PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A
MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

Tracing Fluid Sources and Interactions [and Discussion]

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Tracing fluid sources and interactions

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Methods of evaluating possible sources and interactions of ancient and modern fluids are being significantly improved by the development of new isotopic and geochemical microprobe techniques. Applications of O, C, and S isotopes are benefiting from the development of laser ablation methods capable of 0.1 permil precision on submilligram samples and ion microprobe methods capable of permil precision on nanogram regions of rock sections. The noble gases are proving themselves useful conservative tracers of fluid processes. The ubiquitous presence of air saturated water patterns testifies to the dominance of water originating at the Earth's surface, while the presence of radiogenic isotopes and ^{3}He quantify interactions with crust and mantle respectively. The use of resonance ionisation has increased sensitivity for Xe and Kr analyses to the single atom level. Examples of fluid régimes currently under study are described.

1. Introduction

Diagenetic processes frequently lead to the production of mineral species which are either fine grained or isotopically and chemically heterogenous. The isotopic information they carry concerning the diagenetic fluids and fluid processes involved in their formation are consequently difficult to obtain and to decipher. Diagenetic minerals may also trap formation fluids in fluid inclusions, but here also the amounts of fluid trapped are small and present an analytical challenge to the isotope geochemist. This paper describes some new technical developments applicable to a wide range of geological problems, including the study of diagenesis. The selection of topics is not comprehensive but is biassed by the current activities of the Isotope Geochemistry Group in the University of Manchester.

2. Oxygen isotopes in quartz cements

Authigenic quartz cements are volumetrically the most important porosity-occluding mineral in sandstones worldwide, but despite this common observation, there is much uncertainty surrounding the source of the silica, transport mechanisms and the causes of quartz precipitation. A combination of fluid inclusion thermometry with δ^{18}O measurement can be used to identify the isotopic composition and possible sources of the fluid and, if made with high spatial resolution, an indication of whether the pore fluid evolution was continuous or episodic.

Several micro-analytical techniques have been developed for the study of stable isotopes. Release of carbon dioxide by laser ablation is now widely used for the determination of O and C isotope abundances in carbonates. Analyses with sub-permil precision can be made on 10–100 μg of carbonate with a spatial resolution of the order of 100–200 μm (Smalley *et al.* 1989). δ^{18}O determinations can now be made

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Figure 1

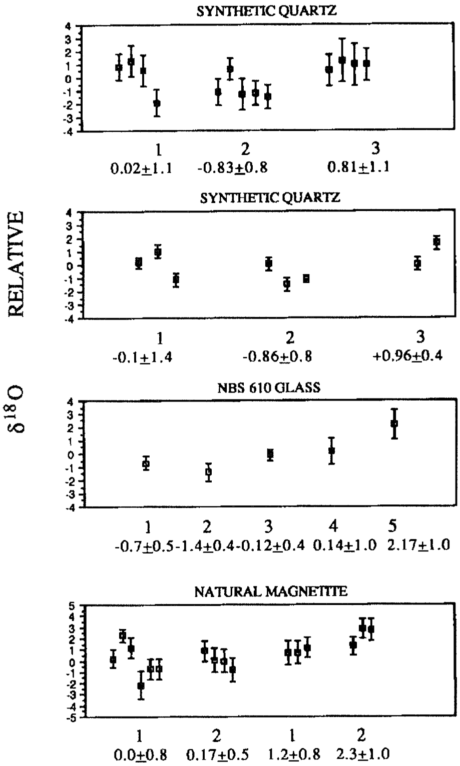

Figure 2

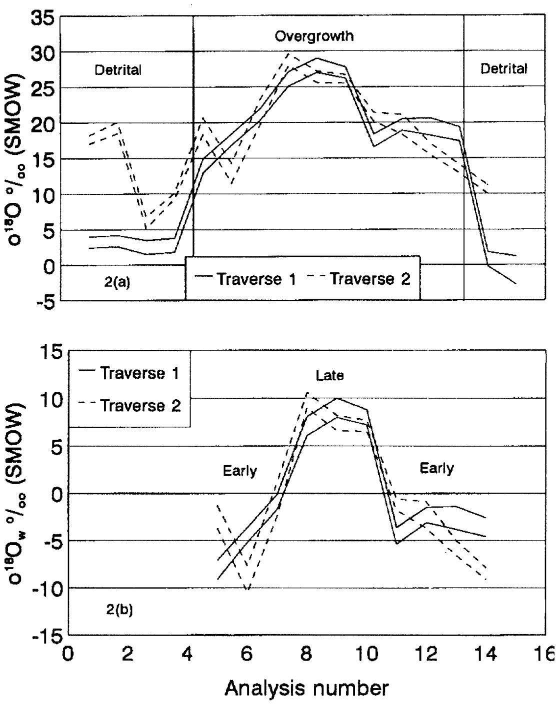

Figure 1. Oxygen isotope analyses on the Isolab 54 Ion Microprobe, showing repeat measurements on single spots and on spots separated typically by a few hundred micrometres.

