Rare Gas Studies of Basin Scale Fluid Movement [and Discussion]

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Rare gas studies of basin scale fluid movement

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Rare gases are conservative tracers of subsurface fluid movement. The mass balance of atmosphere-derived and crustally produced radiogenic and nucleogenic rare gases in natural gas reservoirs allows straightforward constraints to be placed on scales of fluid movement in sedimentary basins. The details of large-scale fluid movements in Neogene sedimentary basins appear to differ according to their thermal structures.

1. Introduction

Fluid movement on scales of tens to hundreds of kilometres occurs in various parts of the crust. This includes sedimentary basins, accretionary prisms, and areas of crustal deformation and metamorphism. The development of hydrocarbon reservoirs and formation of metallic ore deposits are two common expressions of these processes.

There are two basic types of observation used to examine questions of fluid flow in the crust. One of these involves the fossil system where some chemical or isotopic signature which has been imprinted upon the rock by fluid flow is examined. The other involves observations of active fluid systems and emphasizes observations on the composition of the fluid phase itself. The first approach has become commonplace in metamorphic petrology (e.g. Bickle & McKenzie 1987) where from chemical and isotopic gradients in exhumed metamorphic rocks the details of fluid composition and flow are reconstructed. The study of groundwaters at low temperatures in aquifers or at high temperatures in geothermal systems are well-known examples of the second approach. For example, Oxburgh & O'Nions (1987) and O'Nions & Oxburgh (1988) have described the use of ^{3}He in these to identify mantle-derived fluids present in the continental crust of Europe.

This contribution considers the understanding of basin scale fluid movement that has arisen through studies of active fluid systems in young sedimentary basins. Because in this work a basic requirement has been for samples that are well located in the subsurface, the studies are based mostly on areas of hydrocarbon exploration or production where samples could be obtained from existing wells and boreholes. In geochemical tracer studies of fluid movement in the subsurface, the aim is to identify and exploit those chemical and isotopic tracers which provide information on fluid provenance, pathways and rates of movement. The rare gases have proved to be of particular value as natural tracers of subsurface fluids. Because they are chemically inert, their abundances and isotopic compositions are not modified by chemical reaction. They behave as ideal conservative tracers. Their relative abundances are modified, however, in multiphase fluid systems, where for example water and gas, or water and oil phases co-exist. Fortunately the physical chemistry of rare gases is now

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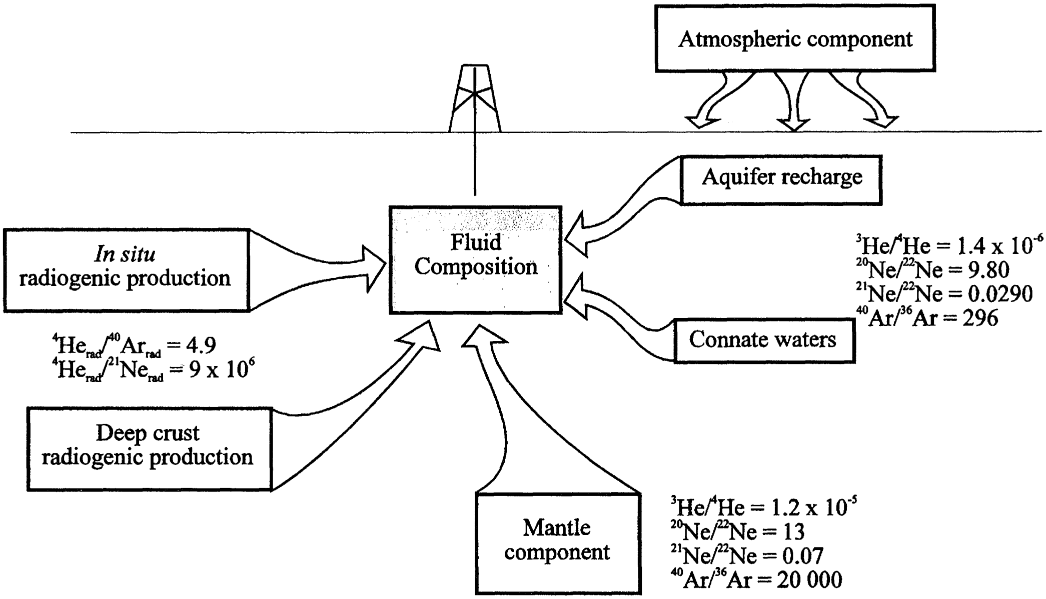

Figure 1. Schematic diagram illustrating the various rare gas components that may be found in a hydrocarbon reservoir or other subsurface fluid. The isotopic compositions of rare-gases in the atmosphere are acquired by connate waters and aquifer recharge through equilibration. The abundances of the rare gases in these waters are controlled by the Henry's coefficients which depend upon temperature and salinity (see Ballentine *et al.* 1991; Bosch & Mazor 1988). Radiogenic rare gases are generated within the fluid reservoir and elsewhere in the crust with ^{4}He/^{40}Ar and ^{4}He/^{21}Ne ratios which are characteristic of the K/U and Th/U ratio of the crust (see Appendix A). Mantle rare gas is relatively enriched in primordial ^{3}He and ^{20}Ne compared to the atmosphere but depleted in ^{36}Ar. In many circumstances the contributions of these various sources to a 'final composition' in a hydrocarbon reservoir may be resolved.

sufficiently well known that their partitioning in these situations may be predicted. The rare gas isotopes are highly diagnostic of fluid provenance; groundwaters which have equilibrated with the atmosphere have rare gas isotope abundances which differ significantly from those produced in association with radioactive decay in the continental crust or those introduced along with melt from the mantle.

This contribution is concerned with the application of rare gas abundances and isotopes to the understanding the scales of fluid movement in Neogene sedimentary basins. The results obtained on several gas fields in the Pannonian, Vienna and Po Basins are emphasised and it is shown how rare gas mass balance provides direct information about scales of movement and the importance of focusing effects that arise from it.

2. Tracers of fluid movements

Of the rare gases only He, Ne and Ar tracers are considered here because more complete abundance and isotope data sets are currently available for these. The stable isotopes of H, C, O, N and S have been widely used as fluid tracers in groundwater, hydrothermal and hydrocarbon systems. These tracers differ from the rare gases in being chemically reactive and therefore non-conservative. As such they cannot normally be used to address the questions of fluid mass balance which is emphasized in the discussion of rare gas tracers below.

