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Isotopic methods and their hydrogeochemical context in the investigation of palaeowaters

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Abstract: Isotope and geochemical techniques are the primary way in which the residence time, recharge conditions and subsequent evolution of palaeowaters can be determined. Isotopic species and noble gas concentrations are used as residence time and palaeoclimate indicators. Among the former, ¹⁴C is pre-eminent in late Quaternary studies because of an age range which covers the Pleistocene–Holocene transition. However, its use is constrained by frequent difficulties in determining the dilution of dissolved ¹⁴C due to water–rock interaction. A combination of ¹⁴C data with ²²⁶Ra and ⁴He results may be useful for Holocene waters but they can also be used to validate the carbon systematics assumed for ¹⁴C dating. For waters beyond the range of ¹⁴C dating, ⁸¹Kr, ³⁶Cl, ⁴He and chemical tracers can be applied.

Stable isotope ratios and noble gas concentrations primarily reflect climatic conditions at the time of recharge. While the noble gases provide absolute values for recharge temperatures, stable isotopes are only relative indicators that vary regionally. The PALAEWAUX programme has examined these aspects in some detail by looking at the $\delta^{18}\text{O}$ shift between Pleistocene and Holocene waters on the European scale, and by calculating $\delta^{18}\text{O}/\Delta T$ ratios from $\delta^{18}\text{O}$ v. recharge temperature plots for aquifers at different distances from the Atlantic Ocean. Indications are that the more positive $\delta^{18}\text{O}$ value of ocean water during the Pleistocene dominates in the more westerly European countries over the negative $\delta^{18}\text{O}$ shift during cooler conditions. There are also indications that air-mass circulation during the Pleistocene was similar to the present day.

The evolution of a palaeowater can best be studied by measuring chemical tracers; this is possible in freshwater aquifers, where a clear trend of geochemical reactions is observed, and in freshening marine aquifers. Chemical and isotopic tracers can also be used to study the movement of the front between palaeowater and younger components that must be identified in coastal aquifers to guarantee a sustainable water use.

Introduction

Isotopic and geochemical methods are used in the investigation of palaeowaters to: (1) determine the origin and the former recharge conditions of groundwaters; (2) determine the flow paths, the evolution of the water and to understand the effects of water–rock interaction; (3) determine mixing components and their age structure; (4) validate

flow models. Two aims can be realized by the combination of hydrogeological and isotopic methods. The first is mainly scientific: information about climate signals can be found stored in palaeowaters. The other aim is a practical application: how to exploit reservoirs of old groundwater in a sustainable way. Such conclusions are possible, for example, from the observation of how fast anthropogenic influences are penetrating into

the reservoir or how fast the interface between palaeowater and Holocene water is moving.

In general, the interpretation of chemical and isotopic signals in groundwater systems is complex. Palaeowaters, however, are even more complicated because, for example, permafrost and ice cover may have changed infiltration conditions, and even subsurface flow parameters such as permeability and flow direction. It is also necessary to consider that atmospheric circulation and atmospheric composition (especially $p\text{CO}_2$), and therefore recharge parameters, may have been different from those of the present day.

For all these reasons it is necessary, wherever possible, to use a combination of techniques. Isotopic, geochemical, hydraulic and modelling data, where these exist, should be interpreted together. For example, when converting isotope results into time information, understanding the geochemical system and its evolution is necessary. Furthermore, isotopic ages need to be compared with time information from hydraulic modelling. It is often the case that isotopic and geochemical data are the primary information available, and the palaeohydrological indications pose further questions for the hydraulic interpretation.

In the first part of this chapter, the present-day knowledge about some selected isotopic and geochemical methods, and their combination relevant to the investigation of old waters is summarized. In the second part, it is shown how these methods are applied to aquifers in Europe with examples taken from those aquifers investigated during the EU-funded PALAEAUX programme. Most emphasis is placed on the identification of a palaeowater and on conclusions obtained during this program referring to palaeowaters. In this second part the examples are arranged proceeding from a local to the European scale.

Present-day knowledge about some isotope and geochemical methods, and their combination

Isotopes and chemical tracers as residence time indicators

Time information is important in order to describe flow systems in a quantitative way. In the PALAEAUX programme, for example, it has been necessary to know how fast the two main fronts are moving, i.e. (1) the interface separating waters with anthropogenic signals from older water, and (2) the interface between palaeowater (defined as of Pleistocene or early Holocene age) and younger

water. The dating techniques for the first front are described in Hinsby *et al.* (2001); recent applications of dating methods to young waters are also described in Cook & Herczeg (1999). The present chapter concentrates on dating methods for waters older than *c.* 100 a, i.e. prior to human intervention.

In Figure 1 the dating ranges of different isotope methods are shown schematically, which shows that overlapping methods exist for young waters up to *c.* 50 a old. It is desirable to combine dating methods (see below) but for older waters usually only a single method is available to cover a dating range. The species ^4He and $^{40}\text{Ar}/^{36}\text{Ar}$ can at present, only be used in a qualitative supporting way, therefore, their ranges are shown by dashed lines in Figure 1.

It is not the aim of this chapter to give a general and comprehensive introduction and survey of isotopes and chemical tracer methods; for this the reader is referred to Cook & Herczeg (1999) and Clark & Fritz (1997). Instead, this chapter mainly provides additional methodological information that has been important, used or developed during the PALAEAUX programme.

Argon-39 and Carbon-14 methods

Argon-39 can be used for the following:

- (1) dating of groundwater in the range of a few decades and *c.* 1000 a, i.e. in the gap between the tracers useful up to *c.* 50 a and ^{14}C (e.g. Andrews *et al.* 1984; Pearson *et al.* 1991; Scholtis *et al.* 1996; Eichinger *et al.* 1999; Loosli *et al.* 1999). This application for groundwater dating is only possible where it can be shown by measurements and/or calculation that the subsurface produced ^{39}Ar activity is small compared to the atmospheric cosmic-ray-produced content;
- (2) determining mixing components, usually in combination with chemical components (e.g. Beyerle *et al.* 1998; Purtschert *et al.* 2001);
- (3) studying how a subsurface-produced nuclide is transferred from the rock matrix into the water phase (e.g. Loosli *et al.* 1992; Lehmann & Purtschert 1997).

The frequently used ^{14}C method is practically the only 'clock' available for the transition from ice age to post-glacial times. The range of ^{14}C dating is limited to *c.* 30 ka because water-rock interaction effects may predominate over simple ^{14}C decay in very old samples.

The problems of converting the measured ^{14}C activity of the total dissolved inorganic carbon (TDIC) into time information are well known and extensively described (e.g. Fontes 1992; Pearson *et al.* 1991; Clark & Fritz 1997; Geyh 2000; Kalin

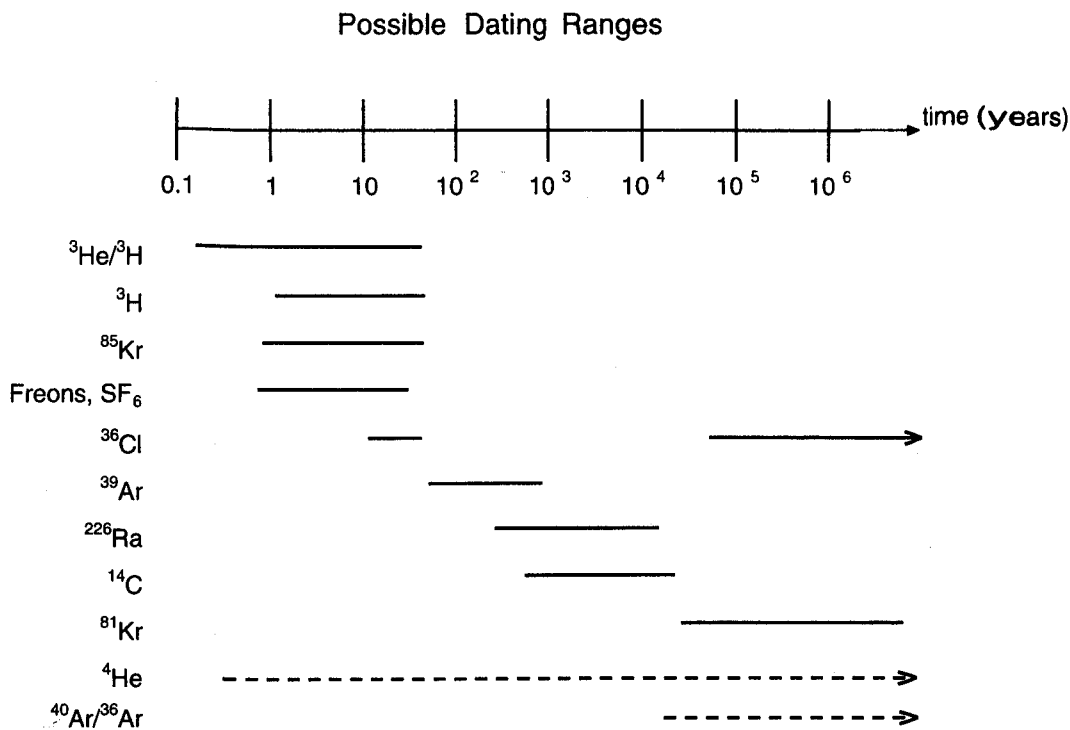


Fig. 1. Isotopic tools potentially available for dating of groundwaters in the range of 10^{-1} – 10^6 a

2000). NETPATH modelling for ^{14}C interpretation is described by Plummer *et al.* (1994).