Figure 2. (*a*) Oxygen isotopic composition measured in two different traverses across a 1 mm wide quartz cement overgrowth between detrital quartz grains. (*b*) Calculated oxygen isotopic composition of water in equilibrium with the quartz overgrowth in (*a*). The fractionation between quartz and water is assumed to be that which corresponds to the measured homogenization temperatures of fluid inclusions in the quartz.

on similar amounts of silicate by combining laser ablation with fluorination techniques (Sharp 1990). When carried out *in situ* the short lived high temperature gradients associated with this procedure lead to large and unsystematic levels of fractionation which restrict precision to the permil level.

Ion microprobes have better spatial resolution and require much smaller amounts of sample but until recently have lacked the necessary precision when applied to insulators such as quartz. Using a VG Isolab 54 ion microprobe with multicollection, we have succeeded in making reproducible $\delta^{18}O$ measurements with a spot size of 20 μm and a precision of 1‰ in synthetic quartz, NBS 610 glass, and magnetite. The measurements illustrated in figure 1 indicate the reproducibility of repeat measurements on a given spot and between different locations of the same specimen separated by intervals of approximately 0.2 mm. We subsequently used the ion probe to measure $\delta^{18}O$ profiles across well characterized quartz overgrowths from North Sea sandstone, in which the pore space is almost totally occluded by authigenic quartz and chalcedony. The sample is taken from close to a major fault, thought to be responsible for the large flow of fluid needed to account for the amount of silica deposited. Across the 1 mm wide overgrowth, $\delta^{18}O$ values increase from +19‰ at the boundaries with detrital grains to +26‰ in quartz crystals near the centre of the pore, with error bars typically 1‰ (figure 2*a*). Corresponding fluid inclusion homogenization temperatures from edge to core increase from 90 °C to 115 °C. Based on the dependence of the quartz–water fractionation on temperature (Clayton *et al.* 1972; Matsuhisa *et al.* 1979) and assuming that the homogenization temperatures accurately reflect the fluid trapping temperatures, these observations indicate that the oxygen isotopic composition of the fluid from which the quartz precipitated evolved from −2‰ to +7‰ (figure 2*b*). The early fluid is similar in composition to meteoric water, while the isotopically heavy fluid indicates evolution through interactions within the sediment pile. A possible alternative source could arise from pore water expulsion from fault juxtaposed evaporites (Burley, personal communication).

3. Noble gas isotopes in crustal fluids

Most of the early interest in noble gas isotopes in natural systems centred on meteorite analyses due in part to the wide variation in isotopic composition observed and the equally wide range of physical processes open to study. Early terrestrial applications involved the investigation of natural gas systems (Zartmann *et al.* 1961). The subject received a major boost with the discovery (Craig *et al.* 1975; Jenkins *et al.* 1978) that primordial ^{3}He was escaping from the Earth's mantle at mid-ocean ridge spreading centres. Since then the subject has developed two major branches. On one hand noble gases trapped in mantle-derived rocks are used to constrain the composition, budgets and fluxes of volatile species in and from the mantle. On the other hand noble gas contents and compositions in contemporary crustal fluids, groundwaters and gases, are used as inert tracers to provide information on circulation patterns, ages and fluxes. The presence of ancient fluids trapped in inclusions in minerals is now being used to extend the study of noble gases in crustal fluids back through the geological column (Kelley *et al.* 1986; Simmons *et al.* 1988) and is the subject of this section.

