Noble gases applied as paleotemperature indicators in the Floridan aquifer system, Naples Florida

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ABSTRACT

Atmospheric noble gases (He, Ne, Ar, Kr and Xe) in groundwater yield valuable information on paleoclimate, in particular temperature at the time of recharge. Dissolved gas concentrations assist in determining the age of the groundwater because they record processes at the time when the water exchanged gases with the atmosphere. These concentrations of dissolved gases also aid in identifying the chemical processes that occur in the subsurface and groundwater flow velocities. There are many applications for atmospheric noble gases in paleoclimatology to reconstruct past climate conditions, in particular temperature during the last glacial maximum. This method was utilized to determine the paleo-temperatures of water entering the Floridan aquifer within Naples, Florida, thus providing constraints to the determined radiocarbon ages to better define the hydrogeologic framework Floridan Aquifer System.

INTRODUCTION

The study area, as shown in Figure 1, covers approximately 175 square miles around the city of Naples, Collier County, Florida. Two of the four Floridan monitoring wells (I75-TW and MIU-MW) were sampled for noble gases. The tri-zone Floridan monitor well (I75-TW), property of the South Florida Water Management District (SFWMD), and three dual-zone Floridan monitor wells, property of Collier County, Florida, were used for this investigation.

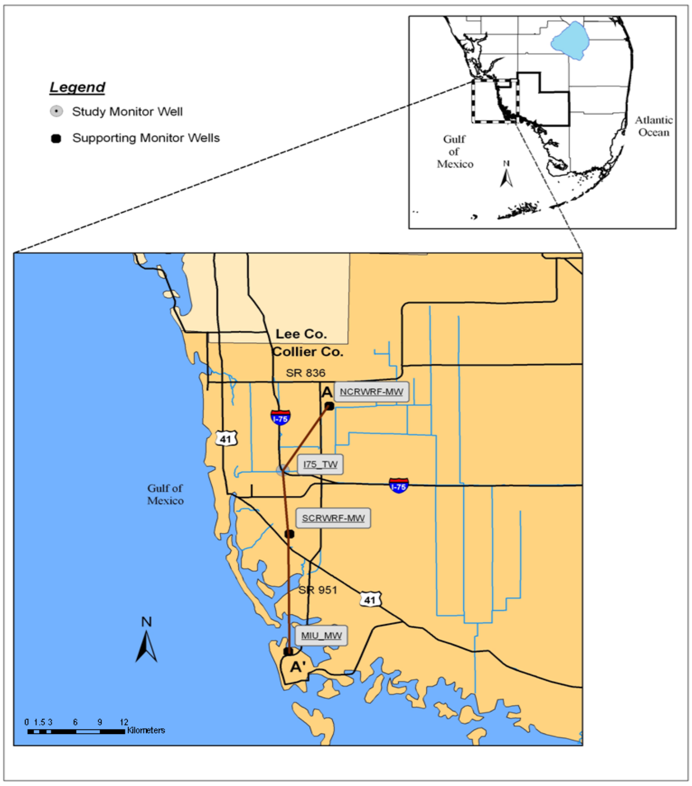

Figure 1. Site Map with Well Locations

This investigation attempts to analyze dissolved gas concentrations to determine the age of the groundwater. These noble gases record processes at the time when the water exchanged gases with the atmosphere. The concentrations of dissolved gases also aid in identifying the chemical processes that occur in the subsurface and groundwater flow velocities.

Hydrogeology

Three major aquifer systems underlie Naples, Florida: the Surficial Aquifer System (SAS), the Intermediate Aquifer System (IAS), and the Floridan Aquifer System (FAS). These aquifer systems are composed of multiple, discrete aquifers separated by low permeability "confining" units that occur throughout this Tertiary/Quaternary age sequence. The aquifers occurring in the Floridan Aquifer System (FAS) are the focus of this study. Figure 2 shows a hydrologic cross-section from north to south across Naples, Florida.