All models currently in use require an estimate of A_0 , an initial ^{14}C activity for each sample, to be used as basis for applying the radioactive decay equation. Otherwise the models differ in their approaches: e.g. the Tamers model is mainly based on mass balances, the Pearson model on $\delta^{13}\text{C}$ balance, while others combine mass and isotope balance (e.g. the Fontes–Garnier and Eichinger models). It must be realized that only model ages can be calculated and the reliability of these will depend on how well the carbon system in individual aquifers is understood. For example, whenever measured $\delta^{13}\text{C}$ values are more enriched than c. -6% , an extensive evolution of the system must be assumed. The isotope exchange reactions between liquid and solid phases may still affect the ^{14}C activity but will not greatly alter $\delta^{13}\text{C}$ values. The reliability of ages calculated for such samples will be low.

In dual porosity aquifers, such as the Chalk aquifer of the UK and France, groundwater dating is difficult because of the mixing between the two component waters (matrix and fracture) of different ages. Incongruent reactions between the incoming water and the reactive chalk sediment also lead to near-surface reaction such that the A_0 values are low, c. 70% modern (Edmunds *et al.* 1992; Kloppmann *et al.* 1998).

From the PALAEAUX studies, supporting information from other isotope methods for the interpretation of ^{14}C data could be obtained: ^{39}Ar can in some cases be used to determine an upper limit of A_0 ; ^{226}Ra , with its different geochemical behaviour, can be used to better understand the effects of water–rock interaction on the carbonate system; and ^4He opens a possibility for expanding the dating range of ^{14}C .

Table 1 gives isotope results from some of the aquifers investigated in the PALAEAUX programme. In each aquifer some samples have low ^{39}Ar activities, showing that underground production is low or negligible (Loosli *et al.* 1999). The almost-modern ^{39}Ar contents of other samples in the same aquifer must therefore be due to atmospheric equilibrium activity, showing that the second sets of samples are young (up to a few decades old). Therefore, in these young samples the measured ^{14}C activities must reflect A_0 values (except in the sample Glattal A, in which some thermonuclear ^{14}C is included). These measured A_0 values can be compared to calculated A_0 values (e.g. using Fontes–Garnier, Pearson or Eichinger models). This comparison shows a general agreement in ^{14}C activity values. However, it also shows that precise conversions of ^{14}C activities into young water ages may be an overinterpretation: e.g. an attempted conversion for Doñana M-8-13 (^{85}Kr and ^3H free) of 54.6 pmc, based on a calculated A_0

Table 1. Isotope data of PALAEAUX waters used to estimate initial ^{14}C values

Name	Lowest $^{39}\text{Ar}_{\text{meas}}$ (%)	$^{39}\text{Ar}_{\text{meas}}$ in young water (%)	$^{14}\text{C}_{\text{meas}}$ in young water (pmc)	$\delta^{13}\text{C}_{\text{meas}}$ in young water (‰)	A_0 calculated young water (pmc)	$^{14}\text{C}_{\text{meas}}$ old water (pmc)	$\delta^{13}\text{C}_{\text{meas}}$ old water (‰)
Switzerland							
Glattal 1	9 ± 5						
Glattal 3	12 ± 3					9.2 ± 0.5	-11.0
Glattal 7	< 18					1.9 ± 0.2	-10.3
Glattal A		109 ± 8	79 ± 1	-15.1	58-61		
Glattal D		92 ± 12	56 ± 0.5	-12.8	48-51		
Spain							
Donana S2	< 10					7.3	-11.0
Donana M-8-13		70 ± 6	54.6 ± 1.3	-11.5	46-54		
England (Triassic)							
Grove I	< 4.6					18.7	-12.3
Rampton	< 3.3					< 0.8	-10.2
Newton I	< 3.2					1.9	-10.6
Far Baulker 2		94 ± 4	58.9	-13.5	59-76		
Ompton 3		57 ± 3	40.6	-13.3	49-76		
Halam 3		55 ± 3	30.9	-10.3	31-54		

of 46 pmc, into a negative age clearly shows the limit of ^{14}C model ages. Such a comparison may also indicate a young (possibly ^3H free) admixture that yields A_0 measured values $> A_0$ calculated values. However, the main conclusion from Table 1 relates to the ^{14}C dating of old waters in the same aquifers, which generally have a low ^{39}Ar activity. If the $\delta^{13}\text{C}$ values of these old samples are similar to the $\delta^{13}\text{C}$ values of the young waters, and if from chemical results an extensive geochemical evolution can be excluded, then a conversion of the low ^{14}C activity value into old ages seems reliable. The calculated and/or measured A_0 value of the young water is an upper limit for the old waters.

A method based on ^{226}Ra , with a half-life of 1602 a, can assist in the validation of ^{14}C ages (compare Fig. 1 for dating ranges). The first condition for this method is that the initial ^{226}Ra content coming from dissolution can be determined; the second condition is that the additional dissolution along the flow path coming from decaying ^{230}Th can be estimated. Barbecot *et al.* (1999) describes how, for an example in southern France, the initial ^{226}Ra content could be determined in the zone of relatively young water and how for very old samples in the same aquifer the (maximal) additional *in situ* contribution was estimated. This *in situ* production could also be determined by measuring U contents in the water and following $^{234}\text{U}/^{238}\text{U}$ and Sr/Ca ratios. Figure 2 compares ^{226}Ra with ^{14}C ages for this example. Up to a few thousand years the dating methods are in good agreement but for most older samples there are discrepancies, for which two explanations are

given: the ^{226}Ra *in situ* production has been underestimated; or (2) the models used to calculate ^{14}C ages do not take into account all of the retardation processes of ^{14}C occurring in the system.

Although the quoted example in southern France investigated during the PALAEAUX programme appears very promising, the application of the ^{226}Ra method is likely to remain restricted because, in general, the geochemical evolution and the water-rock interaction (e.g. sorption or precipitation of Ra) is rather complex.

Helium-4

In principle, ^4He contents should increase linearly with time as a result of the U and Th decay series.

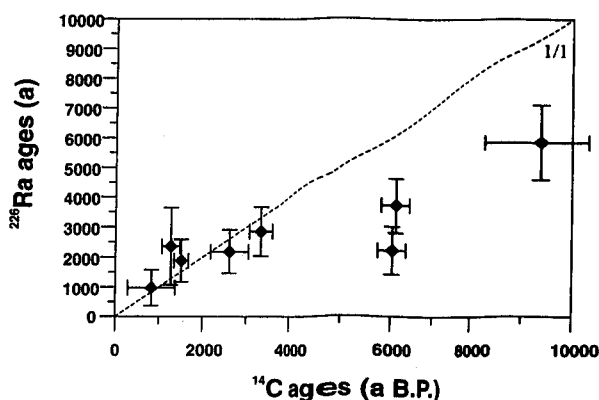


Fig. 2. Comparison of ^{14}C and ^{226}Ra ages for the Astian aquifer, France (Barbecot *et al.* 1999).

The production rate in the rock can easily be determined. It is also well known that the major part of ^4He produced in minerals has escaped from the rock (e.g. Tolstikhin *et al.* 1996) and should be found in the liquid phase. However, if measured ^4He concentrations in moving water are compared with 'known' (e.g. ^{14}C model) ages, a higher increase than that estimated from the *in situ* production rate is usually observed. For the UK East Midlands Triassic aquifer an increase of $c. 10^{-11} \text{ cm}^3 \text{ cm}^{-3}$ water per year has been measured compared with an estimated *in situ* production rate of only half of this value (Lehmann & Purtschert 1997). In the Australian Great Artesian Basin (GAB) the measured rate is $c. 6 \times 10^{-11} \text{ cm}^3 \text{ cm}^{-3}$ per year and in the Milk River aquifer (USA and Canada) it is $c. 1 \times 10^{-10} \text{ cm}^3 \text{ cm}^{-3}$ per year, both higher than the estimated *in situ* production rates (Lehmann *et al.* 1996). In the PALAEAUX programme, the ^4He increase with distance from recharge has been measured in the Ledo-Paniselian aquifer, Belgium (see Fig. 6); an increase of $c. 1 \times 10^{-10} \text{ cm}^3 \text{ cm}^{-3}$ per year can be estimated based on Fontes–Garnier model ages. It has to be assumed that ^4He is admixed with that derived from aquicludes above and especially below. Therefore, at present, a ^4He increase, e.g. with distance from the recharge area, can only be used as a relative and qualitative time indicator (e.g. Solomon 2000). However, it is an important tracer for understanding water–rock interaction and underground processes.

Recently, lower age limits of the order of 10^6 a were calculated (together with the assumed diffusion parameters and scale lengths involved) from ^4He measurements in pore water (Lippmann *et al.* 1998). Assuming ^4He accumulation during sedimentation time and ^4He loss from deep layers into the atmosphere by diffusion, a general agreement between measured and calculated ^4He contents in pore water of a depth profile down to 600 m could be observed (Purtschert 1997).

