Dissolved Noble Gases in Groundwater Hydrology

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ABSTRACT: The studies of dissolved noble gases of atmospheric and terrestrial origin have made important contributions to groundwater hydrology in recent decades. The dependence of noble gas solubility on the physical condition, in particular temperature, at the air-water interface has been successfully used to reconstruct the palaeo-temperatures from ancient groundwaters. An important application of non-atmospheric conservative noble gas components is to date the groundwaters, both, young and old. An emerging application of dissolved atmospheric gases is to estimate the palaeo-aridity based on the excess air, with aridity being one of the important factors governing formation of excess air. This paper summarises some of the important studies demonstrating useful applications of noble gas studies in different parts of the world and dealing with diverse aspects of noble gas applications in hydrology, including the North Gujarat-Cambay basin from India.

INTRODUCTION

The groundwater hydrologists primarily endeavour to obtain reliable information about: (i) past and present conditions influencing recharge; (ii) groundwater storage and availability. Conventional approaches involve processing of hydrometric data such as geophysical parameters, fluctuations of water table and piezometric surfaces, water quality parameters, pump test data, etc. Empirical and physical process models are used with several assumptions regarding complex groundwater-surface water interactions and changing land use pattern. Thus, the conventional approach may have a certain degree of uncertainty which can now be minimised with the application of newer tracer techniques that directly track water movement from within and across hydrological reservoirs, over a wide range of space-time.

In this paper application of dissolved noble and other conservative gases in groundwater hydrology is emphasised because after isolation of groundwater from atmosphere, concentrations of these gases are affected only by physical processes (dissolution/ exolution, mixing and/or radioactive decay) and not by chemical reactions and/or adsorption/absorption within the aquifers. As a consequence, the observed concentration variations can be related to physical processes related to environment and hydrology.

Atmospheric gases enter the meteoric water cycle at air/water interface, by gas partitioning in accordance with their solubility defined by respective Henry coefficients that form a natural baseline. Thus, the gas abundance in water, in most cases, can be understood as a binary mixture of two distinct gas components—a well constrained atmospheric solubility equilibrium component and a residual component that may either be of atmospheric (e.g. trapped air bubbles) or non-atmospheric origin (e.g. radiogenic or terrigenic noble gases).
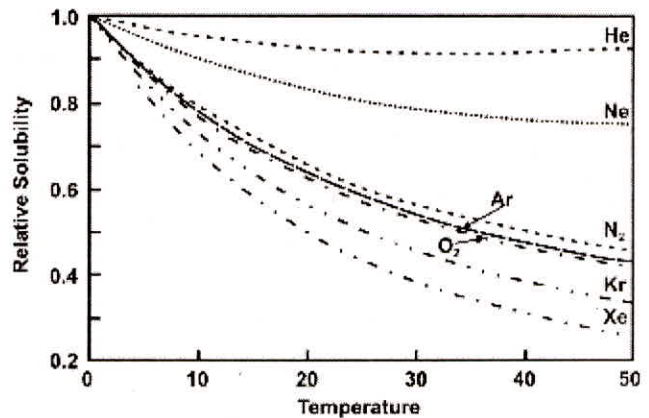

Fig. 1: Variation in noble gas solubility with temperature relative to their solubility at 0ºC. Redrawn from Andrews (1992) and Benson and Krause (1976)

The dependence of noble gas solubility equilibrium on the physical conditions during gas exchange, in particular on temperature (Figure 1), has been successfully used in groundwater studies to reconstruct the soil temperature prevailing during groundwater

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recharge. If an aquifer contains groundwaters that recharged during different climatic conditions in the past, noble gas concentrations provide information about the past temperature (Andrews and Lee, 1979; Mazor, 1972). This approach has been applied to reconstruct the prevailing continental temperature of the Pleistocene/Holocene transition in the tropics (Stute et al., 1995b; Weyhenmeyer et al., 2000) as well as in mid latitudes (Aeschbach-Hertig et al., 2002; Beyerle et al., 1998; Stute et al., 1995a; Stute and Schlosser, 2000).

Additionally, ground waters often contain components of noble gases derived from degassing of earth and/or accumulated from radioactive decay of substances either dissolved or present in the aquifer material. By separating the components according to their origin, one can therefore derive information on time of accumulation of the radioactive component and/or the local degassing of earth. In the following, starting with theoretical considerations some important aspects of the groundwater hydrology using noble gases is described.

THEORETICAL

The measured concentrations of noble gases in ground waters can in principle be described as a sum of the components described in the previous section,

$$C_{i,m} = C_{i,eq} + C_{i,ex} + C_{i,rad} + C_{i,ter} \qquad \dots (1)$$

Where C_i stands for the concentration of the noble gas or isotope i, and the subscripts indicate the components (m: measured (total), eq: atmospheric solubility equilibrium, ex: excess air, rad: radiogenic, ter: terrigenic). The largest component of dissolved gases in ground waters is of atmospheric origin, comprising the atmospheric solubility equilibrium component, and the excess air component.