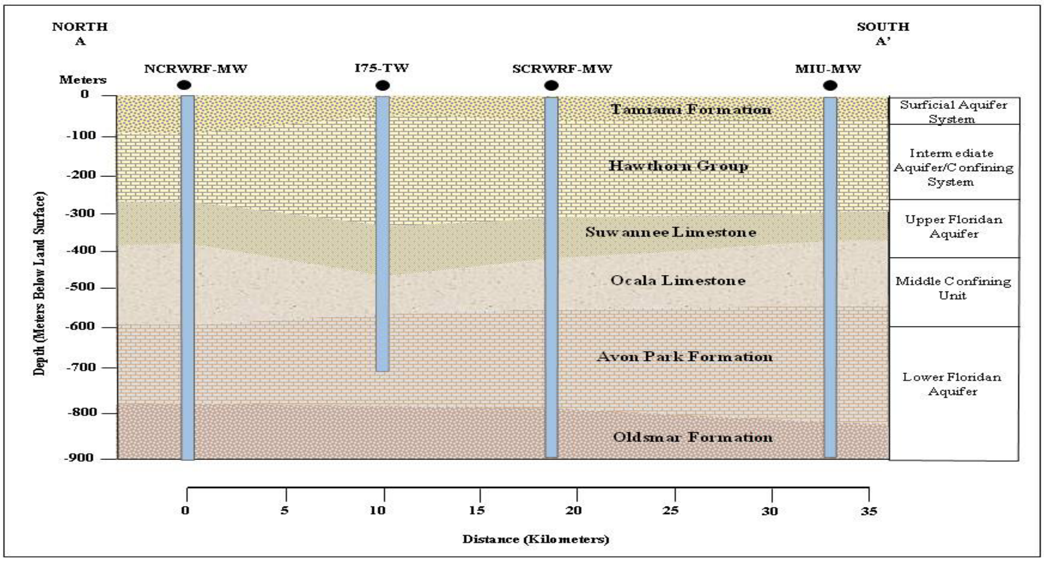

Figure 2. Hydrologic Cross-Section from A to A' through Naples, Florida (line of cross-section shown in Figure 1.)

The FAS in the study area is separated into three hydrostratigraphic units, Upper Floridan aquifer (UFA), middle confining unit (MCU), and Lower Floridan aquifer (LFA). These units are composed predominately of limestone with dolomitic limestone and dolomite. The UFA chiefly consists of permeable zones in the lower Hawthorn Group and Suwannee Limestone (Reese, 1998). The MCU consists of low permeable dolomitic zones in the Ocala Limestone and upper part of the Avon Park Formation (Reese, 1998 and Bennett, 2001). The LFA consists of permeable dolostones in the lower part of the Avon Park Formation, Oldsmar Formation, and the upper part of the Cedar Keys Formation (Meyer, 1989 and Bennett, 2001).

Noble Gases

Noble gas samples were collected at two locations in each well, from the upper and lower portions of the FAS. These samples were collected in approximately 15 ml copper tubes connected to a peristaltic pump and regulator, which reduced aeration of the groundwater sample. Once the copper tubing was flushed with formation water at high pressure, it was sealed at each end with steel pinch-off clamps. The groundwater samples were sent to the Lamont-Doherty Observatory of Columbia University and noble gas concentrations including He, Ne, Ar, Kr, Xe were determined on a MAP 215-50 noble gas mass spectrometer using the method outlined by Stute *et al*. (1995). The system was calibrated using known quantities of air and water standards. Absolute noble gas concentrations were determined with a precision of +/- 1% for Ar and Xe and +/- 2% for He, Ne and Kr.

As water recharges and flows down gradient within the aquifer, there is no longer exchange with other fluid phases and the heavier noble gas concentrations remain unchanged, making them suitable for paleoclimate studies. Helium concentrations in groundwater however change due to radioactive decay of uranium/thorium nuclides within the aquifer (Bottemley *et al.*, 1984; Torgersen and Ivey, 1985, and Bennett, 2004). Helium concentrations increase with time and vary between aquifers making it a useful tool as an approximate chronometer (Clark, 2002). Noble gas temperatures were calculated from concentration data using the inversion method of Aeschbach-Hertig *et al.* (1999).

Results

Noble gas and Carbon-14 were analyzed from the UFA, MCU, and LFA from two of the monitor wells within the study area (Table 1). On average, the LFA water has higher salinities, higher ^{14}C concentrations, lower helium concentrations, and lower noble gas temperatures than those of the UFA (Clark, 2002).

Table 1. Summary of noble gas and carbon-14 results with calculated paleo-temperatures.

