

Alabama Gulf Coast groundwaters: ^4He and ^{14}C as groundwater-dating tools

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ABSTRACT

Analyses of ^4He and ^{14}C in groundwaters from a Miocene quartz aquifer on the Alabama Gulf Coast show the usefulness of ^4He for dating these Holocene groundwaters. In this aquifer system of low alkalinities and low pHs, radiocarbon ages can be used without model correction. The groundwaters studied ranged from 42.3% to 95.5% modern carbon and yielded uncorrected ages of 375–6790 yr. Radiogenic ^4He ages ranged from >50–7500 yr.

Keywords: groundwater, age dating, ^4He , ^{14}C , Baldwin County Alabama.

INTRODUCTION

Knowledge of groundwater ages and recharge rates is important for planning water resource allocation. To understand groundwater age (i.e., the time since recharge), radiocarbon analysis has been suggested as the only practical tool for groundwater-dating studies on time scales to 30 k.y. The usefulness of ^{14}C is reduced by uncertainties in the source of C and by its unsatisfactory application to shorter time scales (Edmunds and Smedley, 2000). Some have proposed that the noble gas ^4He can be a useful indicator of groundwater ages of 100–10,000 yr (Marine, 1979; Andrews and Lee, 1979; Torgersen and Clarke, 1985; Stute et al., 1992; Castro et al., 1998; Cserepes and Lenkey, 1999). The validity of ^4He ages depends upon the presence or absence of external sources, whether ^4He is leaking from grains at a rate in excess of ^4He produced from U and Th decay, or is in steady state (Torgersen and Clarke, 1985; Solomon et al., 1996; Solomon, 2000). Few studies have included the use of both noble-gas isotopic tracers and radiocarbon in the same system (e.g., Castro et al., 2000), and in those in which both tracers have been measured, they have been used for waters of very different ages (Vengosh et al., 2002).

The Baldwin County, Alabama, aquifer system is an ideal quartz aquifer system for age dating by using radiocarbon and for calibrating ^4He with ^{14}C because the aquifer consists almost entirely of quartz. Although not a typical U-bearing mineral, quartz contains significant ^4He and ^{21}Ne , products of U decay. Thus, in this quartz aquifer system, the aquifer solid phase both provides a source of radiogenic ^4He and is low in carbonate, making ^{14}C age dating straightforward with no corrections. Because the protolith age is Miocene, the He release rate nearly equals its production rate from U and Th decay (i.e., steady state). In this paper we present the results of groundwater age dating by both ^{14}C and ^4He . We show the usefulness of He as a groundwater age-dating tool and its good correspondence with measured ^{14}C ages.

PREVIOUS RELATED STUDIES

Helium measured in groundwater is often oversaturated with respect to solubility equilibrium with the atmosphere (Marine, 1979; Andrews and Lee, 1979; Torgersen and Clarke, 1985; Stute et al., 1992; Castro et al., 1998; Cserepes and Lenkey, 1999). Produced by the decay of uranium and thorium in crustal rocks, ^4He concentrations have been shown to increase qualitatively with groundwater age. Several potential

sources exist, including crustal ^4He diffusing from adjacent low permeability U-rich strata (e.g., shales) and in situ production of ^4He from α decay of U and Th series in rocks and sediments and subsequent release into groundwater by diffusion or α recoil.

In the Jurassic Great Artesian Basin, Australia, measured He values in groundwater were shown to result from He diffusing from below the aquifer; accumulation of He over thousands of years resulted in He concentrations 770 times He solubility (Torgersen and Clarke, 1985). In contrast, observed vertical He profiles in groundwater at Sturgeon Falls, Ontario, represented in situ accumulation of He from diffusional loss in He-rich aquifer sediments, not from crustal He diffusing from below (Solomon et al., 1996). The He accumulation in groundwater resulting from diffusional loss from aquifer solids is highly grain-size and age dependent (Solomon et al., 1996).

