

DR2004049

SAMPLING AND ANALYTICAL METHODS

During two campaigns, in 1999 and 2001, 13 groundwater samples (Fig. DR1; Table DR1) were collected and analyzed for the ^{14}C concentration in the dissolved inorganic carbon and for tritium and helium (Dowling et al., 2004). Samples for ^{14}C analyses were collected and preserved following the method of McNichol and Jones (1991) and were kept in the dark at room temperature until analysis at the National Ocean Sciences Accelerator Mass Spectrometry Facility at the Woods Hole Oceanographic Institution. The ^{14}C concentration of the dissolved inorganic carbon was determined by stripping the CO_2 gas from the samples. The CO_2 was reacted with H_2 and an Fe catalyst to form graphite, which was then pressed into targets for analysis in the accelerator, where atoms of ^{14}C are counted directly.

Gas concentrations and isotopic ratio measurements of the groundwater samples were carried out at the Rare Gas Facility at the University of Rochester (Dowling et al., 2004). The dissolved gas was extracted and processed on a high vacuum line (Poreda et al., 1988). The He isotope ratio measurements were made with a VG 5400 noble-gas mass spectrometer by peak height comparison to a calibrated air standard with errors of $\sim 2\%$ (Poreda and Farley, 1992). He isotope ratios are expressed as R/R_{air} , where R is the $^3\text{He}/^4\text{He}$ ratio in the sample and R_{air} is the $^3\text{He}/^4\text{He}$ ratio in the measured air standard. Errors in the reported values of R/R_{air} are $\sim 0.5\%$.

Laboratory helium release experiments

The He-release rate from the aquifer protolith into the surrounding groundwater is highly dependent upon the protolith age and can be established through laboratory diffusion-release experiments (Solomon, 2000; Hunt, 2000). For this study, a step heating procedure was used to determine the diffusional release of ^4He from air-dried soil samples. Approximately 150 grams of aquifer protolith were loaded into stainless steel tube furnaces on the high vacuum line and heated incrementally with an external resistive heater. Temperature was measured with two external thermocouples on the chamber and maintained by a variable transformer. The helium measurements were made on a VG5400 noble gas mass spectrometer by peak high comparison to a measured air standard.

Total concentration and isotopic composition of helium and neon for the sediment samples were determined by fusing approximately 100–200 mg of sample at $1800\text{ }^\circ\text{C}$ in a modified Turner double-walled furnace and measured on a VG 5400 noble gas mass spectrometer (Poreda and Farley, 1992). The He and Ne isotope ratio measurements were made by peak height comparison to a calibrated air standard with errors of $\sim 2\%$ (Poreda et al., 1988).