Solubility Equilibrium

As gas exchange phenomena are fairly fast, with gas transfer velocities of the order of 10^{-5} ms^{-1} (Schwarzenbach et al., 2003), the surface waters of open water bodies are expected to have noble gases in equilibrium with the atmosphere at the prevailing physical conditions. This is supported by experimental evidence (Aeschbach-Hertig et al., 1999; Craig and Weiss, 1971) and is true for all atmospheric gases that have no additional sources or sinks and hence can be considered as bio-geochemically conservative.

Gas partitioning at the free air/water interface can be reasonably well described by Henry's law,

according to which concentrations in the two phases are directly proportional to each other,

$$c_{ia} / c_{iw} = k_i\left(T, c_{jw}, \dots\right) \approx k_i\left(T, S\right) \qquad \dots (2)$$

Where c_{ia} and c_{iw} denote the concentrations of gas i in 'air' and 'water' phase respectively under atmospheric solubility equilibrium condition. In this form, Henry coefficients (k_i) are the inverse of "solubility of a gas in water". Poorly soluble gases have large values of k_i, whereas highly soluble gases have low values of k_i.

If same concentration units (e.g. mol l^{-1}) are used for both phases, the Henry coefficient, k_i is 'dimensionless'. It depends on temperature T and the concentrations of all dissolved species c_{jw} (Ballentine and Burnard, 2002). Because solute concentrations of natural waters are sufficiently low, the dissolved noble gases behave almost as ideal gases so that the total effect of solutes can be expressed by the cumulative dependence of k_i on the salinity S, neglecting chemical interaction between solutes.

Often Henry's Law is formulated in terms of gas partial pressure p_i (atm, bar …) and the corresponding equilibrium concentration of the gas in water $C_{i,eq}$ (cm^3 STP.g^{-1} or mol l^{-1} or mol kg^{-1} or mol mol^{-1},…). In this formulation, with different concentration units for air and water, the Henry coefficients are denoted by H_i as in Eqn. (3),

$$p_i = H_i . C_{i,eq}\left(T, S\right) \qquad \dots (3)$$

The conversion from k_i in volumetric units (e.g. (mol/l$_{gas}$)(mol/l$_{water}$)$^{-1}$) to H_i in units of atm (cm^{3}STP.g^{-1})$^{-1}$ is a simple application of the ideal gas law yielding,

$$H_i = k_i . \frac{T}{T_0} . P_0 . \rho_w \qquad \dots (4)$$

Where $T_0 = 273.15$ K, $P_0 = 1$ atm and ρ_w is the density of water. In these units, the coefficients H_i and k_i have almost the same numerical values, because $\rho_w \approx 1$ g.cm^{-3} and $T/T_0 \approx 1$. The conversion between p_i and c_{ia} and between c_{iw} and $C_{i,eq}$ is temperature dependent and is given by $p_i = RT c_{ia}$ and $C_{i,eq} = RT c_{iw}$; R being the gas constant = 0.082058 atm L mol^{-1} K^{-1}.

To adapt Eqns. (2) and (3) to local conditions, the local atmospheric pressure has to be first estimated based on altitude of the location and then translated into noble gas partial pressures (Gill, 1982; Ozima and Podosek, 1983). It is also required to account for the dependence of the Henry coefficients on the concentration of dissolved ions, the so-called salting out effect (Aeschbach-Hertig et al., 1999; Kipfer et al., 2002).

Excess Air

The excess air is a critical component of the atmospheric (noble) gases dissolved in natural waters (mainly ground waters). It signifies the amount of dissolved atmospheric gases found in excess of that expected from solubility equilibrium. Since various noble gas species have differing solubility, their relative proportion in the analysed water sample differs from the pure atmospheric solubility equilibrium proportion due to excess air.

A convenient and widely used measure for the size of the gas excess, which is independent of its composition, is the relative neon excess, designated as ΔNe,

$$\Delta Ne\,(\%) \;=\; \left(\frac{c_{Ne,m}}{c_{Ne,w}} - 1\right).100 \qquad \ldots (5)$$

Where $c_{Ne,W}$ is the expected equilibrium concentration and $c_{Ne,m}$ is the measured concentration of Neon dissolved in water. Neon is best suited to quantify **excess air because it has almost only atmospheric component and a low solubility**—resulting in a large relative excess. Moreover, because $c_{Ne,w}$ does not strongly depend on temperature (Figure 1), an approximate value for ΔNe can be calculated even if the exact equilibration temperature is not known. Thus, ΔNe is practically an observable quantity. As a rule of thumb, in the case of un-fractionated excess air, 10% ΔNe correspond approximately to 10^{-3} cm^{3}STP.g^{-1} of dissolved air. This thumb rule, however, can only approximately estimate the excess air because its incorporation is governed by several operating hydrological processes that fractionate the dissolved noble gases from their atmospheric equilibration proportions. Several conceptual models have been developed to describe the process of excess air incorporation (Kipfer *et al.*, 2002) and to estimate the optimum value of T (the required recharge temperature) and other model parameters. In particular, a multiparameter inversion technique was introduced by Ballentine and Hall (1999) and Aeschbach-Hertig *et al.* (1999).