The systematics of He, Ne and Ar isotopes in subsurface fluids are relatively

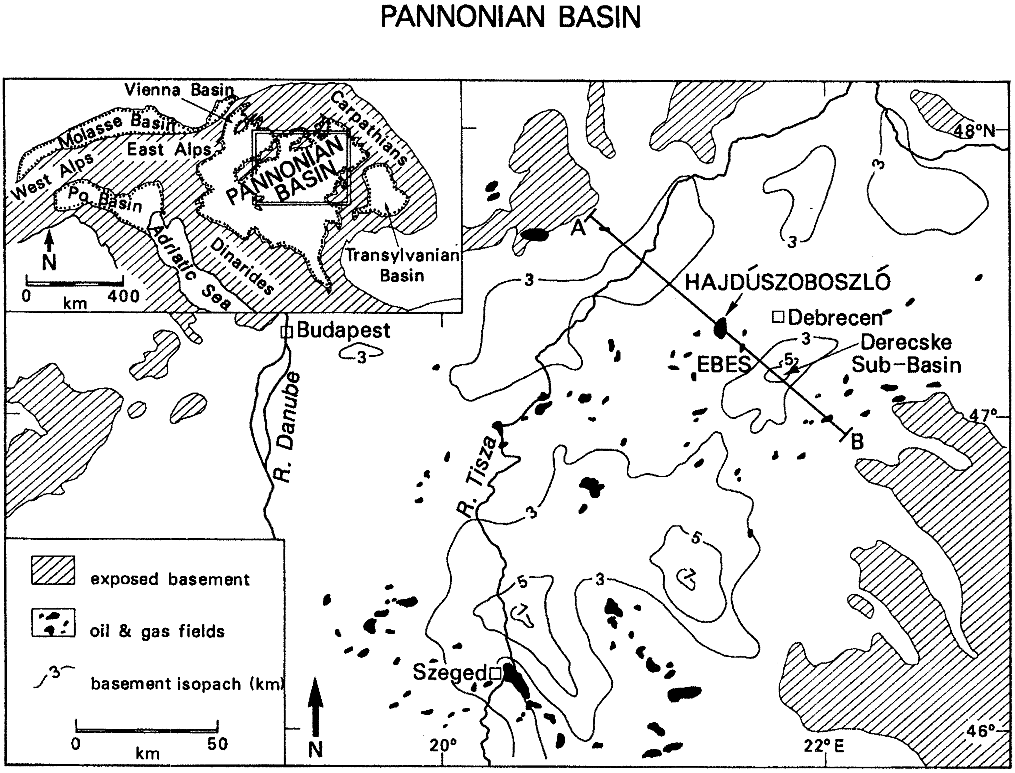

Figure 2. Map showing the distribution of oil and gas fields in the eastern part of the Pannonian Basin, and the location of the Hajduszoboszlo gas field near Debrecen. The section AB across this field is shown in figure 6.

straightforward, and are shown schematically in figure 1. In this diagram distinction is drawn between atmospheric rare gases and their contribution to meteoric and formation waters, radiogenic rare gases produced within the reservoir rocks and elsewhere in the continental crust, and mantle rare gas. These are now considered briefly in turn, but are described in greater detail elsewhere (e.g. Ozima & Podosek 1983).

(*a*) *The atmospheric component*

The atmosphere is well mixed with respect to rare gases, and, with the exception of He, rare gases are retained in the atmosphere by the Earth's gravitational field. The isotopic compositions of atmospheric rare gases are inherited by surface waters upon equilibration with minor, and for the present purposes, insignificant changes in their isotope composition. The ^{40}Ar/^{36}Ar ratio in the atmosphere is lower, and the abundance of ^{36}Ar is higher than in the other parts of the Earth considered here. ^{36}Ar is neither produced radiogenically nor nucleogenically in the Earth (Appendix A) and like ^{3}He is a primordial isotope which has become strongly partitioned into the atmosphere. However, unlike ^{3}He it appears to have been retained quantitatively. An important and diagnostic characteristic of the atmospheric rare gas component carried into the subsurface by groundwaters and connate water is therefore its ^{40}Ar/^{36}Ar ratio.

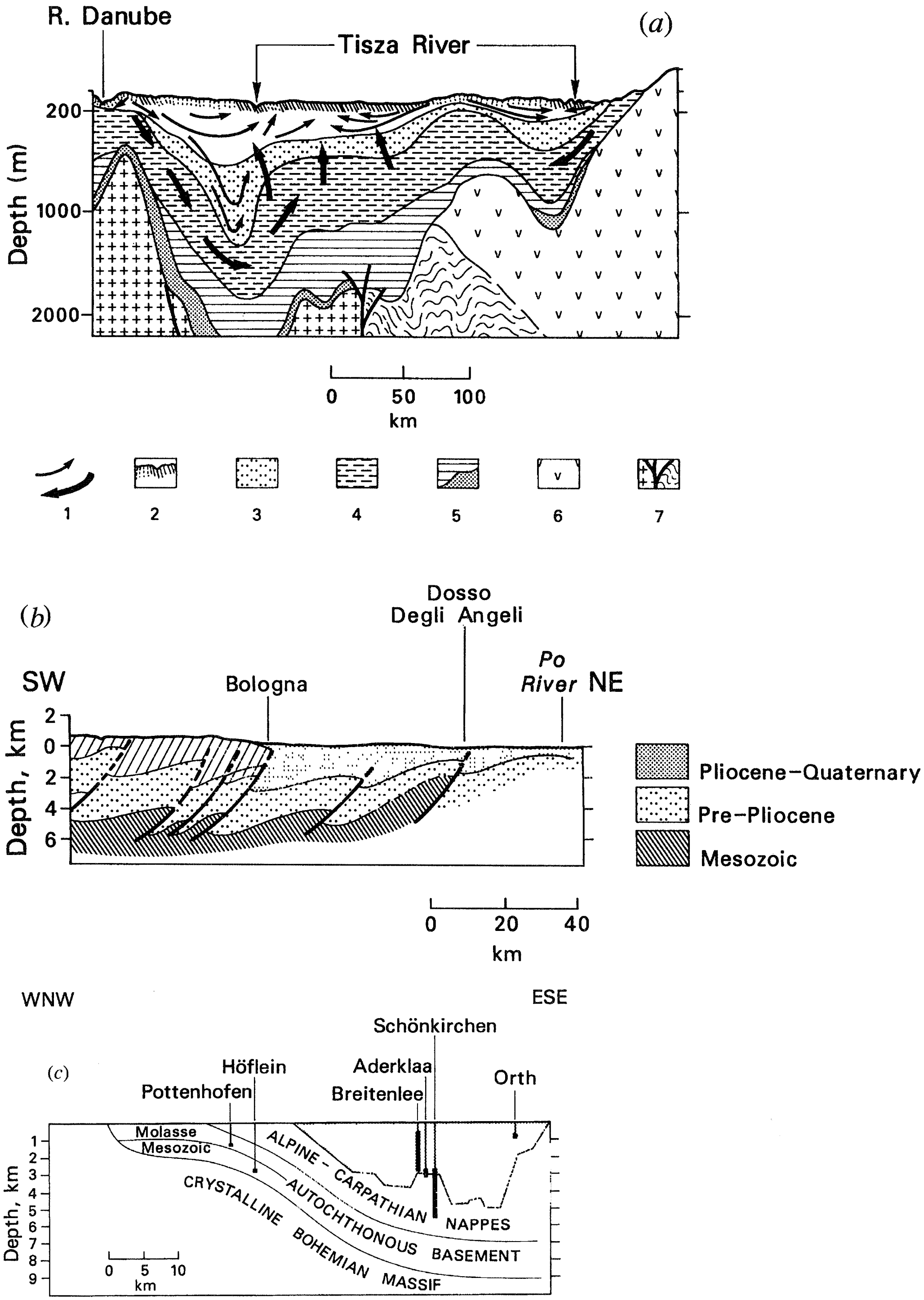

Figure 3. (*a*) Generalized section across the Pannonian Basin from SW to NE showing relationship of post-Miocene Pannonian sediments to Miocene and pre-Miocene basement. The general features of the present-day water flow regimes are indicated. The shallow water flow is topographically driven and supported by aquifer recharges; whereas the deeper régime, which connects locally to