DATA REPOSITORY FIGURE CAPTIONS

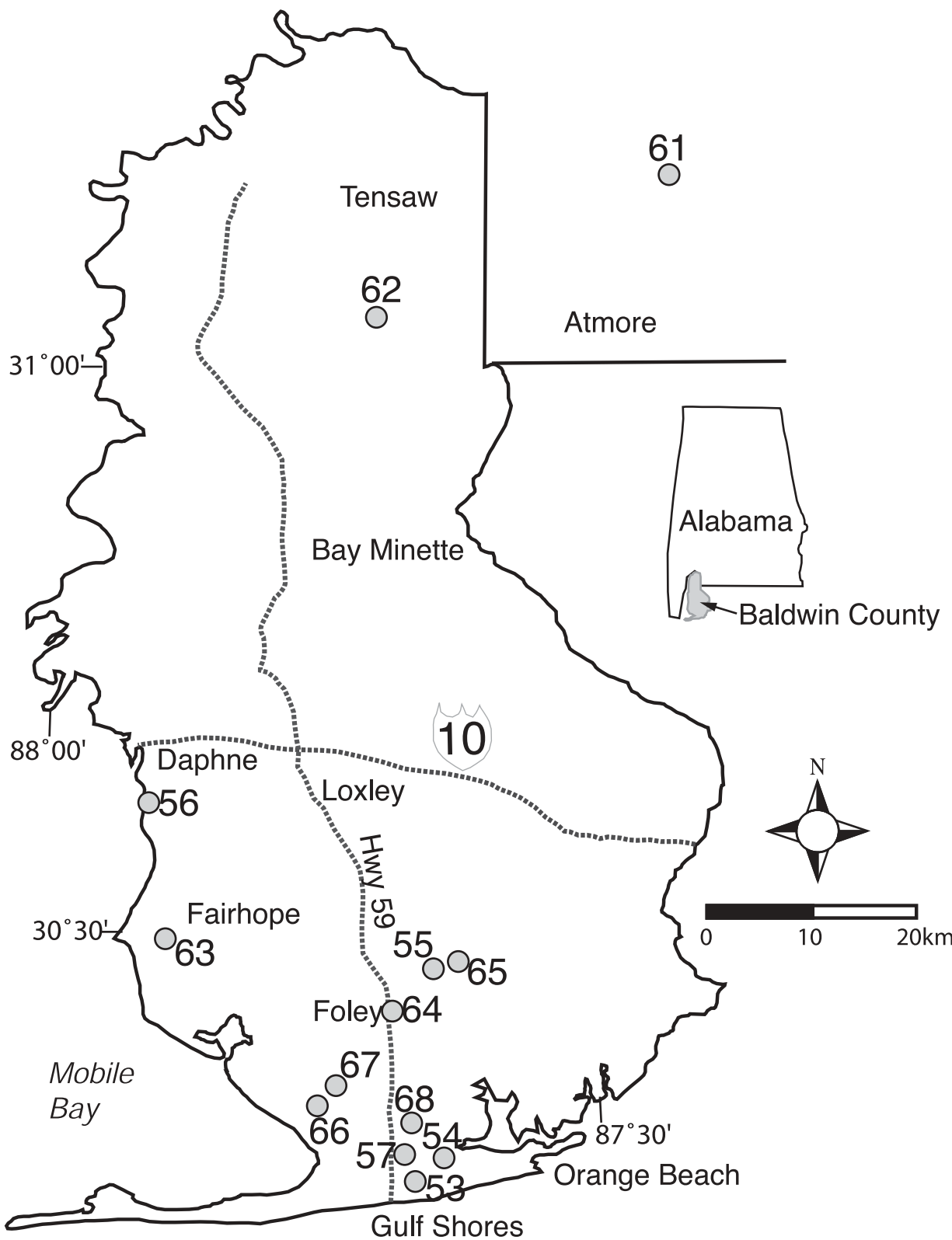
Figure DR1. Map of study area showing location of Baldwin County in southwestern Alabama and the locations of wells sampled for this study. The Atmore well (number 61) is located in Escambia County, Florida. Numbers on map correspond to sample numbers given in Table DR1.

Figure DR2. The modeled helium release rates for select grain diameters ($150\text{--}800\text{ }\mu\text{m}$) are shown using an initial helium concentration of $5\pm 2\text{ }\mu\text{cc g}^{-1}$ and a diffusion coefficient of $1.5\times 10^{-19}\text{ cm}^2\text{ s}^{-1}$ (Dowling et al, 2004, Hunt, 2000). This model shows that the helium release rate from

the quartz grains is $0.0004 \pm 0.00003 \mu\text{cc kg}(\text{quartz})^{-1} \text{ yr}^{-1}$ which is approximately two times greater than the steady state production from U and Th decay.

DATA REPOSITORY REFERENCES CITED

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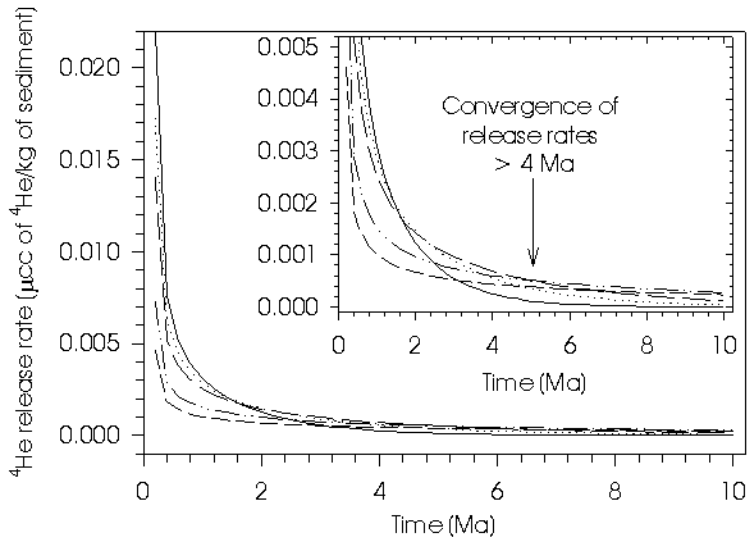


