analytical techniques and applying these techniques to older samples.

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