Lehmann *et al.* (1996) have pointed to an averaged linear relation between He accumulation and Cl^- increase observed for a wide range of old groundwaters. Increasing Cl^- , derived from internal sources such as residual saline fluids within the aquifer and diffusion from more stagnant zones, seems to be accompanied by He accumulation as a result of *in situ* production. Lehmann *et al.* (1996) indicated a difference for Cl^-/He ratios between groundwaters derived from sedimentary and crystalline rocks; this could be due to the fact that Cl^- is more readily leached from sediments than from crystalline rocks. They found that it was possible to explain the observed He and Cl^- concentrations as being derived from local sources, by assuming that neither He nor Cl^- was lost from

the system and that the water, therefore, was more or less stagnant over millions of years.

Krypton-81

For dating very old groundwater ($> 5 \times 10^4$ a), ^{81}Kr is an ideal isotope in terms of half-life and certain other properties. Like ^{39}Ar it is produced by cosmic rays and is available in the atmosphere at its equilibrium activity. This was initially determined by counting (Loosli & Oeschger 1969), and recently confirmed by cyclotron measurements (Collon *et al.* 1999), to be $c. 1.3 \times 10^{-6} \text{ Bq cm}^{-3} \text{ Kr}$. It can be assumed that thermonuclear production in the atmosphere has been negligible and also that subsurface production does not contribute to the activity of this isotope, shielded as it is by ^{81}Br (Collon *et al.* 2000). For ^{81}Kr it is also unnecessary to consider the effects of water–rock interactions. However, the fundamental disadvantage of this method is the low activity of ^{81}Kr ; with only $c. 1$ atom decaying every 300 a in 1 l of recent water. Therefore, measurement by instrumental counting of disintegrations is impossible, especially since any small admixture of recent Kr would introduce a much higher ^{85}Kr activity. The only feasible way of detecting ^{81}Kr is therefore to count the numbers of ^{81}Kr atoms available in a sample, i.e. to measure the atomic ratio of $^{81}\text{Kr}/\text{Kr}$.

Accelerator mass spectrometry (AMS) is not possible because a noble gas does not form negative ions [the recent attempt to measure ^{81}Kr contents was performed using a cyclotron (Collon *et al.* 2000)]. An amount of $c. 0.5 \text{ cm}^3$ of pure Kr was needed for individual measurements, which was obtained in a lengthy extraction process from $c. 16 \text{ m}^3$ of water for each sample. The aquifer selected was part of the Great Artesian Basin in Australia because it was hoped to find, for the first time, ^{81}Kr concentrations below the atmospheric level. Such low concentrations were indeed determined, yielding ^{81}Kr ages of $c. 220\text{--}400$ ka (Collon *et al.* 2000). At present, the interpretation of these results is in progress, especially the comparisons with ^4He , ^{36}Cl , noble gas and other data.

Chemical indicators of groundwater age

Sequential hydrogeochemical changes that can be interpreted in terms of residence time may occur in confined groundwater flow systems. A chemical model is usually required in order to interpret ^{14}C or other age indicators. The integration of geochemical and isotopic indicators is needed to verify numerical hydrogeological models, which can, in turn, provide challenges to their interpretation. The sequential processes that are observed in many

aquifers can be used to provide at least relative age estimates.

Examples to calibrate/chemical evolution by radiocarbon ages and possibly to extrapolate beyond the ^{14}C dating range are presented further on in this chapter (see Hydrochemical evolution) for the East Midlands Triassic sandstone aquifer in the UK, and for the Ledo-Paniselian Tertiary clayey and sandy aquifer in Belgium. The general trend of the chemical evolution with increasing ^{14}C age is clear in both aquifer systems. The conversion of the qualitative to a quantitative dating method has been attempted for the Triassic aquifer (Edmunds & Smedley 2000). The concentrations of the reactive tracers Sr, Rb, Li, Mo and Mn increase approximately linearly with increasing groundwater temperature (a proxy for distance) across the flow length. The data set has been used to construct a chemical timescale as illustrated in a discussion of English aquifers (Edmunds *et al.* 2001, fig. 12). The relatively large scatter already observed in the chemical concentrations, $\delta^{13}\text{C}$ and ^{14}C leads to a correspondingly large scatter of chemical ages. From this it may be concluded that reliable quantitative age values cannot be deduced; however, the calculated chemical ages do at least suggest that recharge was occurring in the Pleistocene within and beyond the reliable ^{14}C dating range (c. 30 ka BP). A Pleistocene origin for these waters is also indicated by the observed jump in noble gas recharge temperatures and in stable isotope composition after c. 14 ka (Edmunds & Smedley 2000).

The conversion of the chemical tracer data into a dating method has also been attempted for the Ledo-Paniselian aquifer (see Hydrochemical evolution later). The chemical concentrations obtained within the framework of the PALAEAUX studies confirm the previously modelled chemical evolution (Walraevens & Cardenal 2001). For these models, piston flow was assumed along the flow path and decreasing ^{14}C activities (and increasing $\delta^{13}\text{C}$ values) were used to obtain chronological information. For the PALAEAUX results, however, HCO_3^- and $\delta^{13}\text{C}$ do not show a clear general trend; instead, two groups with different concentrations and evolutions can be distinguished. The general trend in decreasing ^{14}C activity is still observed but cannot be used for reliable time calibration of the chemical tracer data because of the large scatter of ages.

Stable isotopes and noble gases as indicators of recharge conditions

The ambient temperature fundamentally influences the stable isotopic and noble gas contents of

groundwaters at the time of recharge. They therefore provide important information about palaeoclimatic conditions, but they can also function as qualitative indicators of age where climatic conditions in the past were sufficiently different from those of the present day. The noble gases are absolute indicators of temperature while stable isotopes, though easier to sample and measure, give relative information requiring local calibration for maximum benefit.

Stable isotopes

The O and H stable isotopic compositions of groundwaters, commonly expressed as $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values (e.g. Clark & Fritz 1997), are governed by a variety of physical processes acting mainly during the evaporation–precipitation part of the hydrological cycle that precedes recharge. Changes in climatic conditions have tended to modify the stable isotope signatures of rainfall, thereby providing an important qualitative tool for the identification of palaeowaters. However, the magnitude of any ratio change with time is affected by essentially local factors, and therefore isotopic 'shifts' in waters of the same age may not be identical from area to area. This will be demonstrated below by consideration of examples from the European continent.

Stable isotopic composition of rainfall

As a rain-bearing system moves away from its oceanic source area, preferential rainout of ^{18}O and ^2H isotopes causes the δ values of the remaining moisture to become progressively more negative, i.e. depleted, in these heavy isotopes. Rainout is basically caused by a fall in temperature, such as that affecting a tropically derived air mass as it progresses to higher latitudes, whereby (for example) tropical values of $\delta^{18}\text{O}$ in the range of 0 to -2‰ change to values more depleted than -50‰ in the Antarctic. These changes tend to be most pronounced over the oceans at higher latitudes (e.g. Clark & Fritz 1997). When rain-bearing systems pass over land, however, rainout may be considerably affected by local physiographic factors. A notable effect is the depletion in both $\delta^{18}\text{O}$ and $\delta^2\text{H}$ caused by rainout as air masses cool by moving over high ground. This generally gives rise to progressively more negative δ values with changes in altitude, typically ranging from -0.1 to -0.5‰ $\delta^{18}\text{O}$ per 100 m increase in altitude [data from sources cited in Clark & Fritz (1997)].

Although changing temperature and humidity conditions (i.e. weather) during the evaporation and subsequent condensation of the water vapour can lead to large differences in rainfall isotopic

compositions from event to event, these tend to even out between years [see data in IAEA (1992)]. This results in groundwater recharge in any particular region having an isotopic composition largely characteristic of the climate at the time. Therefore, major changes in climate are likely to be reflected by significant changes in the long-term average stable isotopic composition of recharge.

Effects of air temperature on rainfall isotopic composition

When present-day long-term weighted annual averages are considered, there is a reasonable degree of correlation between air temperature and the isotopic composition of rainfall for different sites, first identified by Dansgaard (1964). With the acquisition of further data, it has been possible to produce different temperature–isotope correlations for different groups of stations, i.e. marine, continental–coastal, continental interior and polar regions. For O-stable isotopes, the $\delta^{18}\text{O}/\Delta T$ effects range from $0.17\text{‰ }^{\circ}\text{C}^{-1}$ for marine stations to $0.90\text{‰ }^{\circ}\text{C}^{-1}$ for the Antarctic Peninsula (Clark & Fritz 1997). For the continental category, which would at present apply to much of Europe, an average of $0.58\text{‰ }^{\circ}\text{C}^{-1}$ was noted by these authors. Concomitant changes in $\delta^2\text{H}$ are observed.

There is also a *seasonal* isotope–temperature effect that may differ in magnitude and degree of correlation from the long-term effect. The reason for this is that the different sources and/or types of rainfall associated with the changing seasons can have quite different $\delta^{18}\text{O}/\Delta T$ relationships (Rozanski *et al.* 1993).

Both the long-term and seasonal isotope–temperature relationships require some consideration if they are going to be applied to palaeowater studies. For example, the present-day $\delta^{18}\text{O}/\Delta T$ value for a particular region may not have remained the same since the Pleistocene owing to climate change. Similarly, changes in the seasonality of rainfall could potentially affect seasonal isotope–temperature relationships (Jouzel *et al.* 2000).