By assuming that release of ^4He was in steady state with ^4He production within the aquifer rock, Bottomley et al. (1984) calculated accumulation rates for He in deep groundwater reservoirs of the Canadian Shield. They found no clear relationship between groundwater age and measured He concentrations. The He accumulation age dates for groundwater were either too young or extremely old when compared with ^{14}C groundwater ages. In studies of the Triassic Bunter sandstone in Nottinghamshire, England, Andrews and Lee (1979) and Andrews et al. (1982) performed ^4He age calculations based on U-Th concentrations in rocks, rock density, and estimated fractional porosity of the rock. Their studies yielded higher ^4He model groundwater ages than measured ^{14}C ages.

In a study of the Paleocene coastal plain Aquia aquifer, Maryland (Aeschbach-Hertig et al., 2002), carbonate shelly debris contributed dead carbon to groundwater, leading to apparent ^{14}C ages much older than those determined by noble-gas thermometry, age dating, and stable isotope data (Chapelle and Drummond, 1983; Hansen, 1974). The ^{14}C ages at this site, calculated by using the Fontes and Garnier (1979) model, suggested a Pleistocene age for the water (most samples were apparently older than 30 ka), whereas other climate-sensitive geochemical analyses (e.g., noble gas recharge temperature and stable isotopes) suggested Holocene ages. Unaccounted-for carbonate exchange processes were used to explain the low percentage of modern carbon (PMC) for ^{14}C results, an unsatisfactory explanation because it cannot be independently verified and does not account for the amount of calcite exchanged with aquifer solid phases. The ^{14}C was deemed to be a useless tool for dating in the Aquia aquifer.

In another study, good correlations were found between ^4He and ^{14}C ages in the Eocene Carrizo aquifer in Texas, the Tertiary Ojo Alamo and Nacimiento aquifers in New Mexico, and the Auob Sandstone aquifer in Namibia (Castro et al., 2000), only if external ^4He source terms are understood. Castro et al. (2000) found some groundwater ages determined by noble-gas data equivalent to the rock age and concluded that most He in these aquifers had external sources (i.e., He diffusion from fine-grained shale beds into aquifer sands), to allow agreement with ^{14}C ages. As in the case of the Great Artesian Basin, external He source can overwhelm in situ sources of ^4He to groundwater.

In previous studies, ignorance of the C source hindered use of radiocarbon in age dating. In studies that combined both age-dating

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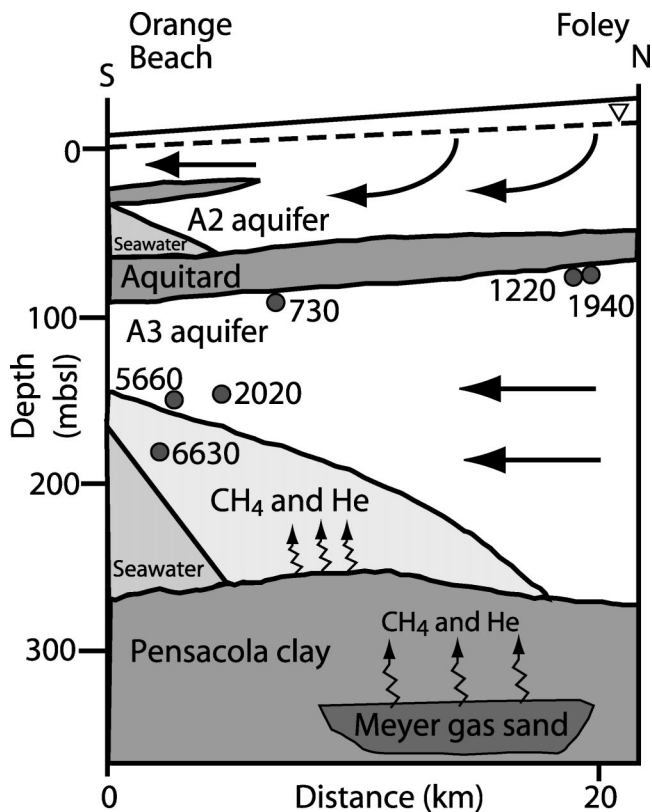