(*b*) *The radiogenic or crustal component*

Rare gases are generated by radioactive decay (radiogenic) and through (α, n) and (n, α) nuclear reactions (nucleogenic) in the Earth in association with the production of heat (Appendix A). However, their rate of production is highest in the continental crust. Because the Th/U and K/U ratios do not vary greatly between the hydrocarbon reservoir rocks and deeper parts of the continental crust the production ratios of ^{4}He/^{40}Ar and ^{4}He/^{21}Ne are easily predicted (Appendix A) and are diagnostic. Rare gases are present in natural gas accumulations with these production ratios only if they were released and transported in this ratio without any relative fractionation.

(*c*) *The mantle component*

Although not considered explicitly here, the mantle rare-gas component is characterized by relatively high ^{3}He/^{4}He and ^{40}Ar/^{36}Ar ratios. These features are deduced from the rare gases present in spreading ridge basalts and are assumed to be applicable to mantle-derived gas present in the continental crust.

(*d*) *Factors affecting inert gas abundances*

There are several processes that may affect the abundances of rare gas components in subsurface fluids. The abundances of rare gases in groundwaters that have equilibrated with the atmosphere are a function of both temperature and salinity. Similarly degassing of a subsurface aqueous fluid through the separation of CH_4 or CO_2, for example, depends not only upon temperature and salinity, but also the mole fraction of gas lost (see Ballentine *et al.* 1991; Ballentine & O'Nions 1993). If one of the phases is oil rather than gas then the behaviour will differ but again in a way that is predictable (Bosch & Mazor 1988). In practice the natural situation is considerably more tractable than might be anticipated from the above considerations because rare-gas components can often be resolved quantitatively from one another (figure 1), and the amounts of each component calculated. The rare-gas abundances for each component may then in turn be compared with those for simple model systems involving one or more fluid phases.

3. Fluids in some neogene basins

To date there have been very few studies of rare-gas isotopes in sedimentary basins which are sufficiently comprehensive to provide information on the scales of fluid movement (Ballentine *et al.* 1991; Ballentine & O'Nions 1992, 1993; Hiyagon & Kennedy 1992; Elliot *et al.* 1993). Ideally the abundances and isotope compositions

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the shallow flow, is saline and possibly connate (modified from Martel *et al.* 1989). 1, principal groundwater flow directions; 2, Quaternary; 3, upper Pliocene; 4, Pliocene with saline pore water; 5, late to middle Miocene; 6, Miocene volcanic; 7, Mesozoic or older.

(*b*) Schematic cross section from SW to NE across the Po Basin from near Bologna to the Po delta (see figure 2 inset). Dosso degli Angeli – the gas field under consideration in the Po Valley lies within the Pliocene–Quaternary sediment section located above the faulted Mesozoic and Miocene basement. The natural gas field at Dosso degli Angeli lies at a depth of 3200 and 3500 m. The thermal gradient in this region is particularly low *ca.* 18 °C km^{-1} (after Elliot *et al.* 1993).

(*c*) Schematic cross section of the Vienna Basin from WNW to ESE showing the location of the natural gas fields referred to in this article (see inset to figure 2). The sedimentary fill to the Vienna Basin is post-Miocene. Sampled natural gas fields are located in both the Pannonian sediments and the Mesozoic basement in the case of the Schönkirchen field (after Ballentine & O'Nions 1992).

of at least two of the rare gases are required in samples from an hydrocarbon reservoir for which the volume is also known. Such data are now available for several situations in the Pannonian, Vienna and Po Basins of Europe, but even here the reservoir properties are not available for the latter two. Gas fields in the Alberta and North Sea Basins have also been investigated (Hiyagon & Kennedy 1992; Ballentine *et al.* 1993, unpublished work) but the present discussion will be restricted to the young Neogene sedimentary basins of Europe.

The locations of the Pannonian, Vienna and Po Basins in relation to the European Alps are shown in the inset of figure 2. The Po Basin, like the Molasse Basin on the north side of the Alps, is a classic loading basin, whereas the Pannonian and Vienna Basins have formed at least in part by extension. All are characterized by a sedimentary fill that is post-Miocene in age, but differ in the presence of mantle-derived He in the extensional basins and its absence in the loading basins (Oxburgh *et al.* 1986; Marty *et al.* 1992).

(*a*) *The pannonian basin*

The Pannonian Basin (figure 2) which occupies the area of the Great Hungarian Plain, consists principally of Pliocene to Quaternary (Pannonian) sediments which have been deposited upon a pre-Miocene basement. Oil and gas fields are distributed widely within the Basin, and the natural gases range in composition from near pure CH_4 to near pure CO_2 with variable amounts of N_2. The present hydrogeological régime in the Pannonian Basin is shown schematically in figure 3*a*, and has been defined through the large number of borehole observations available (Toth 1980). The flow is topographically driven with an upper flow régime consisting of low salinity water which is connected locally to a lower aquifer system containing saline, possibly connate water. The system discharges into the Tisza River at a rate which has been estimated at *ca.* 35 $m^3\ s^{-1}$ (see table 4 and figure 3*a*).

Of particular interest here is the Hajduszoboszlo field in eastern Hungary (figure 2), which has been studied in detail by Ballentine *et al.* (1991). The reservoir is stacked above a basement high adjacent to the Derescke sub-basin (figure 6) over a depth interval between 700 and 1300 m. The reservoir rock volume is 1.5 km^3 and it contains 0.37 km^3 of natural gas at reservoir pressure. In this case sufficient information is available on rare gas concentrations in the field to permit a mass balance to be made. Some of the He, Ne and Ar rare gas isotope data for the Hajduszoboszlo field are shown in figure 4*a*. The most significant feature of these data as far as the present discussion is concerned, is the marked decrease of the atmosphere-derived rare-gas component with depth in the field, as revealed by changes in $^{40}Ar/^{36}Ar$ ratio. The ratio varies from the atmospheric value at the shallowest levels in the field to progressively higher $^{40}Ar/^{36}Ar$ ratios with depth. This pattern is mirrored by the Ne isotope ratios (figure 4*a*). The combined He, Ne and Ar isotope data-set available for this field allows a ready distinction to be made between the atmosphere, radiogenic (= crustal) and mantle components which when combined with concentration data make a mass balance of these rare gas components straightforward.