Air-mass origin and circulation

The humidity of source areas is an important control on the relationship between $\delta^{18}\text{O}$ and $\delta^2\text{H}$. Thus, for example, rainfall derived from evaporation in the eastern Mediterranean will have different characteristics from that originating in the North Atlantic (Gat & Carmi 1970). The subsequent trajectory of air masses will not affect the $\delta^{18}\text{O} - \delta^2\text{H}$ relationship significantly but may have a profound effect on the absolute δ values of rainfall at a particular site, depending on the site's

position along the trajectory (e.g. Sonntag *et al.* 1979).

The isotopic composition of the oceanic source itself may change. During major extensions of ice cover the ocean becomes isotopically enriched because the depleted rainfall of higher latitudes is being more slowly recycled to the ocean than before the glacial episode (Sowers *et al.* 1993; Schrag *et al.* 1996).

The trajectories of moist air masses do not necessarily remain fixed through time. Any changes are most likely to result from modifications in oceanic circulation patterns brought about by long-term climatic trends. Significant changes in land-mass elevation, such as the comparatively rapid uplift of the Himalayas, can also play a part. However, over most of Europe there appears to be little isotopic evidence of gross changes in atmospheric circulation patterns since the Late Pleistocene (see below). Areas most affected by change seem likely to be either in high latitudes (Jouzel *et al.* 2000) or in zones which oscillate between humid and arid conditions, e.g. in the northern Sahara (Sonntag *et al.* 1979).

Identifying palaeogroundwaters from their stable isotopic content

During late Glacial times, proxy evidence points to decreases in the average annual temperature of several degrees in periglacial areas of the Northern Hemisphere. According to evidence cited in Clark & Fritz (1997), such declines in temperature would translate into an easily identifiable depletion in $\delta^{18}\text{O}$ of the order of 2–3‰ (measurement precision is $c. \pm 0.1\text{‰}$). Therefore, in principle, it should be possible to identify palaeowaters using stable isotope data. However, assuming that palaeowaters remain unmixed with modern waters, assessment of the period when recharge occurred on the basis of stable isotopes is not necessarily straightforward for the following reasons:

- (1) the temperature–isotope relationship appropriate for the present day may not apply, e.g. a modern coastal area may have been situated some distance inland during periods when sea levels were much lower owing to extensive glaciation;
- (2) changes in ocean circulation may have had profound effects on the circulation of air masses;
- (3) ice cover or permafrost may have distorted the isotopic composition of recharge, or even prevented recharge altogether.

Because of these factors, waters with the same recharge age may have different stable isotope

'shifts' in different geographical areas. To a considerable extent these apparent anomalies can be resolved by measuring noble gas concentrations to yield a temperature for recharge within certain limits as discussed below. Once this has been done for a local area, a noble gas-stable isotope calibration can be used to interpret further isotopic data.

Noble gases

The solubilities of the noble gases He, Ne, Ar, Kr and Xe are temperature dependent. Therefore, in principle, the mean annual ground temperature can be calculated and information about past climatic conditions can be derived from their content in groundwater (Mazor 1972; Andrews & Lee 1979; Person *et al.* 1991; Stute *et al.* 1995a, b; Cook & Herczeg 1999). For this calculation the recharge altitude has to be assumed and subsurface-produced radiogenic ^4He and ^{40}Ar have to be subtracted. Because the correction for radiogenic ^4He is usually impossible, He is often disregarded in the calculation of the recharge temperature (RT). However, the main problem in calculating RT is the so-called excess air (EA). Gas supersaturation of 10–50% is frequently observed; Ne excess (see below) up to a factor of 4 is measured in the Cambrian–Vendian aquifer in Estonia (Vaikmäe *et al.* 2001). Usually, it is assumed that EA is formed by the forcible dissolution of small air bubbles trapped in soil pores.

Several correction methods for EA are in use: an iterative optimization program for RT calculated from Ne, Ar, Kr and Xe is described in Pearson *et al.* (1991) and Stute *et al.* (1995a, b). A simplified method based only on excess Ne (most sensitive to oversaturation) can be used for a rapid approximation of EA. In the most rigorous approach, the parameters RT and EA are derived from inverse models describing noble gas concentrations in groundwater (Aeschbach-Hertig *et al.* 1999; Ballentine & Hall 1999). This method shows that the assumption of a purely atmospheric composition for EA is often incompatible with the data. Even the model of EA fractionation by diffusive re-equilibration (Stute *et al.* 1995b) does not always describe the data within experimental uncertainty. Recently, a model assuming solubility equilibration in a closed system of initially air-saturated water and a finite volume of entrapped air has been proposed (Aeschbach-Hertig *et al.* 2000).

It is not always possible to calculate a RT from the measured noble gas contents. One reason may be the degassing of oversaturated waters with irregular fractionation; high oversaturation with EA, as in the case of the Cambrian–Vendian aquifer

in Estonia (Vaikmäe 2001), or large contents of CO_2 or CH_4 favour such fractionations. However, several publications describe the successful application of correction models for EA and give convincing conclusions about past climatic conditions, e.g. in the UK, Hungary, Namibia, Switzerland and Oman (e.g. Weyhenmeyer *et al.* 2000). Similar conclusions about palaeowaters investigated during the PALAEAUX programme will be described below, mainly adopting a comparison between RT and stable isotope data.

Applications of isotope and geochemical methods in the PALAEAUX programme

Identification of palaeowaters using isotopic methods: examples from PALAEAUX studies

A palaeowater is defined as a groundwater that infiltrated during the Pleistocene or Early Holocene (Edmunds *et al.* 2001). Therefore, its identification contains both a time and a climate component. The tools to be combined for these two components of identification are summarized systematically in Table 2. Short-lived tracers such as freons, ^3H , ^{85}Kr and ^{39}Ar are omitted as age indicators, since for the following it is assumed that admixtures of young water components are determined by these tracers and taken into account. The question of whether a water is a palaeowater or not should be only decided from the components free of these short-lived isotopes.

Ideally, several age indicators are combined with several climate indicators. As discussed below, this ideal situation is attainable in only a few of the aquifers studied during the PALAEAUX programme. This is mainly due to the fact that usually only (corrected) ^{14}C ages are available for age

Table 2. The identification of a palaeowater is based on a time and a climate signal: possible tools are summarized in a systematic way

Time signals (i.e. age)	Climate signals
^{14}C ($\delta^{13}\text{C}$, C chem.)	RT
U/Th, ^{226}Ra	$\delta^{18}\text{O}$, $\delta^2\text{H}$
^{81}Kr	$\Delta T = 5^\circ\text{C}$
^{36}Cl	Recharge gap
^4He , $^{40}\text{Ar}/^{36}\text{Ar}$	Chemical signals
S and Sr isotopes	
Chemical evolution (if calibrated)	
Models (hydraulic, transport)	

determination. All other dating methods (except ^{81}Kr in Australia) cannot, at present, be used as quantitative tools. In many cases even the corrected ^{14}C ages are questionable, especially if an extensive evolution of the carbonate system has taken place. Radiocarbon ages must also be interpreted carefully when considerable amounts of CH_4 are dissolved in the water because methanogenesis may have shifted $\delta^{13}\text{C}$ in dissolved inorganic carbon (DIC) to more positive values, or if large amounts of CO_2 with unknown origin are admixed.

When considering climate indicators a combination of different signals is desirable (Table 2); most convincing is a consistent correlation between noble gas RT and (adjusted) stable isotope data. It has already been mentioned that the RT calculated from noble gas contents allow a more straightforward calculation of a temperature than by using $\delta^{18}\text{O}$ and $\delta^2\text{H}$. The values of the stable isotopes are determined by the temperature during precipitation and other factors (e.g. continental and altitude effects, circulation of air masses). The shift to more positive values of the water of the oceans during the Pleistocene should also be taken into account. The detection of the typical Late Pleistocene–Early Holocene temperature jump of c. 5°C or more requires a high spatial density of sampling, as does the ‘recharge gap’ possibly found for areas of former ice or permafrost cover.

However, if the temperature jump and/or recharge gap are detected at the expected ^{14}C ages the argument is very convincing. In general, agreement between an age signal and a climate signal is required; a ^{14}C –RT or ^{14}C – $\delta^{18}\text{O}$ plot demonstrates how reliable the identification of a palaeowater is (e.g. Fig. 3). The influence of the distance from the ocean on the $\delta^{18}\text{O}$ shift must also be taken into account.

An assessment follows of palaeowater identification during the PALAEAUX studies based on a traverse from Estonia through the coastal regions of Europe as far as the South of France and Portugal (Table 3). The most convincing cases are based on the results obtained for the Cambrian–Vendian aquifer (Estonia), the Ledo–Paniselian aquifer (Belgium), the East Midlands Triassic aquifer (England), the Aveiro aquifer (Portugal) and the Glatt Valley aquifer (Switzerland). More difficult to interpret are results which indicate only an admixed (and possibly minor) old water component, as then only attenuated climate signals are available. Table 3 summarizes the methods which have been used, with the symbols \blacktriangle \blacksquare \bullet denoting the degree of reliability of identification of a palaeowater. The observations made below are based on the references cited and data given in other chapters of this volume.

