

Molecular diffusion as a source of noble gas fractionation in groundwaters. Hydrodynamic implications. A case study, the Paris Basin

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In recent years, the study of rare gases as natural tracers in deep aquifers, as well as in oil and gas in sedimentary basins, has been used as a complement to hydrodynamic studies (Ballentine *et al.*, 1991; Castro *et al.*, 1998). The general consensus at present (Bosh et Mazor, 1988; Hiyagon and Kennedy, 1992) is that rare gases, of atmospheric as well as of radiogenic and mantle origin found in oil and gas fields originate in the groundwater.

The concentration of He, Ne and Ar in groundwater is very often higher than in water at solubility equilibrium with the air, referred to as ASW (Air Saturated Water). These excesses originate mainly from the crust where the gases are formed by radioactive decay of U, Th and K for ^4He and ^{40}Ar , respectively, as well as by secondary α or n-reactions on target elements such as lithium and oxygen for ^3He and ^{21}Ne . They may be produced inside the aquifer or in deeper layers. In the latter case, the gases must be transported to the upper aquifers. Finally, a mantle flux of gases may sometimes be present (e.g. Oxburgh *et al.*, 1986).

By measuring the concentration and by estimating the flux of certain isotopes in groundwater, it is possible to estimate the residence time of the water in the system and to better understand vertical transport between aquifers. However, ^4He has so far led to higher estimates of the ages than other methods (e.g. Andrews and Lee, 1979). Moreover, when He, Ne and Ar are measured simultaneously, the observed radiogenic $^4\text{He}/^{40}\text{Ar}$ and $^{21}\text{Ne}/^{40}\text{Ar}$ ratios are frequently different from the mean rate of crustal radiogenic production, not only in the water but also in the oil and gas of different sedimentary basins (e.g. Torgersen *et al.*, 1989; Ballentine *et al.*, 1991).

Here, we address the two issues of He dating and of radiogenic elemental fractionation based on the

example of the Paris Basin, France. This large multi-layered system of interbedded aquifers and aquitards is relatively well characterized as this region not only contains exploited hydrocarbon resources, but is also used as a source of low-enthalpy geothermal energy and of drinking water. Thus, this sedimentary basin provides a well constrained framework for studying the behaviour of rare gases. The respective roles of transport by advection and diffusion for each isotope are assessed and further constrained by a quantitative modelling study in a two-dimensional cross-section of the basin. This approach will permit a better understanding of the hydrogeological system and, consequently, a better knowledge of the process of hydrocarbon accumulation in these systems.

Origin of measured isotope excesses. The concentrations and isotopic compositions of helium, neon and argon measured in water samples collected from five overlying aquifers in the Paris Basin (Ypresian, Albian, Neocomian, Dogger and Trias) showed excesses of ^3He and ^4He up to four and five orders of magnitude respectively, as compared to the ASW values. For ^{40}Ar , these excess are smaller and go up to 37.5%. The water in the Dogger and the Trias also present an excess of ^{21}Ne as compared to the ASW values. There is also a vertical gradient of these concentrations throughout the basin. The mean rate of radiogenic production of ^3He , ^4He , ^{21}Ne and ^{40}Ar in the entire sedimentary sequence of the basin was determined on the basis of Li, U, Th and K measurements in the reservoir rocks. Compared to the measured values, this total production is estimated at less than 13% for all the isotopes. The greater part (~87%) of the radiogenic components is thus believed to originate from the bedrock, which means that these isotopes are transported vertically through the entire basin.