(*b*) *The Vienna Basin*

The Vienna Basin, like the Pannonian Basin, consists of post-Miocene sediments which in this case lie above a basement of Carpathian nappes (figure 3*b*). Natural gas fields in the Vienna Basin have been sampled over a greater range of depths than in the Pannonian Basin and include gas reservoirs located within both the basement

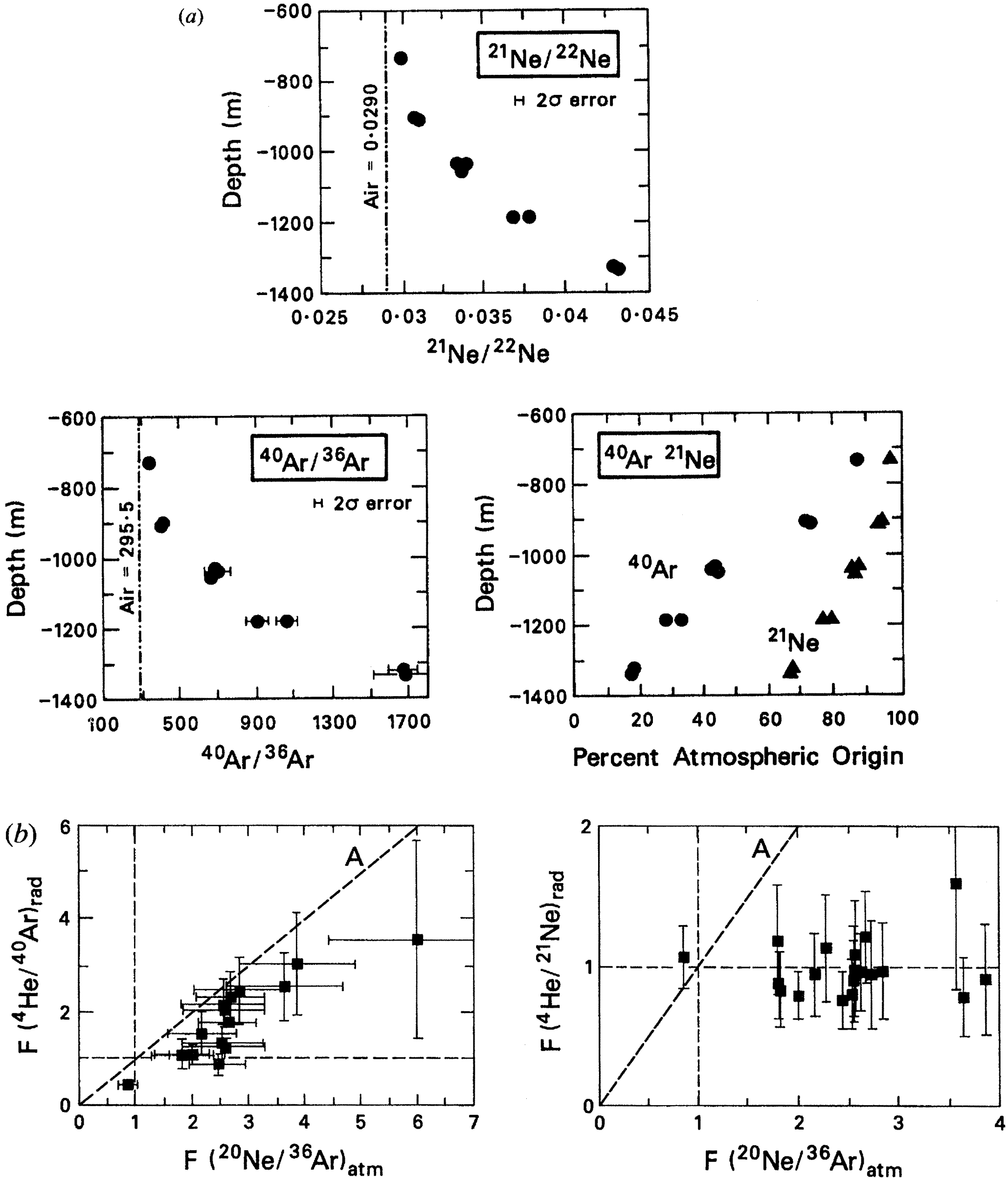

Figure 4. (*a*) Variation of ^{21}Ne/^{22}Ne, ^{40}Ar/^{36}Ar ratios and the corresponding proportions of atmosphere-derived ^{40}Ar and ^{21}Ne in gas samples taken from various depths in the Hajduszoboszlo gas field, Hungary (figure 2). Modified after Ballentine *et al.* (1991). (*b*) Comparison of ^{4}He/^{40}Ar, ^{20}Ne/^{26}Ar and ^{4}He/^{21}Ne ratios in Vienna Basin gases (after Ballentine & O'Nions 1993). The F-values are the measured ratios for a particular rare gas component divided by the same ratio produced through radiogenic production (rad) or introduced by equilibration of groundwater with the atmosphere (atm). The essential feature of these data is the co-variation between He/Ar and Ne/Ar ratio and the constancy of the He/Ne ratio. This is interpreted to be the result of solubility effects arising from the observation that Henry's coefficients of He and Ne are very similar and both greater than that for Ar.

Table 1. *Helium generation in Pannonian and Po gas reservoir rocks*

	res. age[a], T/Ma	$[\mathrm{CH_4}]$ / cc STP $\mathrm{g^{-1}}$	$[^4\mathrm{He}]^{\mathrm{b}}_{\mathrm{obs}}$ / cc STP $\mathrm{g^{-1}}$	$[\mathrm{He}]_{\mathrm{obs}}/[\mathrm{He}]_{\mathrm{T}}{}^{\mathrm{c}}$
Pannonian Basin (Hajduszoboszlo)	5	7.97	7.17×10^{-3}	2.2×10^{3}
Po Basin (Dosso degli Angeli)	3	12.4	1.12×10^{-4}	57

[a] Estimated time of deposition of reservoir rocks (assumed to be free of ^{4}He at time of deposition).

[b] $[^4\mathrm{He}]_{\mathrm{obs}}$ corresponds to 900 p.p.m. He in Hajduszoboszlo field, and 9 p.p.m. in Dosso degli Angeli (Ballentine *et al.* 1991; Elliot *et al.* 1993).

[c] $[\mathrm{He}]_{\mathrm{T}}$ is the He generated over age of reservoir (T), assuming average crust U and Th (U = 2.8 p.p.m.; Th = 10.7 p.p.m.). Generation rate is 6.38×10^{-13} cc ^{4}He (STP) $\mathrm{g^{-1}\ a^{-1}}$.

itself as well as in the sedimentary fill. At shallow levels the natural gases, like those of the Pannonian, have δ^{13}C values indicating a bacteriogenic origin. With increasing depth, however, thermogenic CH_4 becomes more abundant. Although not dealt with in detail here the mantle rare gas component in the Vienna basin is particularly well characterized (Ballentine & O'Nions 1992).