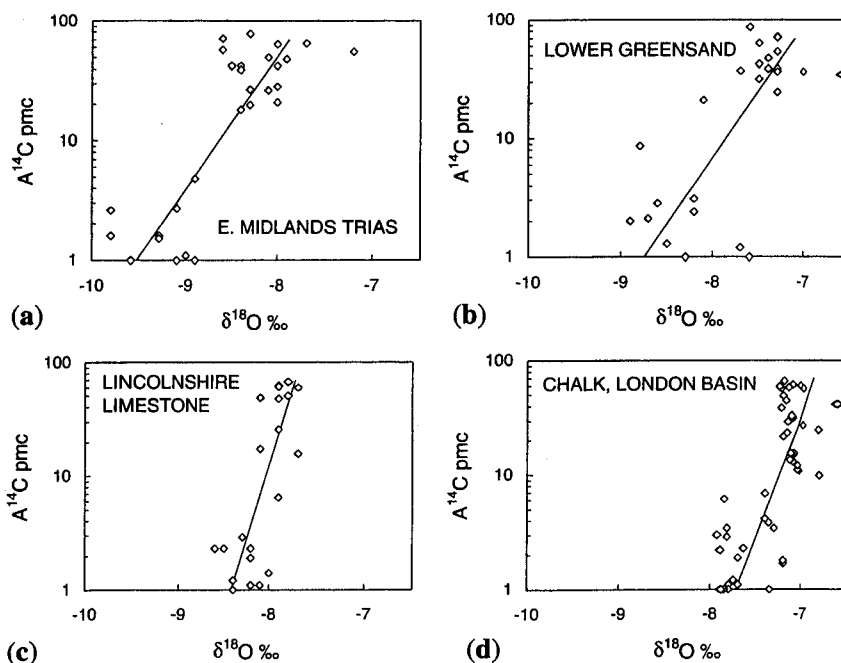


Fig. 3. Plots of ^{14}C activity v. $\delta^{18}\text{O}$ for groundwaters in the four main sedimentary aquifers of England [from data summarized in Darling *et al.* (1997)]. Aquifers (a) and (b) are sandstones, while (c) and (d) are carbonates. There is evidence of a ‘recharge gap’ between older and younger groundwaters in each aquifer, although this is better developed in the sandstones.

Table 3. Indicators of recharge conditions and residence times used in the different PALAEWAUX studies, with an overall 'palaeowater' rating

Aquifer	Noble gas RT *	$\delta^{18}\text{O}$ $\delta^2\text{H}$ *	$\Delta T =$ 5°C *	$\delta^{13}\text{C}$ ⊙	^{14}C ⊙	^{39}Ar ⊙	^{36}Cl ⊙	^4He ⊙	$\delta^{34}\text{S}$?	U series ⊙	Chemical evolution *⊙	Palaeowater water rating
<i>Estonia</i>												
Cambrian–Vendian	√	√		√	√	√		√				▲
<i>Denmark</i>												
Ribe		√		√	√							■
<i>Belgium</i>												
Ledo–Paniselian	√	√	√	√	√			√			√	▲
<i>England</i>												
S Chalk		√		√	√						√	▲
EM Triassic	√	√	√	√	√	√	√	√	√	√	√	▲
<i>France</i>												
Dogger		√		√	√					√	√	●
Astian		√		√	√					√	√	●
<i>Portugal</i>												
Aveiro	√	√	√	√	√						√	▲
Sado–Tagus		√		√	√						√	■
<i>Spain</i>												
Doñana	√	√		√	√	√					√	●
<i>Switzerland</i>												
Glatt Valley	√	√	√	√	√	√		√				▲

*, Climate indicator; ⊙, residence-time indicator.

▲, Strong indications; ■, some indications; ●, few or no indications.

Cambrian–Vendian aquifer, northern Estonia

Palaeowaters are identified by their extremely negative $\delta^{18}\text{O}$ values (c. -20%). Some RT are reliable and are < c. 4°C . Radiocarbon values are difficult to convert into ages because $\delta^{13}\text{C}$ values more negative than -9% are hard to understand if infiltration happened below a glacier. This subglacial recharge mechanism is a possible explanation for the measured high gas oversaturation (up to a factor of c. 4 compared to air-saturated water).

Ribe Formation aquifer, Denmark

Very old groundwaters are suggested by several low radiocarbon activities (≤ 1 pmc) and $\delta^{13}\text{C}$ values similar to young waters (c. -13%), implying that the low ^{14}C values are due to long residence times rather than exchange with 'dead' rock carbonate. However, the $\delta^{18}\text{O}$ shift is small and RT values are not yet available.

Ledo–Paniselian aquifer, Belgium

Samples show an increasing ^4He content in the direction of flow; the corresponding noble gas RT give values close to present-day RT (c. 9°C) for the first 8 km and scattering lower values ($2\text{--}8^\circ\text{C}$) up to c. 20 km. However, the $\delta^{18}\text{O}$ values decrease only from c. -6.5% to -7.1% (Walraevens 1990). Some ^{14}C values are difficult to convert into age information because of elevated $\delta^{13}\text{C}$ values (-4 to $+2\%$) but several convertible low ^{14}C values exist (e.g. 0.5 pmc and -9.2%), demonstrating a Pleistocene age for these waters. A recharge gap is observed based on conventional ^{14}C ages with $A_0 = 70$ pmc (Walraevens 1990) but not for the Fontes–Garnier model ages.

Triassic and Cretaceous aquifers, England

In the East Midlands Triassic sandstone the clear identification of palaeowaters is based on a recharge gap from 10–20 ka BP (corrected ^{14}C ages) and on the corresponding step in $\delta^{18}\text{O}$ and noble gas temperature (Bath *et al.* 1979; Andrews *et al.*

1984). Qualitative support for the nature of palaeoclimatic conditions is given by chemical components and S and Sr isotope values (Andrews *et al.* 1994; Edmunds *et al.* 1996). While ^4He increases along the flow direction, *in situ* production cannot account for the total amount measured; the inferred addition of ^4He from the adjacent strata prevents its use as dating tool (Andrews *et al.* 1984).

The Chalk aquifer probably contains palaeowater concluded from low ^{14}C contents (1–10 pmc) and maximum $\delta^{18}\text{O}$ depletions of *c.* 1‰. The Lower Greensand aquifer has rather better palaeowater credentials with equally low ^{14}C contents but a greater $\delta^{18}\text{O}$ shift (Darling *et al.* 1997).

Dogger aquifers, northern and western France

Groundwater in the highly fissured carbonate aquifer of the Caen area is slightly saline and has so far given a maximum corrected age of *c.* 7.5 ka BP, i.e. Holocene. A $\delta^{18}\text{O}$ -shift of *c.* -0.7‰ has been noted compared to modern waters in the vicinity. Despite the salinity, the groundwaters have no apparent connection with the sea and ^{14}C activities are independent of salinity. Therefore, this aquifer is not currently undergoing a freshening process.

In the Dogger aquifer of the Marais Poitevin, near the Atlantic coastline of western France, less fissured but still calcareous, the chemistry suggests a simple mixing series between fresh groundwater and sea water but isotopic evidence is less clear. The minimum observed ^{14}C activity is 12.1 pmc, indicating a Holocene age.

Astian aquifer, the South of France

The Astian aquifer in this area is a micaceous sand. Mean residence times, based on ^{14}C , range from modern in the recharge zone to 6 ka (earlier Holocene) near the coast. In the eastern part of the aquifer the effects of contamination by 'dead' volcanic CO_2 have been corrected for by the use of ^{226}Ra . A small (0.15‰) depletion in $\delta^{18}\text{O}$ is shown by the oldest waters.

Aveiro aquifer, northern Portugal

Palaeowaters are identified by their apparent ^{14}C ages in combination with their RT. A 5°C drop from present-day RT was observed for waters with modelled ^{14}C ages of *c.* 18 ka BP. Stable isotopes show more positive values for older waters than for shallow recent waters. This is likely to be a reflection of isotopic enrichment of the world's oceans during glacial times.

Miocene Lower Tagus-Sado aquifer, southwestern Portugal

Modelled radiocarbon ages of up to 25 ka were noted for the more saline waters; however, no $\delta^{18}\text{O}$ shift was observed.

Doñana aquifer, southwestern Spain

Few indications of palaeowater were found, although such a component cannot be excluded. The lowest ^{14}C activities are *c.* 7 pmc, converted by Pearson's model (Pearson *et al.* 1991) to 11–15 ka. However, one RT determined for such an old water does not show any difference to present-day precipitation. This is in agreement with a pollen record for the Doñana area covering the last 18 ka, suggesting no major climatic changes since the last glacial maximum (LGM) (Zazo *et al.* 1996).

Glatt Valley aquifer, Switzerland

Admixtures of younger but ^3H -free water components were detected by ^{39}Ar . The old component is clearly identified as a palaeowater by corrected ^{14}C ages, a corresponding temperature shift of 5°C determined from noble gas contents, a corresponding $\delta^{18}\text{O}$ shift and by a recharge gap from *c.* 28–15 ka BP (Beyerle *et al.* 1998).

Hydrochemical evolution: examples from the UK and Belgium

Two types of chemical evolution involving time-dependent water–rock interaction have been investigated in the PALAEAUX programme: (1) downgradient changes in freshwater systems; (2) freshening in formerly saline aquifers. Superimposed effects of sea-level change and of climate changes are included in the following discussion.