Well Name	Interval (meters bls)	Aquifer	He (cc stp/g)	Ne (cc stp/g)	Ar (cc stp/g)	Kr (cc stp/g)	Xe (cc stp/g)	Temp (^{0}C)	^{14}C (pmc)	Uncorrected ^{14}C (years BP)
I75-MZ1	210-231	UFA	2.47E-07	2.13E-07	3.35E-04	7.32E-08	9.84E-09	19.00	0.67	40,130
MIU-MZ1	305-332	UFA	1.37E-07	1.66E-07	3.12E-04	7.32E-08	1.06E-08	18.20	1.53	33,530
MIU-MZ2	454-488	MCU	1.68E-07	1.79E-07	3.16E-04	7.24E-08	1.03E-08	9.10	1.99	31,420
I75-MZ3	701-716	LFA	7.16E-08	1.81E-07	3.21E-04	7.54E-08	1.08E-08	7.70	19.70	13,429
cc stp/g - cubic centimeters of dissolved gas at Standard; Temperature and Pressure per gram of water; ^{0}C - degrees Celsius; pmc – percent modern carbon										

The noble gas paleo-temperature in the UFA samples averaged 18.6° C, 5° C cooler than the present day mean annual air temperature in South Florida (23.6° C), and about 10° C warmer than the LFA samples. These cooler noble gas temperatures suggest that the freshwater recharged the UFA during the cooler glacial period 15,000 to 25,000 years ago (Clark, 2002).

The relatively high helium concentrations (>13 x 10^{-8} cc STP/gr; cubic centimeters of dissolved gas at Standard Temperature and Pressure per gram of water) and low $\delta^{14}C$ concentrations in the UFA support the interpretation based on the noble gas data that the UFA groundwater recharged during the glacial period (Clark, 2002). It is important to note that in the Floridan aquifer from southern Georgia, Clark *et al.* (1997) showed that glacial aged groundwater had helium concentrations greater than 10 x 10^{-8} cc STP/gr (Clark, 2002).

Clark (2002), recognized samples analyzed for stable isotope composition and noble gas temperature (Tables 2 and 4) of the groundwaters in the MCU and LFA in southern Florida were similar to seawater (9.36ºC) collected from depths greater than 1,800 feet in the Straits of Florida. This indicates that post glacial seawater entered the LFA near the bottom of the Straits of Florida and/or Gulf of Mexico as suggested by Kohout (1965). Because the isotope composition of the glacial ocean water (15,000 to 25,000 years ago) was significantly different ($\delta^{18}O_{glacial}$ - $\delta^{18}O_{Holocene}$ > 1‰; Schrag *et al.* 1996; Mashisotta *et al.*, 1999), the seawater must have entered the aquifer after sea level rose to near present day levels subsequent to the last glacial period (Clark, 2002). Hence, the groundwater ages of the seawater circulating through the LFA aquifer must be less than 10,000 years (Clark, 2002). This inference is supported by the relatively low helium concentrations and high $\delta^{14}C$ concentrations found in most LFA samples, both of which suggest short circulation times (Clark, 2002). Absolute ^{14}C ages are difficult to calculate because water rock interactions are difficult to quantify in carbonate aquifers (Clark *et al.*, 1997 and Clark, 2002). Furthermore, standard models are inappropriate because they assume that the groundwater recharged through a soil zone (Clark, 2002).

The noble gas data complements the radiocarbon data for this investigation by identifying two different sources of recharge within the FAS of the study area. The data suggests that within this system relatively old meteoric freshwater circulates in the UFA over relatively young seawater of the LFA (Clark, 2002). The cooler noble gas temperatures, high helium concentrations, and low ^{14}C concentrations suggest that meteoric freshwater recharged the UFA during the last glacial period. The relatively low helium concentrations and high ^{14}C concentrations infer that groundwater in the MCU and LFA is recharged by recent (post-glacial) seawater entering in from the Gulf of Mexico. These results slightly contradict Kohout's (1965) conjecture that seawater entered the LFA from the Straits of Florida and depicts the possibility that recharge into the LFA is not from one particular location. These results support previous investigations by Clark and Fritz (1997), Clark (2002), and Bennett (2004).

CONCLUSIONS

Noble gases (He, Ne, Ar, Kr and Xe) dissolved in groundwater, reliably record information on certain physical processes due to the lack of chemical reactions which affect them. These gases are utilized to estimate temperature at the time of recharge, which can be used to place groundwater age in its paleoclimatic context.

The noble gas analysis was employed to support and add constraints to the radiocarbon data. The data suggested that meteoric freshwater recharged the UFA during the last glacial period and young seawater from the Gulf of Mexico is recharging the MCU and LFA. This geochemical analysis proved to be an essential method to employ when understanding the complex groundwater circulation patterns of the FAS.

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