(*c*) *The Po Basin*

The Po Basin is a classic loading basin, and differs from the other two basins in its rare-gas signature. There is an absence of a resolvable mantle-derived rare gas component as has been found to be the case with other loading basins (Elliot *et al.* 1993; Marty *et al.* 1992). The sedimentary sequence is again mainly Pliocene to Quaternary deposited on a complex Mesozoic basement which includes thrusted nappe structures (figure 3*b*). Natural gas fields occur throughout the Po Basin (Matavelli *et al.* 1983), but so far only the small field at Dosso degli Angeli (figure 3*b*) has been investigated in detail for rare gases (Elliot *et al.* 1993). The rare gas results from Dosso degli Angeli, from samples over a depth interval from 3200 to 3500 m are quite straightforward; the ^{3}He/^{4}He ratios are those expected for radiogenic production (table 1) and the ^{40}Ar/^{36}Ar ratios are atmospheric.

4. Groundwater flow and fluid focusing

Each of the gas fields in the Pannonian, Vienna and Po Basins referred to above has a component of atmospheric rare gas. This is easily identified from the presence of ^{36}Ar, which is a primordial isotope not produced by reactions within the Earth. The ^{36}Ar has been introduced into each of these reservoirs by degassing of a groundwater which has previously equilibrated with the atmosphere – the principal repository of primordial ^{36}Ar (figure 1). These groundwaters could variously be connate waters or the products of aquifer recharge. The current association of atmosphere-derived ^{36}Ar with CH_4 in the reservoirs suggests the possibility that the CH_4 itself also may have been transported by groundwaters.

This possibility is examined in figure 5 where the observed $CH_4/^{36}Ar$ ratios for gases from these three sedimentary basins are compared with the $CH_4/^{36}Ar$ ratios predicted for groundwaters which have first equilibrated with atmosphere and then become CH_4-saturated at reservoir conditions. As can be seen in figure 5 there is little difference between the ratios for brine and pure water. Because the Henry's

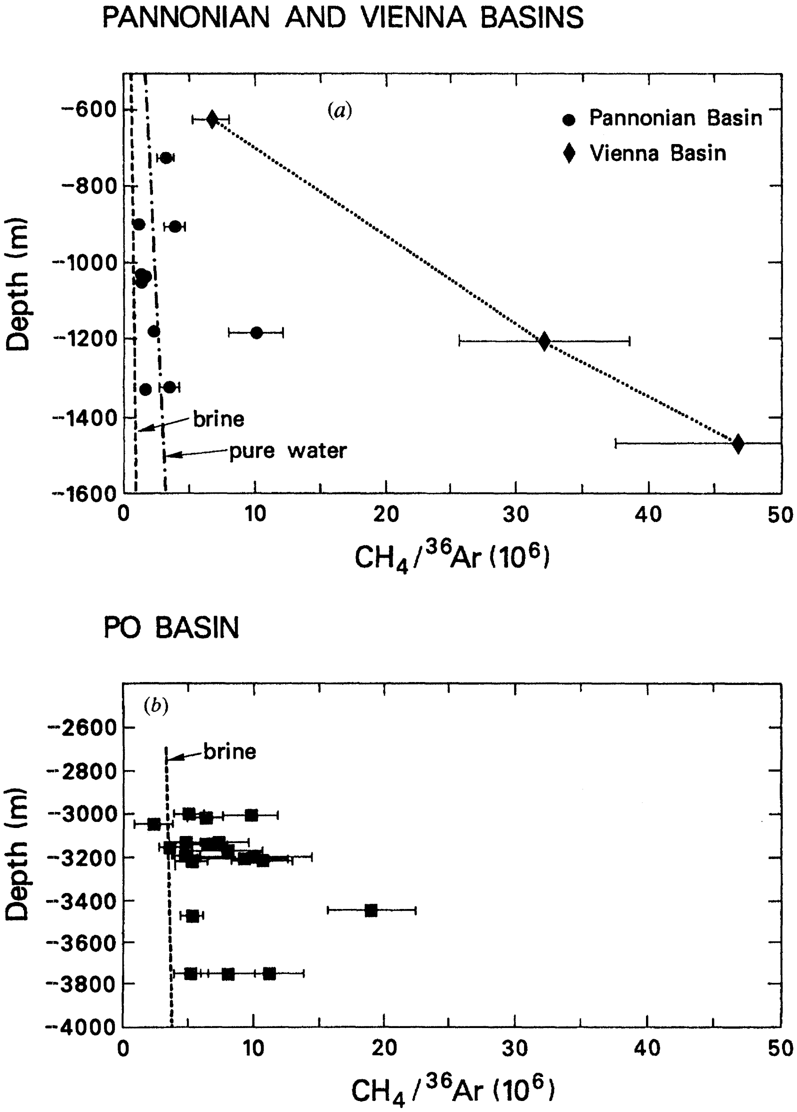

Figure 5. Comparison of $CH_4/^{36}Ar$ ratios in natural gases sampled from various depths in the Pannonian, Vienna and Po Basin gas fields. The measured values are compared with the calculated ratio for a gas exsolved from an atmosphere-equilibrated groundwater which has also become saturated with CH_4 at reservoir conditions. Values are shown for both brine and pure water. Because the Henry's coefficients for CH_4 and Ar are very similar the $CH_4/^{36}Ar$ ratio in the exsolved gas is the same as the dissolved ratio in a closed system. Note that many of the Pannonian and Po gas samples have $CH_4/^{36}Ar$ within a factor of two of those expected for gas transport in a CH_4 saturated groundwater (after Ballentine *et al.* (1991) and Elliot *et al.* (1993)).

coefficients for CH_4 and Ar between gas and water are very similar, the $CH_4/^{36}Ar$ ratio of the evolved gas from a CH_4-saturated groundwater will be the same as the dissolved ratio (Ballentine *et al.* 1991). In the Pannonian and Po Basin gas fields the $CH_4/^{36}Ar$ ratios are mostly within a factor of two of the predicted ratios, indicating that a large part of the accumulated CH_4 could have been transported in groundwater. This simple explanation does not extend to the Vienna Basin data

Table 2. *Radiogenic components of rare gases*

	$({}^{4}\mathrm{He}/{}^{40}\mathrm{Ar})^{a}$	$({}^{4}\mathrm{He}/{}^{21}\mathrm{Ne})^{a}$ $\times 10^{6}$	$R_{\mathrm{He/Ar}}{}^{b}$	$R_{\mathrm{He/Ar}}{}^{b}$
Pannonian (Hajduszoboszlo)	7.7 ± 7.0	10.13 ± 4.2	1.6 ± 1.4	1.02 ± 0.41
Vienna Basin	12.5 ± 11.3	13.3 ± 3.65	2.5 ± 2.3	1.33 ± 0.4
Po Basin[c]	> 33.0	—	$\geqslant 6.7$	—
radiogenic production (ave. crust)[d]	4.9	9.9	1.0	1.0

[a] Data from Ballentine *et al.* (1991) and Elliot *et al.* (1993).