Figure 1. North-south cross section of A2 and A3 aquifers drawn through center of southern Baldwin County (see Fig. DR1 [footnote 1] for site map) using only those wells sampled in center of county. Circles represent both location and depth of well screens in wells from which samples were obtained for ^{14}C and ^4He analysis (mbsl—meters below sea level). Groundwater from deepest samples obtained from A3 aquifer of southern Baldwin County (samples 53 and 54) contains natural gas components attributed to flux of natural gas from methane reservoir within Pensacola clay. Helium and methane dissolved in Pensacola clay pore waters diffuse upward into groundwater of A3 aquifer. High-velocity horizontal groundwater flow in A3 aquifer confines natural gas-derived He and CH_4 close to base of A3 aquifer. Figure is adapted from Dowling et al. (2004).

techniques, ages obtained have lacked agreement either because, as in the Aquia aquifer, the ^{14}C was found to be too low, or as in the Carrizo, external sources of ^4He give unrealistic ^4He ages. To account for carbon interactions with the solid phase generally requires use of modeled ages (e.g., Fontes and Garnier, 1979) to determine actual time since recharge. In other studies, interpretations of ^{14}C concentrations have been deemed to represent the extent of water-rock interactions (Clark et al., 1997) rather than time since recharge. In Clark et al.'s (1997) study of the Floridan aquifer in southeastern Georgia, few samples analyzed had ^{14}C values greater than the detection limit of 1.4 PMC owing to extensive water-rock interactions.

SITE DESCRIPTION

The A2 and A3 (Fig. 1) aquifers of Baldwin County, Alabama (Fig. DR1¹), important water resources of southwestern Alabama, are composed of shallow, unconsolidated Miocene and younger sediments deposited in fluvial and shallow-marine environments (Grubb and Carrillo, 1988). Cenozoic sediments forming the aquifers of the East Gulf

Coastal Plain were deposited in shallow-marine environments of Cretaceous to late Tertiary age. These deposits are estimated to dip gently toward the Gulf of Mexico at $\text{S}28^\circ\text{W}$ at a rate of 18.5 m/km (Robinson et al., 1996). These aquifers are part of the Citronelle Formation and undifferentiated Miocene sedimentary deposits (Chandler et al., 1985). In general, the groundwater flows from north to south and to southwest (Robinson et al., 1996).

The upper, or A2, aquifer ranges in thickness between 60 and 75 m and is the main source of water in southern Baldwin County. Agriculture is a major land use in the southern part of the county. Irrigated agriculture has been conducted as early as the 1940s (Reed and McCain, 1971) and much acreage is currently devoted to turf grass production. Intensive irrigation for agriculture, heavy precipitation, and highly conductive sediments result in large vertical velocities in the upper aquifer (Dowling et al., 2004). The deeper, or A3, aquifer is an undifferentiated Miocene stratum that ranges between 100 and 150 m in thickness.

The lithology of the Miocene deposits forming the southwest Alabama aquifers is distinct from those of the marine carbonate deposits of the Florida Miocene sediments (Isphording, 1977). Miocene sands of southwest Alabama are fine to coarse, containing gravels predominantly of quartzite and chert (Isphording, 1977). Mineralogical evidence suggests that these Alabama aquifer sands and gravels have multiple sources—reworked older coastal-plain sediments, Cumberland Plateau Paleozoic rocks, and Southern Appalachian and Piedmont metamorphic rocks (Isphording, 1977). These sedimentary aquifers are underlain by the Pensacola clay, a middle Miocene unit (Raymond, 1985) with commercial natural gas. There has been no CaCO_3 described in the aquifer solid phase (Isphording, 1977). The Upper Floridan aquifer is absent in this part of Alabama (Planert et al., 1993).