TABLE DR1. CARBON-14 AGE DATES FROM BALDWIN COUNTY GROUNDWATER SAMPLES

| Well name | Gulf sample number | NOSAMS accession # | $\delta^{13}\text{C}$ (‰) | Fraction modern carbon ^a | Fraction modern carbon error ^a | Uncorrected age (yrs) ^a | Age error, (yrs) ^a | $\Delta^{14}\text{C}^a$ | Radiogenic ^4He ($\mu\text{cc/kg}^a$) ^b |
|--------------------|--------------------|--------------------|------------------------------|-------------------------------------|---|------------------------------------|-------------------------------|-------------------------|--|
| Gulf State Park | 53 | OS-22532 | -17.52 | 0.4378 | 0.0025 | 6630 | 45 | -564.77 | 1287–1381 ^{c,e} |
| Orange Beach deep | 54 | OS-22533 | -15.73 | 0.4945 | 0.0048 | 5660 | 80 | -508.46 | 71–73 ^{c,e} |
| Woerner Big Bertha | 55 | OS-22534 | -19.92 | 0.8593 | 0.0036 | 1220 | 35 | -145.80 | 0–5.4 ^e |
| Daphne #2 | 56 | OS-22535 | -19.92 | 0.6725 | 0.0031 | 3190 | 35 | -331.48 | 14.2 ^e |
| Craft Farms deep | 57 | OS-22536 | -18.41 | 0.7780 | 0.0034 | 2020 | 35 | -226.61 | 13.7 ^e |
| Atmore Fountain #2 | 61 | OS-22537 | -20.31 | 0.9545 | 0.0045 | 375 | 40 | -51.15 | 0.0 |
| Rabun | 62 | OS-22538 | -20.22 | 0.4294 | 0.0047 | 6790 | 90 | -573.11 | NA ^d |
| Fairhope #6 | 63 | OS-32311 | -19.58 | 0.8963 | 0.0034 | 880 | 30 | -109.2 | 0.0 |
| Riviera #12 | 64 | OS-32312 | -20.12 | 0.7851 | 0.0025 | 1940 | 25 | -219.7 | 6.03 |
| Woerner Leiterman | 65 | OS-32313 | -20.28 | 0.7856 | 0.0037 | 1940 | 40 | -219.3 | 5.21 |
| Woerner Tindall | 66 | OS-32314 | -19.36 | 0.4597 | 0.0032 | 6240 | 55 | -543.1 | 12.7 |
| Woerner Kaiser | 67 | OS-32315 | -19.48 | 0.4225 | 0.0028 | 6920 | 50 | -580.1 | 16.6 |
| GSU #9 | 68 | OS-32316 | -18.5 | 0.9133 | 0.0034 | 730 | 30 | -92.3 | 0.00 |

| | | | | | | | | | |
|------------------|----|----------|--------|--------|--------|-----|----|-------|------|
| GSU #9 duplicate | 68 | OS-32317 | -18.49 | 0.9064 | 0.0033 | 790 | 30 | -99.2 | 0.00 |
|------------------|----|----------|--------|--------|--------|-----|----|-------|------|

^aSamples for ¹⁴C analysis were prepared and analyzed at the NOSAMS Facility at the Woods Hole Oceanographic Institution. Fraction modern carbon is defined as the deviation from 95% of the ¹⁴C/C ratio of a sample from modern, which is defined as the radiocarbon concentrations (in A.D. 1950) of NBS oxalic acid normalized to $\delta^{13}\text{C}_{\text{VPDB}} = -19\text{‰}$ (Olsson, 1970). Stable isotope measurements of $\delta^{13}\text{C}$ were also performed at the NOSAMS Facility. Data are reported following the convention of Stuiver and Polach (1977) and Stuiver (1980). Radiocarbon ages are calculated using 5568 years as the half-life of the radiocarbon and are reported without reservoir correction or calibration to calendar years. The reported $\Delta^{14}\text{C}$ activities are corrected to 1950.

^bData from Dowling et al. (2004).

^cPresence of natural gas in these samples precludes determination of radiogenic ⁴He model age.

^dNot analyzed

^eValues reported are from analyses of the same well performed from other samples, not the same sampling time as when the ¹⁴C samples were collected.