[b] $R_{\mathrm{He/Ar}}$ and $R_{\mathrm{He/Ne}}$ are the $^{4}\mathrm{He}/^{40}\mathrm{Ar}$ and $^{4}\mathrm{He}/^{21}\mathrm{Ne}$ observed ratios divided by the production ratio in average crust.

[c] Minimum value, maximum is infinity.

[d] Average Crust is taken to have $\mathrm{K/U} = 1.2 \times 10^{4}$ and $\mathrm{Th/U} = 3.8$. The production ratios of $^{4}\mathrm{He}/^{40}\mathrm{Ar}$ and $^{4}\mathrm{He}/^{21}\mathrm{Ne}$ depend only on these ratios (Appendix A).

(figure 5), where the gases at *ca.* 1500 m have $\mathrm{CH_4}/^{36}\mathrm{Ar}$ ratios that are a factor of 10 higher than the predicted ratios for brine or pure water. In this case $\mathrm{CH_4}$ is much in excess of that which a $\mathrm{CH_4}$-saturated and air-equilibrated groundwater could have supplied.

The association of atmosphere-derived $^{36}\mathrm{Ar}$ with $\mathrm{CH_4}$ in these natural gas reservoirs and the details of the $\mathrm{CH_4}/^{36}\mathrm{Ar}$ ratio relationships suggests that a close connection exists between groundwater flow and natural gas migration, in which case groundwater flow has certainly been responsible for focusing $^{36}\mathrm{Ar}$ into the reservoirs and possibly $\mathrm{CH_4}$ also. A more quantitative statement about these focusing effects is possible for the Hajduszoboszlo data because in this case information on the reservoir volume and porosity are available. The total amount of $\mathrm{CH_4}$, $^{20}\mathrm{Ne}$ and $^{36}\mathrm{Ar}$ in the Hajduszoboszlo field have been estimated (table 2) by Ballentine *et al.* (1991), from which the minimum volumes of groundwater required to provide the $^{20}\mathrm{Ne}$ and $^{36}\mathrm{Ar}$ in the reservoir are calculated, making the simplifying assumption that the groundwaters degassed completely. The estimated water volume of 50 km^3 is a minimum and some 150 times greater than the reservoir volume itself. It would occupy more than 500 km^3 of rock with a typical porosity of 10%. Comparison of this volume of rock with the 3000 km^3 present volume of sedimentary fill in the adjacent Derescke sub-basin (figure 6) emphasizes the scales involved and the efficiency of groundwater focusing. Evidently the amount of $^{36}\mathrm{Ar}$ in the Hajduszoboszlo reservoir is vastly greater than that which could have been derived from its own pore volume if it were initially water-saturated.

5. Scales and mechanisms of crustal degassing

The question of the scales over which the products of crustal degassing are transported is essentially one of the mass balance of the radiogenic (or crustal) component of the rare gases in a particular reservoir (Appendix A).

In those situations where the reservoir porosity is known it is straightforward to examine the radiogenic rare-gas balance. This is shown for Hajduszoboszlo and Dosso degli Angeli in table 1. The observed amount of radiogenic $^{4}\mathrm{He}$ per gram of reservoir rock is compared to the amount that the same rock is likely to have generated from the time of its deposition to the present day. The calculation assumes

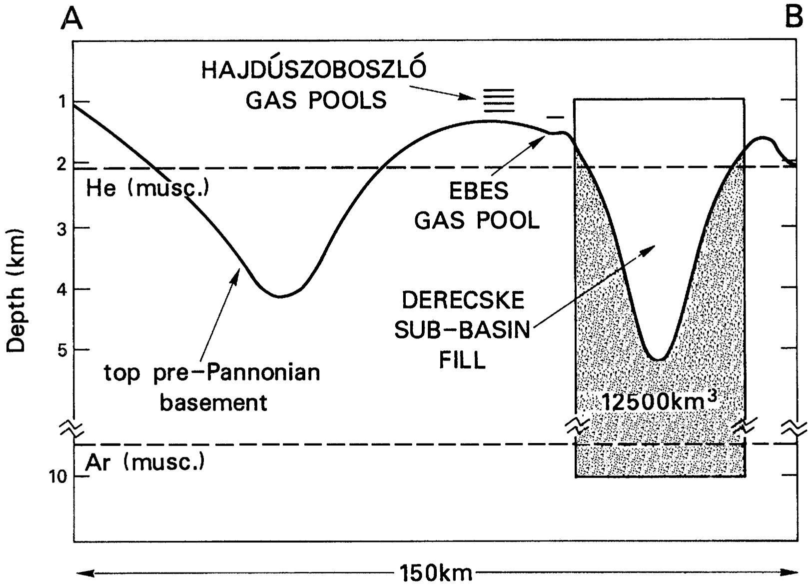

Figure 6. Schematic section across the Hajduszoboszlo gas field along the section line A to B shown in figure 2. The location of the stacked reservoir is shown positioned above a basement high adjacent to the Derecske sub-basin. The total reservoir occupies a rock volume of approximately 1.5 km^3, and the gas volume at reservoir pressure is 0.37 km^3. The mass balance of ^{36}Ar and ^{20}Ne (table 3) corresponds to complete degassing of 50 km^3 of air-equilibrated groundwater into the reservoir. This water would occur in a rock volume of 500 km^3 with a porosity of 10%, a significant portion of the 3000 km^3 fill to the Derecske Basin. Similarly the radiogenic ^{4}He in the reservoir (table 3) if generated over a 5 Ma interval would be the total production in some 2×10^4 km^3 of Pannonian sediment (table 3). This exceeds the volume of crust which extends from the reservoir down to 10 km as shown. This diagram is intended to emphasise the efficiency of fluid focusing and the relative scales of transport that must have operated rather than identify the particular sources of radiogenic ^{4}He (after Ballentine *et al.* 1991). The depths corresponding to the closure temperatures for Ar and He diffusion in muscovite are shown (see figure 7).

Table 3. *Rare gas mass balance in Hajduszoboszlo Field*

reservoir gas km^3	rare gas m^3 STP	source[a]
$CH_4 = 0.367$	1. Atmosphere derived	
	$^{20}Ne = 7.3 \times 10^3$	50 km^3 ASW[b]
$CH_4(STP) = 33.0$	$^{36}Ar = 1.3 \times 10^4$	17 km^3 ASW[b]
	2. Radiogenic	
	$^4He = 23 \times 10^6$	2×10^4 km^3 crust in 5 Ma

[a] Volume of air saturated seawater that must degas completely to provide ^{36}Ar and ^{20}Ne in reservoir. The volume of crust required to generate ^{4}He in reservoir is calculated for 5 Ma, the age of the sediments, and assumes that they were initially ^{4}He-free.