In Figure 4 downgradient increases for two elements and for $\delta^{13}\text{C}$ are illustrated as examples for reactive tracers, described in more detail for the East Midlands Triassic sandstone aquifer by Edmunds & Smedley (2000). Manganese, Rb and Mo also show a significant increase along flow lines, whereas the increase of Si and Cs are less clear. These changes are explained by a progressive release from rock to water by incongruent or disproportionation reactions from carbonate, silicate or oxide minerals. Solubility does not limit the upper concentration of these trace elements and no plateau is reached due to partitioning between solid and aqueous phases, and thus their increases may be interpreted qualitatively in terms of residence times.

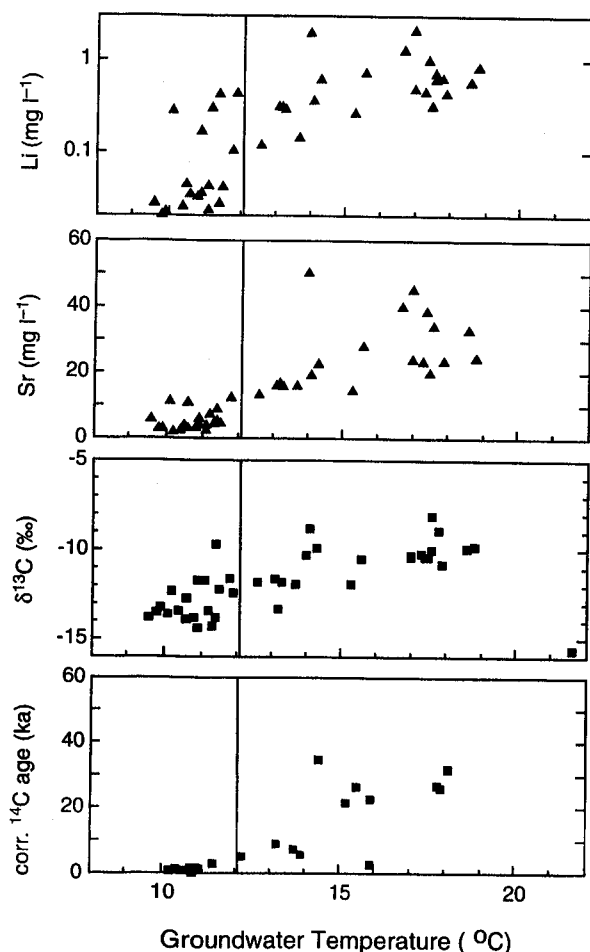


Fig. 4. Downgradient plots of Li, Sr and $\delta^{13}\text{C}$ from the East Midlands Triassic sandstone aquifer (groundwater temperature serves as a proxy for distance). These linear increases have been calibrated in terms of age using the corrected ^{14}C ages (see fig. 12a, Edmunds *et al.* 2001 – p. 86 of this volume).

Chloride, Br and other halogen elements are used as inert tracers (like noble gases – see below) to study atmospheric or anthropogenic inputs in the East Midlands Triassic sandstone aquifer. Chloride concentrations are significantly higher down to c. 200 m depth in the aquifer, showing the anthropogenic impact. Deeper in the aquifer a constant and low Cl content is measured. This is interpreted as a demonstration of constant rainfall concentration, even back to the Devensian glacial period (Edmunds & Smedley 2000). Br/Cl and $^{36}\text{Cl}/\text{Cl}$ ratios are used to reach conclusions for recharge and climatic conditions in the Late Pleistocene: a slightly elevated Br/Cl ratio in old waters indicates a greater distance to the open Atlantic Ocean during the ice age and a reduction of evapotranspiration by almost 50% was deduced from the $^{36}\text{Cl}/\text{Cl}$ ratio for the Late Pleistocene.

Figures 5 and 6 illustrate results in a freshening aquifer measured during the PALAEAUX programme. Freshening aquifers are those in which a marine-derived water is being replaced by freshwater, a situation that applies to many of the coastal aquifers studied during PALAEAUX. In the typical case of a freshening aquifer, two end members are involved: a saline NaCl-type marine water initially filling the aquifer and a fresh Ca-carbonate-type recharge water resulting from rainfall in which CaCO_3 has been dissolved.

After the fresh recharge water has started to infiltrate into the aquifer, the first process consists of the gradual dilution of the original marine porewater. This will result in the development of a salt water–freshwater interface, which will be more or less sharp according to the extent of hydrodynamic dispersion. The interface will move in the direction of groundwater flow. Downgradient, the initial sea water will persist. The freshwater–saline water interface in the Ledo-Paniselian aquifer is clearly observed in Figure 5 at c. 15 km distance from the recharge area – a sharp increase in Cl^- concentration is measured, associated with a similar Na^+ increase. Upgradient of the interface, evidence appears of the different stages of cation exchange, resulting in a chromatographic pattern, when a sequence of Na^+ -, K^+ -, Mg^{2+} - and, finally, Ca^{2+} -rich waters is observed. Involved cation exchange processes are described in more detail in Appelo (1994) and Walraevens (1990).

Geochemical modelling of the chromatographic pattern observed in the Ledo-Paniselian aquifer has been performed (Walraevens & Cardenal 2001). The calculations take into account a lower flow velocity in the second part of the aquifer due to gradual escape of water from the aquifer through the overlying aquitard. In agreement with results plotted in Figure 5, the model predicts a K^+ peak c. 10 km from the recharge area due to $\text{K}^+/\text{Ca}^{2+}$ exchange, and a Mg^{2+} peak c. 5 km due to $\text{Mg}^{2+}/\text{Ca}^{2+}$ exchange. Towards the recharge zone, Ca^{2+} is gradually reaching equilibrium concentrations resulting from CaCO_3 dissolution during infiltration.

Other examples from PALAEAUX

Being predominantly coastal, most other aquifers studied within the framework of PALAEAUX are freshening aquifers. Several of them are of marine origin and connate seawater may still be an end member contributing to the groundwater chemistry, e.g. the Chalk of the English south coast. Other aquifers have a continental origin but were intruded by salt water as a result of later marine transgression, e.g. the Doñana aquifer in southern

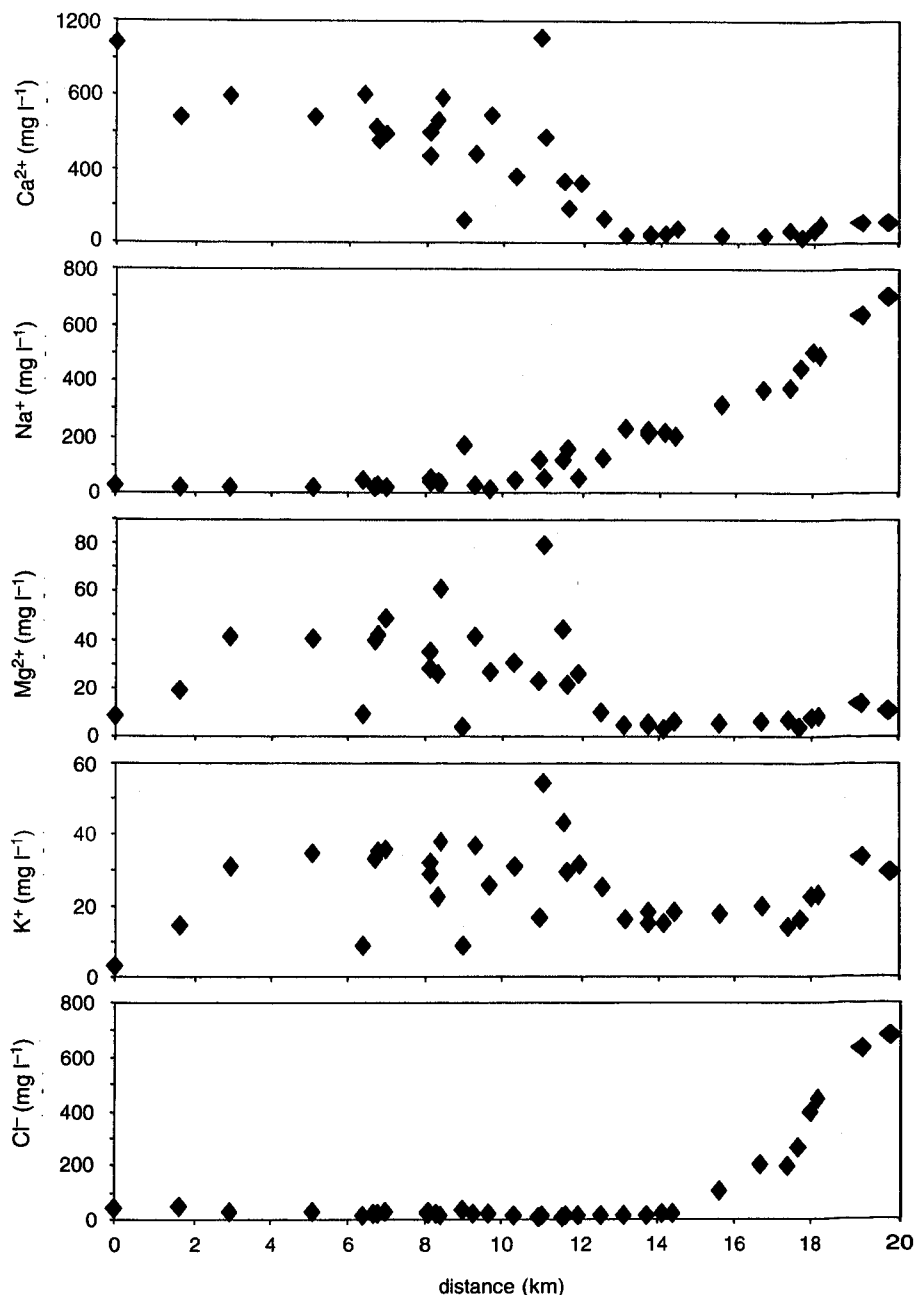


Fig. 5. Chemical data for the Ledo-Paniselian aquifer approximately in the flow direction obtained during the PALAEAUX programme. These results generally confirm the previously modelled evolution (Walraevens & Cardenal 2001).