Non-atmospheric Components

Having obtained best estimates of the atmospheric components of various noble gases and the related environmental parameters, the non-atmospheric components can be estimated through use of Eqn. (1).

An important simplification results from the fact that components of the radiogenic and the terrigenic origin are significant only for certain isotopes. With the exception of helium, all stable noble gases have at least one isotope that usually is only of atmospheric origin (e.g. ^{20}Ne, ^{36}Ar, and virtually all Kr and Xe isotopes). The non-atmospheric component can be reliably estimated following certain mathematical procedures (Kipfer *et al.*, 2002), if measurements of several noble gas isotopes and elemental and/or isotopic composition of individual components are made.

EXPERIMENTAL

The experimental part of studying the dissolved noble gases in water can be divided into four successive steps: (i) sample collection, storage and transportation to laboratory; (ii) gas extraction from the water sample; (iii) purification and separation of the extracted gases; and (iv) quantitative mass spectrometric analysis.

Considering characteristic physical properties of noble gases such as permeation through and interaction with the material of the container, special field procedures and protocols have been devised for collection, storage and transport of water samples for noble gas analyses. The principal aim of each of such procedures is to prevent the loss of the dissolved gas and its interaction with the atmosphere or the material of the container during collection and storage.

For extended discussions of methods for noble gas analysis in waters (and other terrestrial fluids) reference it made to Bayer *et al.* (1989); Beyerle *et al.* (2000); Clarke *et al.* (1976); Gröning (1994); Ludin *et al.* (1997); Rudolph (1981); Stute (1989).

PALAEOCLIMATIC STUDIES

Use of dissolved atmospheric noble gases in groundwater as an archive of palaeoclimate was first suggested in a study in the Jordan Rift Valley in Israel, which showed that noble gases dissolved in thermal ground waters were retained over many thousands of years and reflected the modern air temperature in their recharge areas (Mazor, 1972).

The first reliable tropical noble gas paleo-temperatures record found a last glacial maximum (LGM) cooling of about 5°C (Aeschbach-Hertig *et al.*, 2000; Stute *et al.*, 1995b). Other noble gas studies from tropical sites also yielded similar cooling at LGM (Andrews *et al.*, 1994; Edmunds *et al.*, 1998; Weyhenmeyer *et al.*, 2000), suggesting that the tropics and subtropics (Clark *et al.*, 1997; Stute *et al.*, 1992; Stute and Talma, 1998) cooled rather uniformly by around 5°C during the LGM. In yet another study, a cooling of around 5°C (Figure 2a) was estimated, for

ground waters recharged >15 kyr ago i.e. of glacial origin in the confined Stampriet sandstone aquifer in south-eastern Namibia (Aeschbach-Hertig et al., 1999; Heaton, 1984; Heaton et al., 1983; Stute and Talma, 1998; Vogel et al., 1981). The noble gas record of the aquifer also showed a clear trend in the concentrations of excess air (Figure 2b). The peak in ΔNe reaches values of up to 225% around 6,000 ^{14}C yr ago, indicating a transition from a drier to a wetter climate, which probably caused the water table to rise and consequently to trap and dissolve air. Such a transition is also indicated by independent palaeoclimatic evidence. The glacial period in groundwater of Stampriet aquifer is also characterized by an increased δ^{18}O (Figure 2c), suggesting that the dominating moisture source shifted from the Atlantic to the Indian Ocean at the transition from the Pleistocene (>10,000 yr) to the Holocene (<10,000 yr). The concentrations of non-atmospheric helium showed an increase as a function of radiocarbon age which is initially dominated by in situ production and later by the accumulation of a crustal helium flux (Figure 2d).

EXCESS AIR PARAMETER

The recent development of different models for the formation of excess air, and the methods to distinguish between these models and to determine their parameters based on field data (inverse fitting, isotope ratios) provide the basis for further investigations of the information potentially available from the excess air (Aeschbach-Hertig et al., 2001). The models suggest that excess air is related to physical conditions in the quasi-saturated zone, where air is trapped during groundwater infiltration. Potentially important parameters are the air/water volume ratio, the pore size distribution, and the pressure in this zone. The pressure acting on the entrapped air may in turn be related to the amplitude of water table fluctuations and thus ultimately to the amount or variability of recharge.