Isotope fractionation and vertical diffusion. For the Trias, the radiogenic production ratios $^4\text{He}/^{40}\text{Ar}$ and $^{21}\text{Ne}/^{40}\text{Ar}$ are close to the mean production rate in the crust (4 ± 3 and 0.96×10^{-7} , respectively). For the overlying Dogger, however, these ratios are much higher, up to 6 and 14.2 times the mean value of the crustal production for, respectively, $^4\text{He}/^{40}\text{Ar}$ and $^{21}\text{Ne}/^{40}\text{Ar}$. The diffusive fluxes for ^4He , ^{21}Ne and ^{40}Ar between the Trias and the Dogger were calculated taking into account the temperature dependence of the diffusion coefficient. There is a clear gradient of the calculated diffusive fluxes of $\phi(^{21}\text{Ne})/\phi(^{40}\text{Ar})$ and $\phi(^4\text{He})/\phi(^{40}\text{Ar})$ similar to that of the measured $(^{21}\text{Ne}/^{40}\text{Ar})_{\text{rad}}$ and $(^4\text{He}/^{40}\text{Ar})_{\text{rad}}$ ratios; in particular, the calculated diffusive flux ratios for $(^{21}\text{Ne}/^{40}\text{Ar})_{\text{rad}}$ and $(^4\text{He}/^{40}\text{Ar})_{\text{rad}}$ show variations that are weaker for the former (between 4.3×10^{-7} and 8.2×10^{-7}) but stronger for the latter (between 7.9 and 16.5). These observations strongly suggest that differences in the vertical diffusive flux of ^4He , ^{21}Ne and ^{40}Ar are at the origin of the high ratios observed in the Dogger. In the vertical direction, ^4He is transported mostly by diffusion, whereas ^{40}Ar is transported mostly by advection. ^{21}Ne represents an intermediate situation. Diffusion seems also to be at the origin of higher water residences times obtained with ^4He when this transport mechanism is neglected.

Estimates of vertical fluxes. Transport of ^3He , ^4He and ^{40}Ar isotopes was simulated in steady and transient states. The model included seven aquifers separated by seven aquitards, in a steady-state flow regime on a 2-D vertical cross section approximately following the flow direction in the aquifers. Crustal fluxes of ^3He , ^4He and ^{40}Ar in the basin were estimated at 4.33×10^{-13} , 4.0×10^{-6} and $2.52 \times 10^{-7} \text{ mol m}^{-2} \text{ yr}^{-1}$, respectively, by trial and error fitting on the observed rare gases concentrations. The model results confirmed that diffusion is an important mechanism for vertical transfer through the aquitards for helium isotopes. ^{40}Ar and ^4He fluxes are, respectively, one and two orders of magnitude lower in the shallowest aquifer as compared to these flux values in the Trias. This decrease toward the surface is the result of a dilution of the radiogenic component, as it migrates vertically upwards, by the atmospheric one contributed by recharge water in each aquifer.

Influence of the diffusion coefficient on the R/Ra ratio. The simulation of the ^3He and ^4He transport showed that the R/Ra ratio (value of the measured $R = ^3\text{He}/^4\text{He}$ ratio normalised to the atmospheric ratio, Ra) entering at the base of the Trias from the bedrock

remained constant while crossing the basin except in the zones close to the recharge areas where it is influenced by the atmospheric component. This constancy is due to the low radiogenic/nucleogenic production rate of these isotopes inside the basin, as compared to the crustal flux.

Initially, both helium isotopes were given, for simplicity the same diffusion coefficient. Since their masses are different, it is clear that they have different coefficients: that of ^3He is slightly higher. As is the case for all other gases, the difference between the respective coefficients increases when the temperature decreases. Tests were then done for different diffusion coefficients for these two isotopes. We first tested a case of a 5% increase for ^3He compared to ^4He . The results show a gradient in the center of the basin between the Neocomian and the Albian (absent when the diffusion coefficients are identical) with a R/Ra ratio ranging between 0.08 and 0.1 (i.e. an increase of around 20% in the Albian as compared to the fitting values) and increasing toward the surface. The ^3He and ^4He diffusion coefficients, which are approximately inversely proportionate to the square root of the atomic mass, should in reality differ by 13%, which is in agreement with results obtained by Jähne *et al.*, 1987. Consequently, if we assume proportionality to calculate the effect on the R/Ra ratio of such an increase, it would mean an increase of around 50% of R/Ra in the Albian, compared to the fitting values. Note that the gradient caused by the difference in diffusion coefficients becomes more marked as the distance travelled by the two isotopes increases. If this is verified, it could explain some of the measured R/Ra values in the waters of the Albian and Ypresian in the central and southern parts of the basin that are as high as 0.1–0.2. Evidence of the existence of such a process is very important and further investigations are needed. Nevertheless, if such an effect on the R/Ra ratio caused by diffusion is confirmed, this will have important implications for determining the origin of ^3He , whether radiogenic or mantelic. Indeed, and typically, the existence of a mantle component for ^3He is generally accepted when measured R/Ra values are higher than 0.1. Our preliminary results seem to show that a process such as diffusion can significantly alter the R/Ra ratio thus eliminating the need for a mantle component to explain such high values.

References

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