Spain and the Cambrian–Vendian aquifer in Estonia. In all of these cases, freshening started after regression of the sea, allowing freshwater, derived from rainfall in the recharge areas, to enter the aquifer.

From the radiocarbon activity and the Cl content in groundwater of the Dogger aquifer in western France, three end members have been inferred: sea water (intruded during the Flandrian transgression) and two freshwaters – a fresh water older than

Flandrian that was recharged into the aquifer before the marine transgression and a modern freshwater (Dever *et al.* 2001).

The chromatographic pattern may be obscured by flow conditions in the aquifer (e.g. mixing of water of different flow lines or hydrodynamic dispersion). In general, the most important cation exchange process, i.e. $\text{Na}^+/\text{Ca}^{2+}$ exchange, will be most readily detected, resulting in the NaHCO_3 water type, e.g. in the Ledo-Paniselian aquifer in

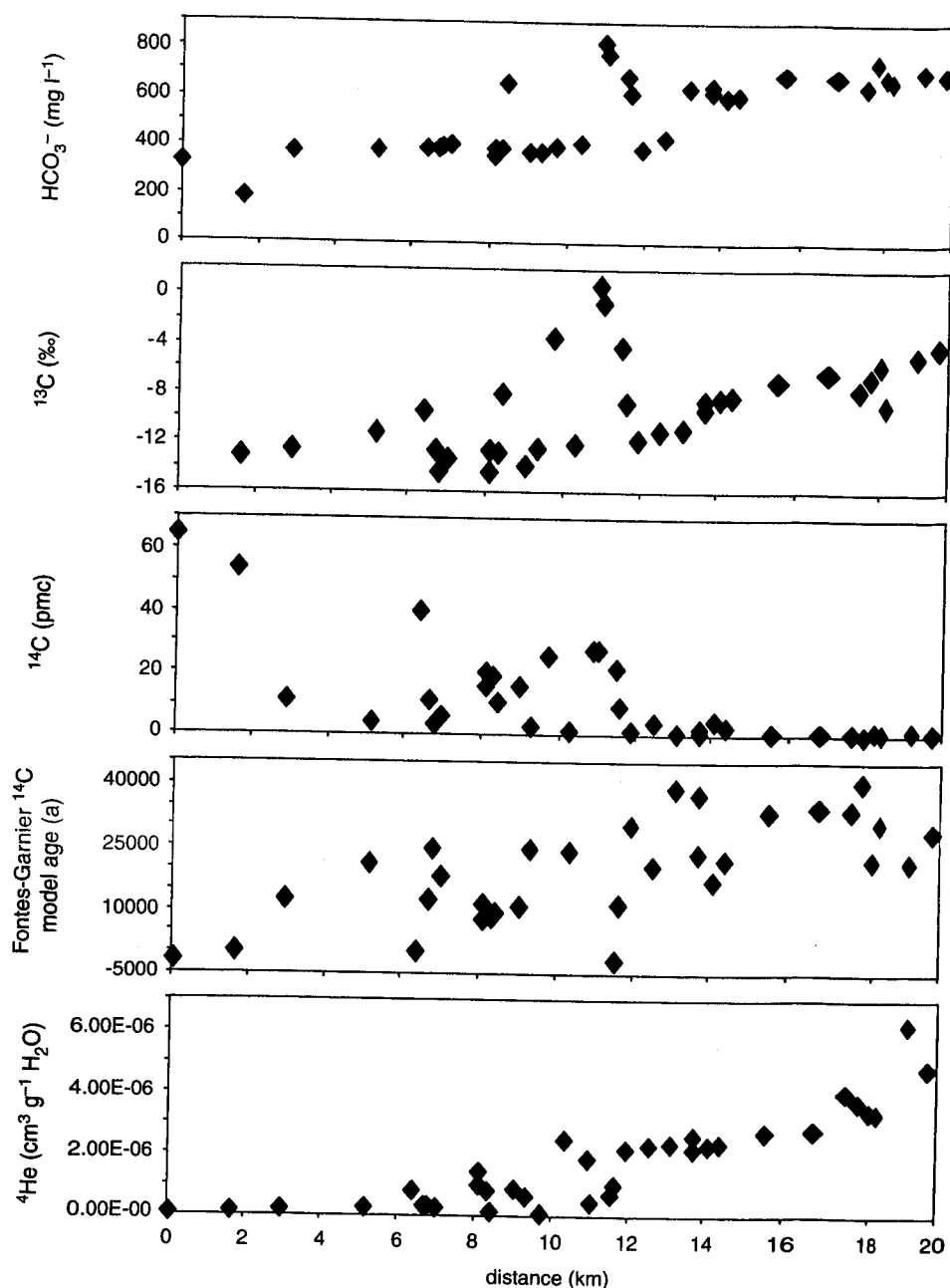


Fig. 6. Isotope and additional data for the Ledo-Paniselian aquifer obtained during the PALAEAUX programme. These data are used to attempt dating by chemical tracers in connection with chemical evolution (see text).

Belgium, the Aveiro aquifer in Portugal and the Ribe Formation in Denmark.

In several of the aquifers studied, overexploitation is leading to local salinity increases, mostly due to upconing of saline groundwater from greater depths or to direct sea-water intrusion. This local salinization is disturbing the regional freshening of the aquifer, e.g. in the Landenian aquifer in southern France and the Cambrian-Vendian aquifer in Estonia.

Conclusions at the European scale from the application of stable isotopes, noble gases and geochemical evolution

Stable isotopes

Due to the wide diversity in climate, relief and geology, the European continent has a variety of groundwater environments and habitats. Many of these have received close attention over the past 30 a in terms of isotopic characterization, providing

good illustrations of the ways of interpreting isotopes in terms of change or, in some areas, lack of change during the transition from past to present climates.

In Figure 3 a comparison of palaeowaters in English aquifers reveals differences due to aquifer lithology. However, the plots can also be interpreted from a palaeoclimatic viewpoint. Examination of Figure 3a and b reveals that there is an offset in $\delta^{18}\text{O}$ between the two sandstone aquifers. This is presumed to be a rainout effect; the recharge area for the East Midlands Trias lies to the north of the recharge area of the Lower Greensand and therefore receives a somewhat more isotopically depleted rainfall as a result of rainout from the predominantly southwesterly source of moisture. The ^{14}C data show that this offset is maintained into the past, implying that there was no fundamental change in air-mass movement. The 'old' $\delta^{18}\text{O}$ data thus reflect a lower annual average rainfall temperature, possibly supplemented by an element of extra rainout resulting from a somewhat greater distance between the recharge areas and the ocean due to the fall in sea level that accompanied the growth of the ice caps.

While the above discussion gives an indication of the amount of information that stable isotopes can provide about individual areas, a Europe-wide perspective requires the comparison of data from different areas. Figure 7 shows the way in which the $\delta^{18}\text{O}$ of groundwaters has changed across Europe between the Late Pleistocene and the present, based on data from the PALAEWAUX programme and other studies. A transect from the southwest (Portugal) to the northeast (Estonia) is represented, using data projected from coastal or near-coastal aquifers in which the maximum $\delta^{18}\text{O}$ shifts for the given area appear to have been preserved. Data from more continentally-influenced aquifers from Switzerland to Hungary are also shown on a separate transect. For the coastal aquifers, it is clear that at the present day there is a progressive depletion from the southwest to the northeast, related to rainout acting on a southwesterly source of moisture. It is equally apparent that in the Late Pleistocene, a southwest-northeast change was also occurring. However, this seems to have had three separate elements:

(1) an isotopic enrichment in Portugal. This is likely to have been the result of a relatively small temperature drop at this latitude (owing to ocean buffering) coupled with the ice-cap-related raising of the oceanic $\delta^{18}\text{O}$ value. Additionally, there was little change in the Portuguese coastline during the Late Pleistocene, so that depletion effects related to rainout over the 'extra' land would not have