Varying amounts of excess air up to 10^{-2} cm^{3}STPg^{-1} in several aquifers of South Africa, representing different lithologic, hydrologic, and climatic environments have been found (Heaton and Vogel, 1981). In the Nossob aquifer (Heaton et al., 1983) larger concentrations of excess air than in South Africa were found. Their work showing systematic variation of excess air with groundwater age in the Stampriet Auob aquifer has already been mentioned. A comparison of the neon excess from aquifers in different lithologies and climates revealed that rather than temperature, other climatic factors such as precipitation or frequency of flooding were likely to influence the excess air content of groundwater (Wilson and McNeill, 1997).
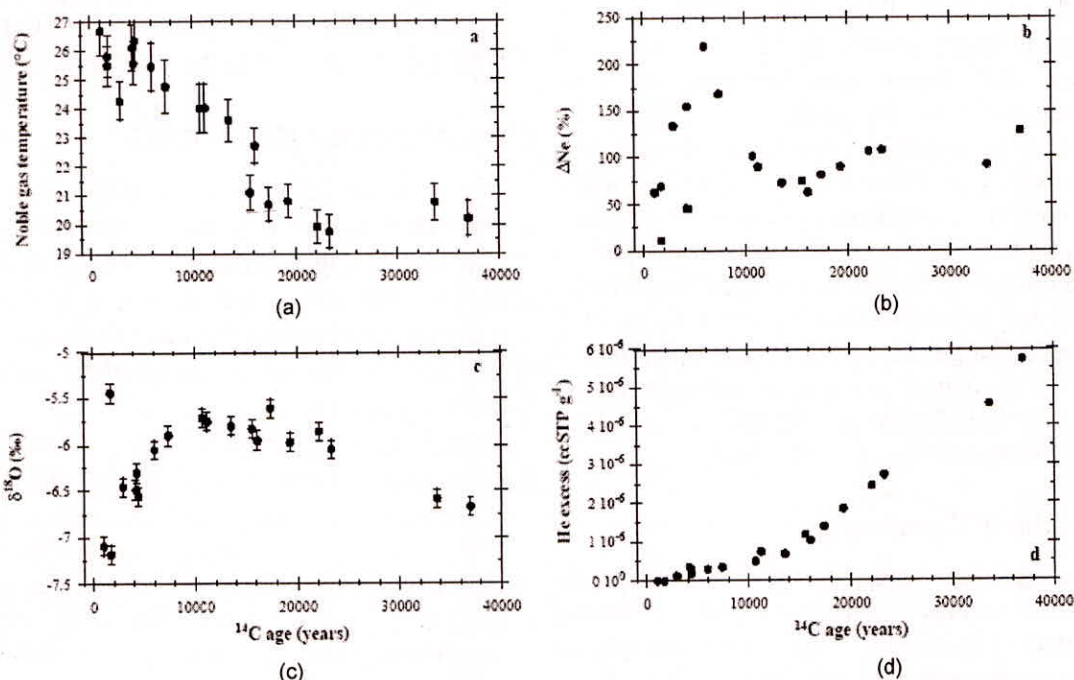

(a)

(b)

(c)

(d)

Fig. 2: Noble gas temperatures, ΔNe, δ^{18}O, and He excess as a function of radiocarbon ages derived from groundwater in the Stampriet aquifer, Namibia (Hinsby et al., 2001; Stute and Talma, 1998). The Noble gas temperatures were re-evaluated for excess air (Aeschbach-Hertig et al., 2000)

GROUNDWATER DATING

Dating of groundwater is the major application of the non-atmospheric conservative gas components. The aim is to estimate the residence time of the water in the subsurface. Dating applications fall into two major categories: (i) Young groundwater with residence times of months to about 50 years can be studied with the ^3H-^3He technique as well as with the anthropogenic radioisotope ^{85}Kr and also using CFCs and SF_6. The natural radioisotope ^{222}Rn can be used to extend the age range to the study of very young groundwater (up to 20 days). (ii) Old ground waters with residence times of thousands to millions of years are studied by using the accumulation of stable radiogenic ^4He and ^{40}Ar, or by the long-lived radioisotope ^{81}Kr. Another radioisotope, ^{39}Ar, covers the time range between about 100 and 1000 years that otherwise is very difficult to access. An understanding and quantification of fluxes of terrigenic noble gases into aquifers is a prerequisite for dating applications of noble gases. Conversely, the study of non-atmospheric helium and argon isotopes in groundwater contributes to our understanding of the degassing of the Earth's mantle and crust. At this point, the field of noble gases in groundwater is strongly linked to the noble gas geochemistry of other crustal fluids and the solid Earth (Ballentine and Burnard, 2002).