Wells sampled for this study (Fig. DR1; see footnote 1) were primarily production wells for municipal drinking water (samples 54, 56, 61, 62, 63, 64, 68) or irrigation wells located in turf grass farms (samples 55, 57, 65, 66, 67). Most of the municipal wells were also located in agricultural areas of the county, adjacent to turf farms. Only the Gulf State Park well (sample 53) fell in neither category. It is an irrigation well located on a golf course.

RESULTS

The ^{14}C in waters sampled from groundwater wells of Baldwin County, Alabama (Fig. DR1; see footnote 1) ranged from 42.2 to 95.4 PMC (Table DR1; see footnote 1). Uncorrected C ages were from 375 to 6920 yr before present. We have chosen to use uncorrected C ages (Fig. 2) in our data analysis and discussion because the most widely used model for correcting the ages is inappropriate (Fontes and Garnier, 1979). The solid phase of this aquifer consists solely of quartz sand. Consequently, water-rock interactions do not contribute C that requires correcting the initial C concentration, and this results in very low C levels in the waters. The very low measured alkalinities and pHs of these waters demonstrate that nearly all dissolved inorganic C exists as aqueous CO_2 from equilibration with vadose-zone soil CO_2 at the water table. Such aquifers need a factor of 0.9 to 1 to correct the very low measured C concentration (Clark and Fritz, 1997; Vogel, 1970). If we use 1, then the uncorrected ages equal the correct ages (Table DR1; see footnote 1). Use of 0.9 as the correction factor produces model ^{14}C ages older (nominally 10% older) than the uncorrected ages. Three wells (samples 61, 64, 68) have model ages that are just pre-nuclear (<100 yr, containing no tritium or tritogenic ^3He). Their radiocarbon ages of 400–900 yr appear to reflect the age of soil organic carbon and soil-zone processes, including oxidation of organic C and dissolution of any carbonate phase (if present).

The $\delta^{13}\text{C}$ values of $\sim -20\text{‰}$ are consistent with the oxidation of dominantly C3 organic C of grasses. The $\delta^{13}\text{C}$ values in most of our

¹GSA Data Repository item 2004049, analytical methods, Table DR1, and Figures DR1–DR2, is available online at www.geosociety.org/pubs/ft2004.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301-9140, USA.

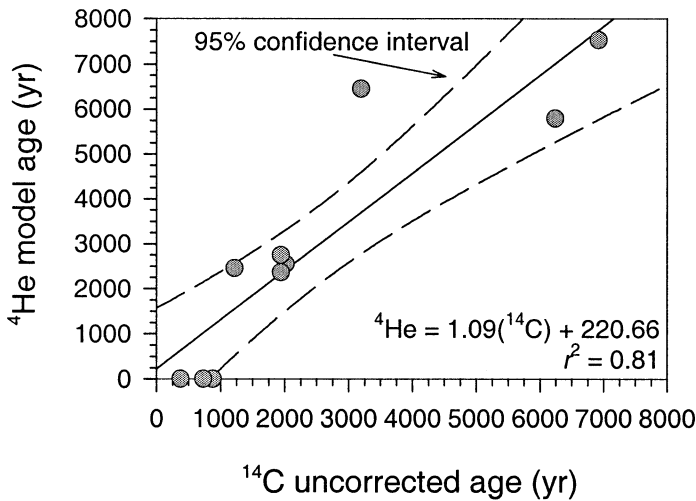


Figure 2. Plot of ^{14}C uncorrected age versus ^4He model ages. Solid line indicates calculated linear regression, and dashed lines indicate 95% confidence interval on line.

water samples are close to -20‰ , reflecting the pure C3 grass crop ($\delta^{13}\text{C}$ of -20‰) rather than a typical soil $\delta^{13}\text{C}_{\text{CO}_2}$ of $\sim -24\text{‰}$. Another possible reason for the observed $\delta^{13}\text{C}$ values is that respired CO_2 has caused dissolution of a minor amount of soil carbonate (-12‰) of greater age and lower ^{14}C content or the influence of some C4 coastal vegetation prior to the initiation of turf grass agriculture.