[b] ASW, air-saturated seawater.

that the sediments contained no ^{4}He at the time of their deposition. The ratio of observed to generated ^{4}He in Hajduszoboszlo is 2.2×10^3, and 57 for Dosso degli Angeli. In both cases the ^{4}He present is in excess of that which could have been generated in the reservoir itself and in the case of the Pannonian samples vastly so. These differences may well reflect either differences in the volumes of crust that

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Table 4. *Helium discharge from Pannonian Basin*

aquifer discharge (5×10^4 km^2)		flux (^{4}He) mol km^{-2} s^{-1}
(*a*) Hydraulic[a]	35 m s^{-1}	1.8×10^{-7}
(*b*) Tisza River Tritium[b]	17 ± 11 m^3 s^{-1}	$8.7 \pm 5.7 \times 10^{-8}$
heat–helium production ratio[c]		6×10^{-8}

[a] Values for hydraulic discharge from Martel *et al.* (1989).

[b] Calculated for dilution of tritium budget in Tisza River by aquifer discharge by Deák (1974).

[c] Assumes heat production equivalent to average crust and heat–helium relationship given in Appendix A.

degassed ^{4}He, the efficiency of the scavenging mechanism, or both. The question may be pursued further at Hajduszoboszlo again because both the reservoir volume and the porosity are known. The mass balance of radiogenic ^{4}He is examined in table 4 in a manner similar to that undertaken for ^{36}Ar except that the generation rate of radiogenic ^{4}He enters in. For 5 Ma of ^{4}He generation some 2×10^4 km^3 of crust must degas to supply the ^{4}He in the reservoir (table 3). This volume is compared with the volume of the Derescke sub-basin in figure 6 without any intended implication as to the actual source of radiogenic ^{4}He supply. In table 4, estimates are given for the total ^{4}He discharge from the Pannonian Basin aquifer system into the Tisza River. These agree surprisingly well with the expected ^{4}He production rate in the crust and suggests that ^{4}He is very efficiently scavenged and transported from the Basin by the aquifer system.

Some further and interesting insights into the scales of crustal degassing are obtained when radiogenic ^{40}Ar is considered along with ^{4}He. The observed ratios of radiogenic ^{4}He/^{21}Ne and ^{4}He/^{40}Ar in the Pannonian and Po Basin gas reservoirs are summarized in table 2. These are compared to the predicted production ratios for average continental crust (table 2, Appendix A). Within error, the observed ratios for the Pannonian gases agree with the predicted production ratios. In the Po Basin in contrast essentially all the He present is radiogenic and all the Ar is atmospheric. Therefore it is only possible to set a lower limit on the ^{4}He/^{40}Ar ratio at *ca.* 30, but this may in fact be infinity (table 2). It would seem that this difference is related to the very different thermal structures of these two basins. The Pannonian Basin has a relatively high thermal gradient of *ca.* 35 °C km^{-1}, a factor of two higher than the Po Valley in the vicinity of Dosso degli Angeli which is *ca.* 18 °C km^{-1}. These differences will influence the diffusion rates of He, Ar and other rare gases as a function of depth in these sedimentary basins (figure 7). This question may only be viewed from a qualitative or semi-quantitative view at present because of the paucity of appropriate diffusion data for He and Ar. If it is assumed to a first approximation that ^{40}K and therefore radiogenic Ar generation will be concentrated in common K-bearing minerals such as muscovite (illite), feldspar, and hornblende, then at temperatures lower than their ^{40}Ar closure temperatures the ^{4}He/^{40}Ar ratio available in the pore volume is unlikely to be the same as the production ratio. At temperatures above the relevant ^{40}Ar closure temperatures He and Ar should be available at their production ratio. Although few diffusion data for He are available for any minerals, and particularly for minerals in sediments at low temperatures, it is reasonable to assume that the effective closure temperatures will be lower than those for Ar (Lippolt & Weigel 1988). The presence of radiogenic ^{4}He/^{40}Ar ratios in

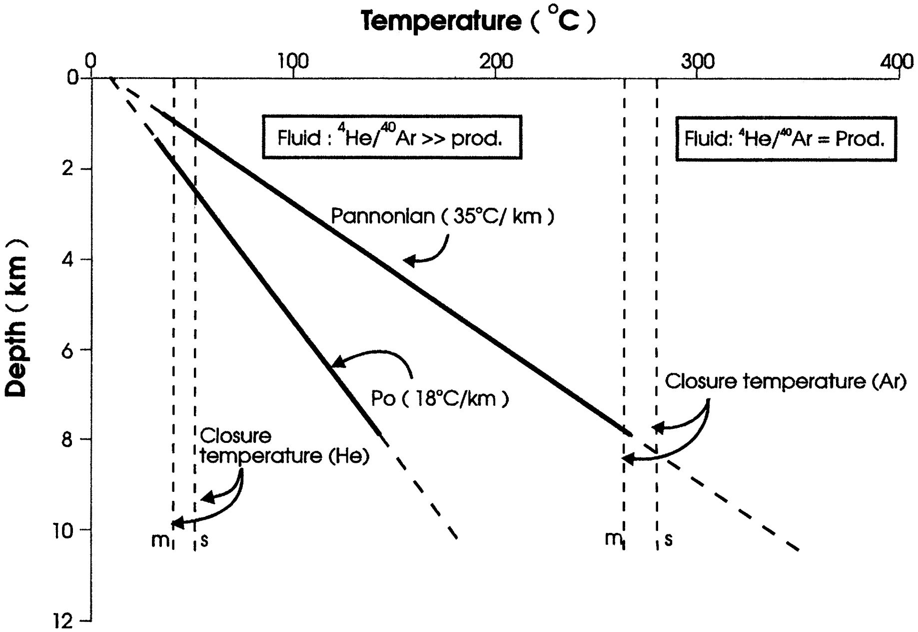

Figure 7. Comparison of thermal gradients in the Pannonian Basin and the Po Basin in the vicinity of Dosso degli Angeli. These are compared with the theoretical closure temperatures (Lippolt & Weigel 1988) for He and Ar in 500 μm grains of muscovite (m) and sanidine (s). At present there are very few diffusion data for He and Ar in the mineral phases of interest. Data for muscovite and sanidine are used to illustrate the *expected* relative behaviour of He and Ar in sedimentary basins rather than to propose a rigorous solution to the observation. At temperatures of 250–300 °C radiogenic ^{4}He and ^{40}Ar should be available in the pore volume at their production ratio of *ca.* 4.9 (Appendix A)). At lower temperatures of 100 °C or less ^{40}Ar should be strongly retained by mica (or illite) and feldspars and the ^{4}He/^{40}Ar available for fluid transport should be greater than production. The differences in ^{4}He/^{40}Ar ratios in the Po and Pannonian samples (table 2) are likely to reflect the control exerted by diffusion release from minerals.

the Pannonian Basin gas field at their production rates reflects the transport of He and Ar from regions of the crust where neither the non Ar are significantly retained by minerals and this may only occur where temperatures exceed *ca.* 250 °C. In the Po Basin on the other hand rare gases have not been transported in quantity from the even greater depths where those temperatures are attained. These contrasting effects are expected to arise from differing thermal structures in the Pannonian and Po Basins are illustrated in figure 7.