Dating of Young Ground Waters

Tritium-helium-3 Method

The excess tritiogenic helium ($^3He_{tri}$) resulting from the decay of ^3H continuously escapes into the air as long as the water is in contact with the atmosphere,. However, after isolation of a water parcel from the atmosphere, the $^3He_{tri}$ starts building up and the $^3He_{tri}/^3H$ ratio steadily increases with time. The $^3He_{tri}$ can be fairly easily separated if the other helium components are dominated by atmospheric sources with only small additions of radiogenic or mantle helium. The neon concentration is used to estimate the atmospheric helium components. The equations for Ne, ^4He, and ^3He are linked by the elemental composition $L_{ex} = (He/Ne)_{ex}$ of the excess air component as well as the isotopic compositions $R_{ex} = (^3He/^4He)_{ex}$ and $R_{ter} = (^3He/^4He)_{ter}$ of both the excess air and terrigenic helium components. Further introducing $R_{eq} = (^3He/^4He)_{eq}$, we can write Eqn. 1 explicitly as,

$$c_{Ne,meas} = c_{Ne,w} + c_{Ne,ex} \quad \ldots (6a)$$

$$c_{4He,meas} = c_{4He,w} + L_{ex} \cdot c_{Ne,ex} + c_{4He,ter} \quad \ldots (6b)$$

$$c_{3He,meas} = R_{meas} \cdot c_{4He,meas}$$
$$= R_{eq} \cdot c_{4He,w} + R_{ex} \cdot L_{ex} \cdot c_{Ne,ex} \quad \ldots (6c)$$
$$+ R_{ter} \cdot c_{4He,ter} + c_{3He,tri}$$

In Eqn. 6(c), rather than using ^3He concentration, the ratios are used as these usually are measured with higher precision than the concentrations. Estimated value of $c_{Ne,ex}$ from Eqn. 6(a) is inserted into Eqn. 6(b) to obtain $c_{4He,ter}$, and finally $c_{3He,tri}$ is obtained from Eqn. 6c. The equilibrium components $c_{Ne,w}$ and $c_{4He,w}$ can be calculated if the recharge temperature is known or estimated. The elemental and isotopic compositions of the excess air component (L_{ex} and R_{ex}) are usually assumed to be atmospheric ($L_{air} = 0.288$; $R_{air} = 1.384 \times 10^{-6}$). Finally, the terrigenic helium component usually originates from the crust and a typical value of $R_{ter} = 2 \times 10^{-8}$ is assigned. However, these traditional assumptions should be critically assessed in each particular case (Holocher *et al.*, 2001). The expression for groundwater age, τ, is easily obtained from the law of radioactive decay (Tolstikhin and Kamenskiy, 1969),

$$\tau = \frac{1}{\lambda} \cdot \ln\left(1 + \frac{^3He_{tri}}{^3H}\right) \quad \ldots (7)$$

Where λ is the decay constant of tritium (half-life 12.32 yr; $\lambda = 0.05626$ yr^{-1}; (Lucas and Unterweger, 2000)). ^3H is usually given in TU (tritium units, 1 TU is equivalent to a $^3H/^1H$ ratio of 10^{-18}). Since $c_{3He,tri}$ is in mol l^{-1} or cm^{3}STP.g^{-1}, it has also to be converted to TU to give $^3He_{tri}$ as follows (for fresh water): 1 mol l^{-1} = 9.0026×10^{15} TU or 1 cm^{3}STP.g^{-1} = 4.019×10^{14} TU. The $^3He_{tri}/^3H$ ratio is a unique function of the ^3H–^3He water age 'τ' that measures the isolation time of the water parcel.

^3H–^3He ages have been used to determine groundwater flow velocities in different situations. Vertical ^3H–^3He profiles allowed determination of groundwater recharge rates (Schlosser *et al.*, 1988; Solomon *et al.*, 1993; Solomon and Sudicky, 1991). Horizontal transects of ^3H–^3He ages with increasing distance from rivers served to quantify river infiltration (Beyerle *et al.*, 1999; Stute *et al.*, 1997). ^3H–^3He data have also been used for the estimation of hydraulic conductivity, effective porosity, and dispersivity on a range of scales (Solomon *et al.*, 1995). Another important application of the method is to provide chronologies for records of past environmental change, in particular histories of groundwater contamination (Aeschbach-Hertig *et al.*, 1998; Böhlke *et al.*, 1997; Dunkle Shapiro *et al.*, 1998; Johnston *et al.*, 1998; Schlosser *et al.*, 1998). ^3H–^3He data can also provide constraints on mixing of

different water components, e.g. in aquifers affected by river infiltration (Holocher *et al.*, 2001; Plummer *et al.*, 1998; Plummer *et al.*, 2000). In fractured rock aquifers ^{3}H-^{3}He dating has been applied to typically encountered problems, namely, their extreme heterogeneity, double porosity causing differences between hydrodynamic and ^{3}H-^{3}He age, and geochemical complications due to the presence of other helium sources (Aeschbach-Hertig *et al.*, 1998; Cook *et al.*, 1996).