Any input of C to the aquifer from shell carbonate ($\sim 1\text{‰}$) can be assessed by the ^{13}C values. Shell carbonate will increase the $\delta^{13}\text{C}$ of the dissolved inorganic carbon by contributing C with a ^{13}C content of $\sim 1\text{‰}$, whereas initial C contributed by soil organic matter is expected to be $\sim -20\text{‰}$. Only in the deep Orange Beach well (sample 54) was a slightly enriched ^{13}C measured ($\delta^{13}\text{C}$ of -15.73‰), which may reflect a slight influence of seawater carbonate and elevated salt content from seawater intrusion (that well is located adjacent to the brackish Intracoastal Waterway).

Modeled ^4He ages from radiogenic ^4He in these same waters range from 0 to 7500 yr B.P. (Table DR1; see footnote 1) (Dowling et al., 2004). The ^4He ages were determined on the basis of the measured ^4He release rate of $0.0004 (\pm 0.00003) \mu\text{cm}^3 \cdot \text{kg}^{-1} \cdot \text{yr}^{-1}$ from the Miocene, low-U quartz sand from the Ecor Rouge sediment. The laboratory-determined release rates are consistent with the modeled release rate based on grain size, ^{21}Ne content, and Miocene depositional age (Fig. DR2; see footnote 1).

DISCUSSION

^4He Data and Release Rate

Groundwater samples with no measurable tritium and with radiogenic ^4He (corrected by using Ne and Ar concentrations for “excess air” by Dowling et al., 2004) were examined in the light of an He release model (after Solomon et al., 1996; Hunt et al., 2000). We estimate the release of He from quartz by modeling diffusional release over time (Dowling et al., 2004). The technique, which assumes that He initially stored within quartz grains is released and accumulates in groundwater over time, is effective in areas of moderate groundwater recharge and where deep-crustal sources of ^4He can be ruled out. The spherical-release model assumes that a sediment grain has a uniform distribution of ^4He . Initially diffusional release of ^4He follows an exponential decrease with time, then becomes linear over long time intervals after deposition, and eventually reaches steady state with its production from U decay. Laboratory release experiments were performed on sediment samples from the cliffs of the Ecor Rouge (A2 aquifer in Fairhope, Alabama) and from Geological Survey of Alabama

drill core 5386 from the Pensacola clay and extrapolated to 20°C (Dowling et al., 2004). In addition, model He release curves were calculated at 5 Ma for a range of grain sizes based on the measured diffusion in quartz at 20°C and an initial ^4He concentration based on measured ^{21}Ne (Fig. DR2; see footnote 1). The use of the known $^4\text{He}/^{21}\text{Ne}$ production ratio in silicates assumes complete retentivity for ^{21}Ne over time. In low-U sands such as the A3, the release rate at 5 Ma approaches, but still remains about 2 times higher than, the steady-state release rate equivalent to the in situ production rate and is not very sensitive to grain size over a diameter range of $100\text{--}800 \mu\text{m}$ (Fig. DR2; see footnote 1). Based on two independent laboratory methods to estimate the release of He, groundwater ages for the 5 samples containing excess He range from 2000 to 7500 yr; the ages become progressively older in wells deeper and closer to the sea.

We have excluded groundwater samples 53 and 54 from the He accumulation model. Both samples have He concentrations to 10 times higher than other A3 wells and have measurable CH_4 . We attribute their high levels of ^4He and ^3He to an external flux of natural gas (methane plus He) from the Pensacola clay, and not to diffusional release of ^4He from quartz grains. The R/R_{air} ratios in these two wells are similar to the ratio measured in a natural gas sample ($95.53\% \text{CH}_4$) from the nearby West Magnolia Springs gas production well ($R/R_{\text{air}} = 0.548$) tapping the Meyer gas sand. This points to the importance of methane analysis in evaluating the source of ^4He . Analysis of variance at $\alpha = 0.05$ of the measured R/R_{air} ratio among three groups of wells—A2 wells, A3 wells, and wells excluded from the analysis—shows that there is greater variance among these three groups of wells than within the groups at a high level of significance ($P = 8 \times 10^{-9}$, $F = 56.63$).