6. Mechanisms of transport

The clear association of atmosphere-derived rare gases with methane in natural gas accumulations points immediately to the importance of groundwater advection in the transport of the rare gases and probably methane also. Because in each of the three cases discussed above some products of groundwater degassing are present in the reservoir, then some influences of solubility effects on rare-gas abundances are to be anticipated. In effect this means that the differences in Henry's coefficients between the rare gases should be evident particularly in those situations where the gas/liquid ratio approaches zero. At this limit fractionation of rare gases between gas and liquid will be in the ratio of the Henry's coefficients. The Henry's coefficients for

He and Ne are very similar and as a consequence fractionation of He/Ne ratios should always be less than the He/Ar or Ne/Ar ratios where solubility effects dominate (Ballentine *et al.* 1991; Ballentine & O'Nions 1993). A good illustration of this behaviour is shown by rare gases in the Vienna Basin fields (figure 4*b*). Here solubility effects appear to control the abundance of both the atmospheric and radiogenic rare gas components (Ballentine & O'Nions 1993).

It is interesting that these predicted effects of solubility control often extend to the radiogenic and even mantle rare gases (Ballentine *et al.* 1991; Ballentine & O'Nions 1992, 1933). These observations point to the involvement of groundwaters at some stage in the transport of all the rare gas components. These simple observations also suggest that the relative abundances of these rare gases have not been modified greatly by diffusion which is expected to result in mass-dependent fractionation patterns rather than the relationships seen in figure 4*b*.

Lastly it is emphasized that the rare gases may provide useful information on scales of transport in sedimentary basins but do not provide directly information on the rates. The question arises as to whether the rates of groundwater movement are adequate to focus gases from such large volumes into gas fields such as Hajduszoboszlo on reasonable timescales. Consider the present day rate of groundwater discharge of *ca.* 35 $m^3\ s^{-1}$ from the Pannonian Basin into the Tisza river (table 4). The Hajduszoboszlo gas field requires a minimum of 50 km^3 of water to degas its Ar and Ne quantitatively into the reservoir. This corresponds to only 46 years of the total groundwater outflow. It would appear that at present-day rates of groundwater flow, all the rare gas and methane required for 1000 fields the size of Hajduszoboszlo could be supplied in *ca.* 50000 years, if the groundwaters were CH_4-saturated and then degassed totally. If the degassing is incomplete as seems most likely then the time would be proportionately greater.

7. Conclusions

Rare gases have been studied in natural gas fields and sedimentary basins for many years. The classic studies of Zartman *et al.* (1961) recognized a number of the important principles that have been mentioned here. It has been only recently, however, that rare gases have been used in a more systematic way to address questions relating to basin scale fluid movement. As conservative tracers with well-characterized isotopic composition for the various atmospheric crustal and mantle components involved, the results obtained are unambiguous and the mass balance calculations straightforward. Some of these early results in this subject summarized above are perhaps surprising in terms of the scales and transport distances that must be involved in actively spreading basins.

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Appendix A. Radiogenic and nucleogenic rare gases

Helium

$$^{238}\mathrm{U} \rightarrow 8\ ^{4}\mathrm{He} + {}^{206}\mathrm{Pb}, \quad ^{235}\mathrm{U} \rightarrow 7\ ^{4}\mathrm{He} + {}^{207}\mathrm{Pb}, \quad ^{232}\mathrm{Th} \rightarrow 6\ ^{4}\mathrm{He} + {}^{208}\mathrm{Pb}.$$

The radiogenic production rate is

$$^{4}\mathrm{He} = 1.207 \times 10^{-13}[\mathrm{U}] + 2.867 \times 10^{-14}[\mathrm{Th}]\ \mathrm{cm^3\ STP\ g^{-1}\ a^{-1}}.$$

Argon

$$^{40}K \rightarrow {}^{40}Ar + {}^{40}Ca.$$

The production rate is

$$^{4}Ar = 3.885 \times 10^{-18}[K] \text{ cm}^3 \text{ STP g}^{-1} \text{ a}^{-1}.$$

Helium/Argon

The production ratio is

$$^{4}He/^{40}Ar = [3.11 + 0.738(Th/U)] \times (U/K) \times 10^4.$$

Neon

$$^{18}O(\alpha, n)^{21}Ne \text{ and } ^{24}Mg\ (n,\ \alpha)^{21}Ne.$$

The production rate is

$$^{21}Ne = 8.006 \times 10^{-21}[U] + 3.96 \times 10^{-21}[Th] \text{ cm}^3 \text{ STP g}^{-1} \text{ a}^{-1}.$$

Helium/neon

The production ratio of $^{4}He/^{21}Ne$ is

$$^{4}He/^{21}Ne = [1.207 + 0.2867(Th/U)] \times 10^8/[8.006 \times 3.86(Th/U)].$$

Average continental crust ratios

$$K/U = 1.2 \times 10^4; \quad Th/U = 3.8;$$

$$[U] = 2.8 \text{ p.p.m.}; \quad [Th] = 10.7 \text{ p.p.m.};$$

$$^{4}He/^{40}Ar = 4.9; \quad ^{4}He/^{21}Ne = 9.96 \times 10^{-6}; \quad ^{21}Ne/^{40}Ar = 4.94 \times 10^{-7}.$$

Heat–helium relationship

10^{12} atoms ^{4}He/joule for K/U and Th/U given for average crust (above) (O'Nions & Oxburgh 1993).

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Discussion

G. TURNER. Please note, my *F*-values (elemental ratio relative to ^{36}Ar) were normalized to air but Professor O'Nions' were normalized to water. What happens to ^{40}Ar coming from below the Pannonian Basin; does it move sideways?

R. K. O'NIONS. Perhaps a little: the fluid circulation probably does not extend deep enough or far enough.

A. HALLIDAY. There is apparent agreement for He and Ar, but U and K are in different minerals.

R. K. O'NIONS. We only have He data for sanidine and muscovite. I agree that U and K are in different minerals. At shallow levels we need to know exactly what happens to, for example, U in illite. We need to know more about gas release behaviour in rocks.

D. P. MCKENZIE. What about mechanisms of gas release: how does it happen?

R. K. O'NIONS. The determined degree of radiogenic/atmospheric rare gases requires a low volume ratio of CH_4:H_2O (approximately 0.001 for degassing). Therefore the water volume must be very large, which is unlikely. In the Hungarian gasfields, methane-saturated water does exist.

M. L. COLEMAN. Knowing things like ages and permeabilities, has Professor O'Nions done any calculations to determine the flow rates needed to move that volume of gas into one place?

R. K. O'NIONS. 35 $m^3 s^{-1}$ is the present total water discharge in the Pannonian Basin. A maximum of a few Ma would be needed.

M. L. COLEMAN. But that implies a totally efficient process.