Krypton-85 Method

Although ^{85}Kr is radioactive, the age information is not derived from the radioactive decay itself, but from the increase of the atmospheric concentrations since the 1950s (Figure 3). In this regard, the method has strong similarities with the transient tracer methods based on ^{3}H, CFCs, and SF$_6$. In comparison with these related techniques, the ^{85}Kr-method has some advantages, namely, (i) the input function is still steadily increaseing; (ii) locally enhanced atmospheric concentrations occur only near the sources (nuclear fuel reprocessing plants e.g. in Europe (Weiss *et al.*, 1992); (iii) local contamination is unlikely and subsurface production is usually small; (iv) being a noble gas, conservative behaviour can be taken for granted; and (v) the ^{85}Kr method is unaffected by excess air and recharge temperature, because only the ^{85}Kr/Kr ratio and not the absolute concentration is relevant.
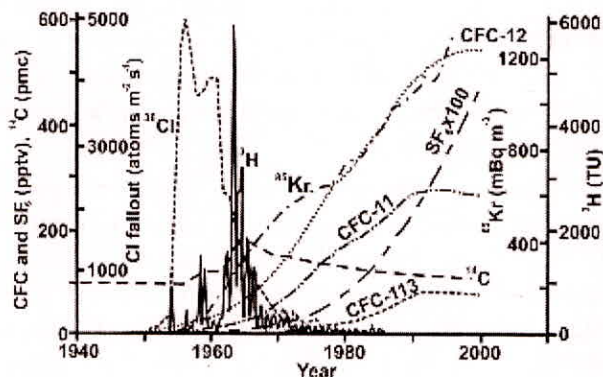

Fig. 3: Concentration variation of several environmental tracers in the atmosphere during the period 1940–2000. These tracers are applied as relative or absolute groundwater dating tools. Redrawn from (Clark and Fritz, 1997; Hinsby *et al.*, 2001)

In spite of this, ^{85}Kr has not been applied as widely as ^{3}H, 3H – ^{3}He, or CFCs because of the technical difficulties of detecting its minute concentrations in natural waters. Sampling large volumes of water is time-consuming and not always feasible.

Radon-222 Method

Due to its short half-life (3.8 d), the use of ^{222}Rn for dating is restricted to the study of the first few weeks after groundwater infiltration. This age range is hardly accessible by other methods but nicely complements the range of the 3H – ^{3}He method. In addition, ^{222}Rn can also be used in older groundwater and in surface water as a tracer to study hydrological and geochemical processes. For a more comprehensive review of the ^{222}Rn-method in subsurface hydrology, reference is made to (Cecil and Green, 2000). As a dating tracer, ^{222}Rn has in particular been applied to study the infiltration of river water into alluvial aquifers. Such aquifers are often exploited because of their high yield, but the quality of the groundwater can be threatened by the possibility of break through of contaminated river water. A difficulty of the ^{222}Rn dating method is to distinguish between changes of the ^{222}Rn concentration that are due to actual aging of a water parcel and variations that merely reflect different mixing ratios between Rn-rich groundwater and virtually Rn-free surface water. This problem was solved by using chloride as an additional tracer to quantify the mixing ratios (Bertin and Bourg, 1994). The large contrast in ^{222}Rn concentrations between ground and surface water enables this isotope useful for the study of groundwater/surface water interaction. In ground waters with residence times above about 20 days, the concentration of ^{222}Rn is at equilibrium with the production rate in the aquifer matrix. Instead of age information, ^{222}Rn then conveys information about the characteristics of the aquifer matrix, such as U content, porosity, grain size distribution, and release efficiency for ^{222}Rn (Andrews and Lee, 1979). Because both radiogenic ^{4}He and ^{222}Rn originate from the U decay series, the study of ^{222}Rn may support the application of ^{4}He as a dating tool (Agarwal *et al.*, 2006; Torgersen, 1980).

Dating of Old Ground Waters

The most common method to date ground waters in the age range of 10^3–10^4 yr is ^{14}C-dating of the dissolved inorganic carbon in the water. However, due to the complexity of the geochemistry of carbon in aquifer systems (Fontes and Garnier, 1979; Vogel, 1967), this method is difficult and not always reliable. The situation is probably even worse for ^{36}Cl, which has been explored as a dating tool in the range of 10^5–10^6a (Cresswell *et al.*, 2001; Sturchio *et al.*, 2004). Therefore, noble gases are very welcome additional tracers that help to constrain long groundwater

residence times. In the following, results of radio-carbon, ^{4}He and ^{4}He/^{222}Rn dating of groundwater in the North Gujarat-Cambay basin are discussed. For details of experimental procedure adopted in this study reference is made to Deshpande, (2006) and Agarwal *et al.* (2006).