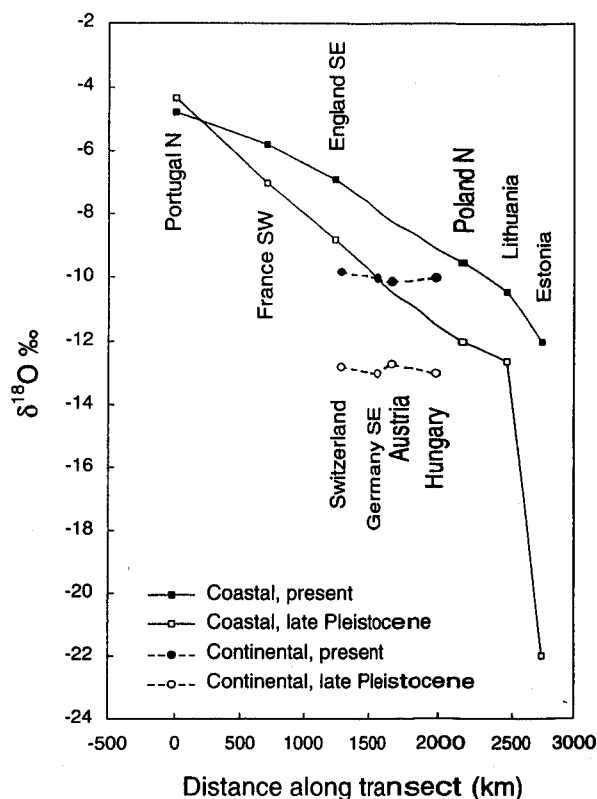


Fig. 7. Differences in European groundwater $\delta^{18}\text{O}$ values between the present day and the late Pleistocene, following an approximately southwest-northeast transect from Portugal to Estonia. Data from: Portugal, Carreira *et al.* (1996); France, Le Gal La Salle (1996); England, Darling *et al.* (1997); Poland, Rozanski (1985); Lithuania, Mazeika & Petrosius (1998); Estonia, Punning *et al.* (1987); Switzerland, Beyerle *et al.* (1998); Germany, Bertleff *et al.* (1993); Austria, Andrews *et al.* (1985); Hungary, Stute & Deak (1989).

occurred. Thus, it would have been possible for $\delta^{18}\text{O}$ to increase slightly;

- (2) a west-east European trend, terminating in Lithuania, giving a depletion gradient similar to the present-day value, confirming the interpretation of the data from England (Fig. 3 and above) that there have been no large-scale changes in air-mass circulation between the Late Pleistocene and the present;
- (3) a considerably greater change in Estonia than can be explained by rainout effects alone. It is considered that Late Pleistocene recharge in this area must have been the result of the infiltration of isotopically depleted glacial meltwater, either in the outwash plain of the ice cap or as the result of subglacial melting. Recharge of this depleted water may have affected other parts of the present Baltic littoral: e.g. waters with $\delta^{18}\text{O}$ values some 3‰ more negative than the palaeowaters generally

encountered in northern Poland (see Fig. 7) were sampled from the Hel Peninsula in the extreme northeast of the country (Zuber *et al.* 1990), and palaeowaters with $\delta^{18}\text{O}$ contents down to -18‰ have recently been reported from southern Finland (Casanova *et al.* 1999). However, Estonia remains the location with the most isotopically depleted water so far encountered.

By contrast, the continental transect in Figure 7 is almost flat. It might perhaps have been expected that the mountainous centre of Europe would have had a more profound effect on isotopic compositions between Switzerland and Hungary, particularly in Late Pleistocene times, but clearly air-mass trajectories were, and remain, such that isotopic effects are minimized.

Palaeoclimatic information from noble gas RT and stable isotopes at the European scale

The measurement of noble gases to derive RT values is a relatively specialized technique and comparatively few data exist for Europe. One of the

main aims of the PALAEWAUX programme has been to extend knowledge of noble-gas-derived RT in order to gain a wider perspective on conditions of recharge for Europe as a whole.

The importance of obtaining RT data from these areas is illustrated by the plot in Figure 8, which shows gradients of RT v. $\delta^{18}\text{O}$ for some European aquifers. While countries from England to Hungary have positive gradients with subparallel trends showing roughly similar amounts of isotopic depletion for a given drop in RT between the present and Late Pleistocene, those from Belgium and Portugal are almost flat and negative, respectively. Two conclusions emerge:

- (1) the generally similar (RT) temperature gradients in northwestern and central Europe lead to averaged-out shifts in stable isotopes of c. $-0.35\text{‰ }^{\circ}\text{C}^{-1}$ drop in temperature, less than the $-0.58\text{‰ }^{\circ}\text{C}^{-1}$ figure for present-day rainfall mainly because of the rise in oceanic $\delta^{18}\text{O}$. However, since the errors of the determined $\delta^{18}\text{O}$ v. RT slopes are still rather large, this difference is not yet firmly established;
- (2) the barely positive gradient in Belgium and the negative gradient in Portugal show that it cannot be assumed that a decline in RT will always be accompanied by a drop in $\delta^{18}\text{O}$; regional factors must be taken into account.

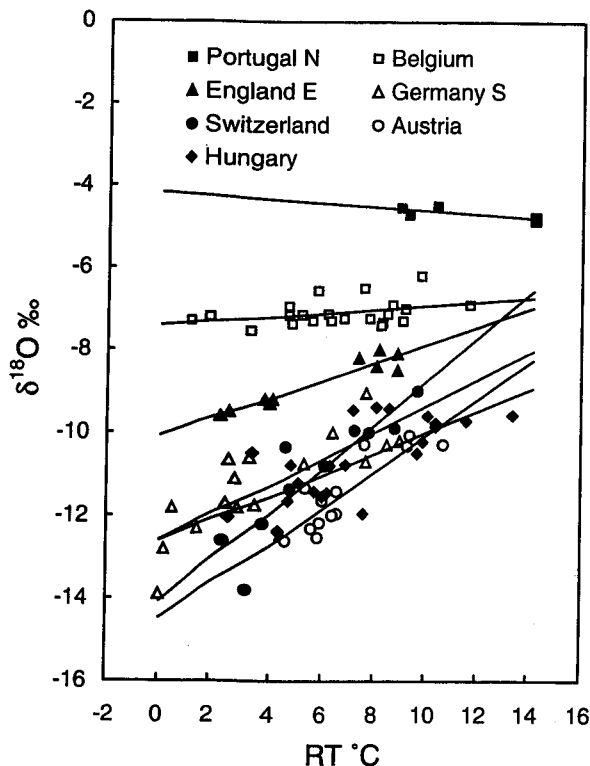


Fig. 8. Plot of $\delta^{18}\text{O}$ v. recharge temperature (RT) showing the gradients between the present day and the Late Pleistocene for various European countries. Data sources as for Figure 7, plus relevant chapters in this publication.

It is apparent from the various points considered in this section that stable O and H isotopes can only be qualitative indicators of palaeowater RT; therefore, it is important that they are calibrated locally by measurements of noble gas RT. However, it is also clear that stable isotopes have a major role to play in establishing the climatic context of past recharge.

Overall conclusions

This chapter has reviewed, at regional and European scales, the tools and methods used to investigate palaeowaters. The main questions covered are the identification of a palaeowater, the movement of the front separating palaeowater from younger water, the calibration of flow models and the application of all this information to reach sustainable water use. The PALAEWAUX studies demonstrate that recharge conditions can be determined most effectively by combining stable isotope results with noble gas RT, and that the evolution of a palaeowater can be described by analysing chemical tracers, but that residence times can sometimes only be estimated with great uncertainties.

Progress has been achieved during the PALAEWAUX programme by using the stable isotopes to study climate information on the

European scale (Fig. 7) and by combining $\delta^{18}\text{O}$ and noble gas RT to calculate $\delta^{18}\text{O}/\Delta T$ ratios for countries at different distance from the Atlantic (Fig. 8). Indications are that the more positive $\delta^{18}\text{O}$ value of the ocean water during the Pleistocene predominates in western countries over the expected negative $\delta^{18}\text{O}$ shift accompanying cooler conditions. There are also indications that no significant changes of air-mass circulation occurred between the Pleistocene and Holocene. However, some RT could not be calculated, indicating that further studies are needed to better understand subsurface processes influencing noble gas concentrations.

The evolution of a palaeowater can be best studied by measuring chemical tracers; this is possible in freshwater aquifers, where a clear signal of geochemical reactions is observed, and freshening in previously marine aquifers. Relationships between specific hydrochemical parameters and residence times are valid only for the flow path from which they have been derived and require recalibration for each aquifer being considered. The observation of chemical parameters is the most important tool in investigating the movement of the front between palaeowaters and younger components, which need to be known for model calibration.

The PALAEAUX studies confirmed that dating of palaeowater is still a weak point, even if several methods are combined; the ^{14}C results are often difficult to convert into ages because of water-rock interaction. Therefore, a more frequent combination of ^{14}C with ^{226}Ra , ^4He and $^3\text{He}/^4\text{He}$ -ratios, and with ^{36}Cl results is necessary. Another important conclusion from the PALAEAUX programme is that the combination of time and climate signals reinforces both and that, in addition, the geochemical processes need to be understood.

From the viewpoint of aquifer management, it is desirable to have easily accessible indicators of groundwater age; however, the the PALAEAUX studies have demonstrated that the traditional relatively simple methods (e.g. ^3H and stable isotopes) are not usually sufficient for studying palaeowaters. Whether the water use is sustainable or not can be best investigated by applying calibrated flow and transport models. To recognize early a change in water quality the combination of all available information is required: isotope techniques, chemical tracers and calibrated models are, at present, the most powerful basis for a good management of waters and especially of palaeowaters.

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