Comparison of Dating Methods

A plot of ^4He versus ^{14}C (Fig. 2) shows the good correlation ($r^2 = 0.81$) between the groundwater ages from these two methods in the Baldwin County aquifer system. The slope of 1.09 ± 0.43 ($|t| = 5.84$, $P = 0.0004$) and intercept of 220 ± 1433 yr ($|t| = 0.36$, $P = 0.73$), at the 95% confidence level, show that ^4He ages are in good agreement with ^{14}C ages. Most samples fall within the 95% confidence intervals. We have plotted ^{14}C ages on the x-axis, considering those as the data with error assumed to be negligible. Age errors for all ^{14}C measurements are in the range of 30–90 yr, or errors of 0.7%–10.7%. All errors are $< \pm 4\%$ except for sample 61, whose ^{14}C age of 375 ± 40 yr was the youngest ^{14}C age measured (Table DR1; see footnote 1).

This close association between radiogenic ^4He and ^{14}C indicates that $^4\text{He}_{\text{rad}}$ is a viable method for dating groundwater. However, several conditions must be met before the model based on He accumulation in groundwater may be applied. The release rate from the aquifer protolith should be determined experimentally because the He stored within quartz grains is released into groundwater at a rate greater than the steady-state production from U. Even in this pure quartz sand, after 5 m.y. the release is still twice the production rate. The ^{21}Ne concentration can be used as a proxy for the initial ^4He in the model as long as the age of deposition is known, and thus serves as a check for the laboratory release value. One must know the aquifer hydrogeology, and in those cases where a vertical gradient in ^4He can be established, it can be an aid in estimating the age. As revealed by the samples having high ^4He and low R/R_{air} (samples 53 and 54), the technique can only be used in areas of moderate recharge with no external source of He.

Most samples whose modeled ^4He ages were 0 (samples 61, 63, and 68) had measurable $^3\text{H}\text{--}^3\text{He}$ ages (Table DR1; see footnote 1). For sample 68 there was no tritium analysis, but when sampled in November 1998, this well had a tritium age of >50 yr (Dowling et al., 2004). Unlike the Sturgeon Falls, Canada, aquifer (Solomon et al., 1996), the $^4\text{He}_{\text{rad}}$ release rate from the Baldwin County aquifer solids is low, requiring a long period of time for measurable ^4He to accumulate in

the groundwater. The laboratory-measured ^4He release rate obtained with quartz separates (Dowling et al., 2004) and the He release model for this Alabama groundwater system indicate that it would take ~ 450 yr to accumulate $1 \mu\text{cm}^3 \cdot \text{kg}^{-1}$ of ^4He , about the minimum observable excess ^4He concentration after the air correction. The present study contrasts with the data from Sturgeon Falls aquifer from the Canadian Shield whose ^4He release rate is ~ 300 times greater than supported by in situ decay of U-Th decay series. As shown in the Sturgeon Falls groundwater study, it is difficult to use ^4He release when the sediments are recently deposited (i.e., since the last glacial), because the He release rate has not approached steady state. The ^4He release rate changes dramatically over the time scale of centuries, especially for fine-grained sediments.

CONCLUSIONS

The Baldwin County aquifers constitute an actively flowing Holocene groundwater system with rapid recharge. The analysis of ^{14}C and ^4He in the same groundwater samples shows the usefulness of ^4He as a dating tool for Holocene groundwaters, particularly in regions of rapid recharge and high groundwater flow velocities. In aquifers with little carbonate in the solid phase, the groundwaters can be reliably dated without need for model corrections to ^{14}C ages. The good correlation between ^{14}C ages and ^4He model ages, particularly for waters older than 1000 yr, shows the usefulness of ^4He as a groundwater age-dating tool.

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