CASE STUDY: NORTH GUJARAT–CAMBAY BASIN

North Gujarat Cambay region (71.5°–74° E and 22°–24.5° N) is a 'Graben' characterised by a NNW-SSE trending major fault system and successive down faulting along sympathetic faults that run parallel to the major trend line and many orthogonal faults cutting across (Merh, 1995). Within the Cambay Basin, Quaternary alluvial sediments with alternating sand and silty-clay layers constitute the regional aquifer system having its recharge area in the foothills of Aravalli Mountains and discharge area in the Little Rann of Kachchh—Nalsarovar – Gulf of Khambhat region (LRK-NS-GK).

The estimated groundwater radiocarbon ages are seen to increase roughly westwards from the Aravalli foothills up to the LRK-NS-GK corridor. Further west, lower groundwater ^{14}C ages are encountered. It is also seen that ^{4}He ages (for no crustal flux of ^{4}He) are in close agreement with the ^{14}C ages (Figure 3b). This is supported by the findings of other workers that

relatively young groundwater are dominated by in situ ^{4}He production. The distribution of estimated groundwater ^{4}He/^{222}Rn ages using measured concentration ratio of [Th]/[U] = 7.1 ± 4.3 is shown in Figure 5a. Because the source of both ^{4}He and ^{222}Rn is the same parent ^{238}U in the aquifer formation, these ages are independent of porosity, density and U concentration but depend on Th/U of the aquifer material. Additionally, the ^{4}He/^{222}Rn ages also depend on the release factor ratio ($\Lambda_{Rn}/\Lambda_{He}$) and accumulation rate ratio (A_{Rn}/A_{He}) of ^{4}He and ^{222}Rn.

As in the case of ^{14}C ages, a gradual age progression from the recharge area towards the West Cambay Basin Boundary Fault (WCBBF) is observed in the major part of the study area. These ^{4}He/^{222}Rn ages (Fig. 5a) were obtained using $\Lambda_{Rn}/\Lambda_{He} = 0.4$ to give the best match with the ^{14}C age gradient (Fig. 5b) across the Cambay basin. This gradient matching approach was chosen because the inferred groundwater flow velocities in the confined aquifer by the two methods match when age gradients match. This also ensures that the uncertainties related to, for example the initial activity of ^{14}C in the recharge area or the 'excess He', have as little influence on matching as possible. The groundwater age estimates by the three methods (^{14}C, ^{4}He and ^{4}He/^{222}Rn) indicated present to < 2 ka ages in the recharge area along the Aravalli foothills. The ages progressively increased in the general flow
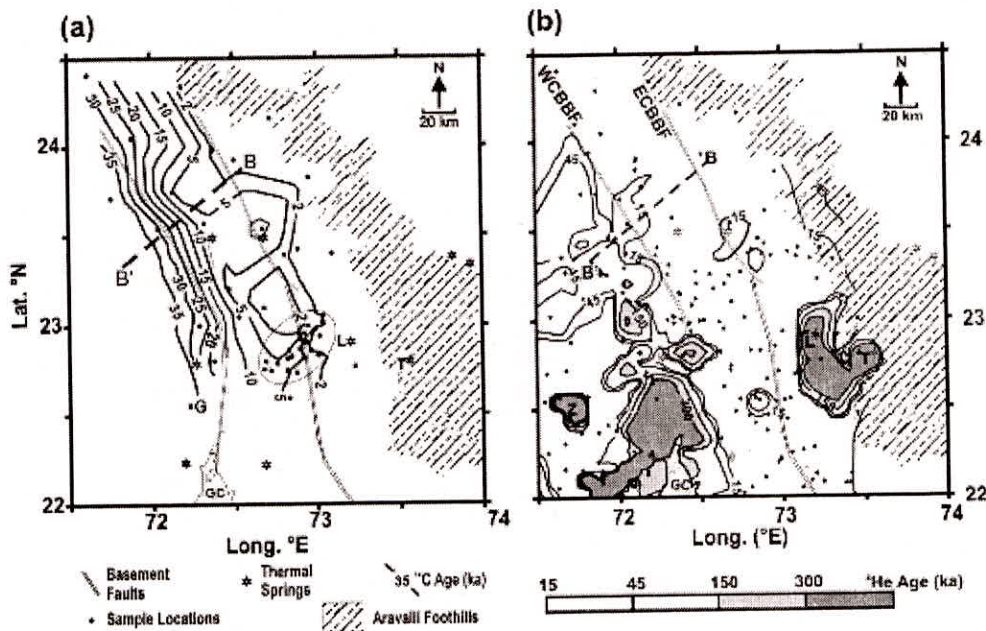

Fig. 4: (a) Isoline map of groundwater ^{14}C ages. Within the Cambay basin the groundwater ^{14}C ages increase progressively towards the WCBBF, beyond which a limiting ^{14}C age of >35 kaBP is observed. (b) Isoline map of estimated ^{4}He ages of groundwater (for helium release factor; $\Lambda_{He} = 1$). The groundwater age gradient along BB' is shown in Figure 5b
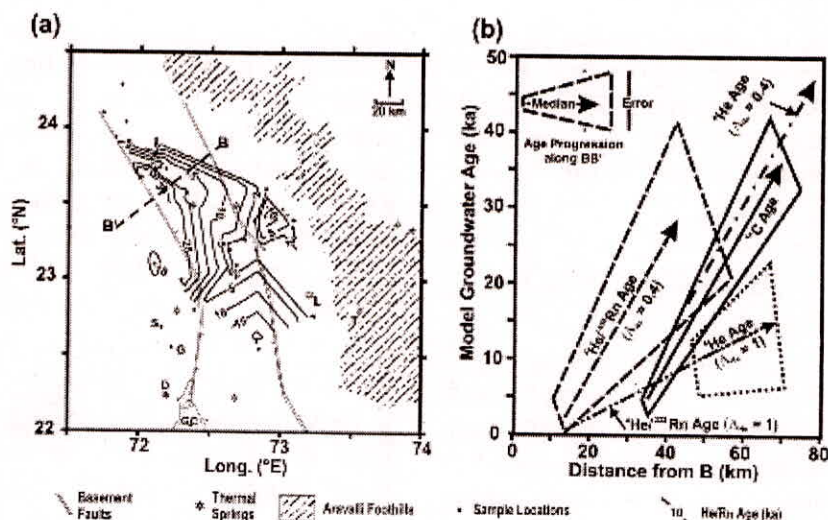
Fig. 5: (a) Isoline map of groundwater $^4He/^{222}Rn$ ages in the NGC region. (b) Plot of groundwater age progression along line BB' for comparing the age gradients for model ^{14}C ages, ^4He ages for $\Lambda_{He} = 1$ and $^4He/^{222}Rn$ ages both for $\Lambda_{He} = 1$ and for $\Lambda_{He} = 0.4$

direction of groundwater, approximately south westward in the Cambay Basin, reaching a limiting value of ~35 ka for ^{14}C near the WCBBF. The ^4He method also indicated further west-southwards progression of groundwater ages up to ~100 ka. In the entire study area, there was correspondence in age estimates by the three dating methods within ~50% uncertainty for both ^4He and $^4He/^{222}Rn$ methods.

Gupta *et al.* (2005) and (Deshpande, 2006) have identified imprints of past enhanced aridity in the NGC region around the LGM in the form of higher values of fluoride concentration and EC, higher values of $\delta^{18}O$ and δD, and lower value of *d*-excess of groundwater recharged around 20 ± 5 ka BP. Their inferences from chemical and isotopic palaeoclimatic proxies in groundwater tally with the evidence of other palaeoclimatic studies from the region (Juyal *et al.*, 2006; Juyal *et al.*, 2003; Pandarinath *et al.*, 1999; Prasad and Gupta, 1999; Sridhar *et al.*, 1994; Wasson *et al.*, 1983) It will, therefore, be interesting to see how the known changes of humidity in the NGC area over the past ~100 ka are reflected in the excess air and noble gas temperature records.

CONCLUSIONS

The strong dependence of gas solubility in water on its temperature and salinity ensures that equilibrium concentrations of noble gases implicitly carry information on the physical properties of the water during gas exchange at the air/water interface, i.e. air pressure, temperature and salinity of the exchanging water mass. Ground waters in contrast to surface waters almost always contain atmospheric gases in excess of the quantity expected from solubility equilibrium. New concepts link the formation of excess air with the physical processes that control air/water partitioning at the transition between the unsaturated and the saturated zone in soils. The major application of the atmospheric noble gas components in groundwater is palaeo-temperature reconstruction, i.e. determination of the temperature at which the infiltrating groundwater equilibrated with the atmosphere in the past. Dating of groundwater is the major application of the non-atmospheric conservative gas components. This aims to give the residence time of the water in the subsurface.

Groundwater dating in the regional aquifer system of North Gujarat-Cambay region using dissolve ^4He and $^4He/^{222}Rn$ is shown to give ages that are consistent with the radiocarbon ages and help extend the range of observed ages to >100 ka – well beyond the limit (~35 ka) of radiocarbon dating.

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