Three distinct sources contribute to the elemental and isotopic signatures of the noble gases in natural systems. Most water present in the Earth's crust has at some time or other been in contact with the atmosphere and carries with it, into the crust, noble gases with elemental ratios corresponding to their relative solubilities. The concentrations of noble gas in air saturated water (ASW) are dependent on the temperature and salinity at recharge. Relative abundances are usually expressed as F-values, the measured elemental ratio relative to ^{36}Ar divided by the corresponding ratio in air. Solubilities increase in the progression from neon to xenon and the corresponding F-values between 0 and 25 °C for fresh water range from 0.23 to 0.33 for neon, from 2.07 to 1.74 for krypton, and from 4.20 to 3.09 for xenon. Solubilities and the degree of elemental fractionation are reduced slightly in sea water. In saturated brines the solubilities are reduced by factors of up to 2, and are relatively insensitive to temperature. There are many processes which can modify the elemental ratios carried into the crust and it is one of the aims of noble gas studies to identify these processes. Possible causes of fractionation include; phase separation, e.g. water–steam, water–CO_2, water–oil; hydration reactions leading to removal of water; metamorphic reactions leading to the evolution of water; adsorption effects; mixing of isotopically distinct fluids, etc. Fractionation during the formation of the diagenetic minerals under study is a potential complication which has so far received little attention.

Nuclear processes provide a second source of noble gases in crustal fluids. ^{4}He and ^{40}Ar are produced by radioactive decay of U, Th and K, and heavy xenon isotopes by the spontaneous fission of ^{238}U. Other noble gas isotopes are generated by a variety of nuclear reactions (see Ozima & Podosek 1983), the principal ones being themselves the result of α-particles produced in U and Th decay (e.g. $^{18}\mathrm{O}(\alpha, \mathrm{n})^{21}\mathrm{Ne}$) or neutrons generated by α-particle interactions (e.g. $^{6}\mathrm{Li}(\mathrm{n}, \alpha)^{3}\mathrm{H}(\beta^{-})^{3}\mathrm{He}$). Because of this the nucleogenic component is characterised by isotopic ratios which show only limited variation (Kennedy *et al.* 1990), usually related to variations in target chemistry. The ^{3}He/^{4}He ratio is controlled by Li content and is typically between 0.05 and 0.02 R_a (where R_a is the air ratio 1.39×10^{-6}).

The third major source of noble gases in crustal fluids is the mantle. Mantle input is most readily observed in the case of helium because of the extremely low abundance in the atmosphere and the characteristically high ^{3}He/^{4}He ratio of mantle helium, between 5 and $30R_a$. The large difference between the isotopic composition of helium produced in the mantle and crust allows ^{3}He/^{4}He ratios to provide a unique insight into processes which add mantle volatiles to the continental crust and has been extensively used to trace and quantify these processes in different tectonic settings (Kennedy *et al.* 1985; Poreda *et al.* 1986). Mantle gases are also characterized by very high ^{40}Ar/^{36}Ar ratios, and moderate enhancements of ^{21}Ne/^{22}Ne, ^{20}Ne/^{22}Ne and ^{129}Xe/^{130}Xe (Allegre *et al.* 1983; Staudacher *et al.* 1989). These are less easily detected in crustal fluids though the neon isotopes have been used recently by Ballantine *et al.* (1992) to investigate contributions of mantle gases to fluids in the Vienna basin.

Mass spectrometric techniques for analysing small amounts of the noble gases were pioneered by Reynolds in the 1950s (Reynolds 1956). Since then developments have been essentially evolutionary, with improved resolution of interferences, use of low level ion counting, and the development of ultra low blank extraction techniques, in particular methods involving laser ablation. The only fundamentally new development in mass spectrometry has been that of resonance ionisation mass spectrometry, a topic discussed later in the paper.

The system in operation in Manchester is designed to combine most of these developments in one laboratory. Gases can be released by laser ablation, *in vacuo* crushing, or stepped heating. One extraction system uses a capacitance manometer and a quadrupole mass spectrometer to make precise measurements of the amount and composition of active gases released (principally water and carbon dioxide). It also has a spike system which uses a cocktail of noble gas isotopes, ^{21}Ne, ^{38}Ar, ^{80}Kr and ^{128}Xe, to measure elemental abundances to a precision of 1% or better (Burnard *et al.* 1992). A second instrument is devoted to precise isotopic analyses, unaffected by spike gas, while a third, developed for ^{40}Ar–^{39}Ar dating, is used to measure relative abundances of noble gases, halogens, K, Ca and U, by analysing noble gases in neutron-irradiated samples. Examples of applications of these techniques are presented below.

4. Air saturated water signatures in inclusion fluids

There are many examples of the application of noble gases to the study of modern groundwaters. Andrews & Lee (1979), for example, measured recharge temperatures for the Bunter sandstone aquifer in the English Midlands, corresponding to recharge during the last period of glaciation. Low abundances in groundwaters from wells in

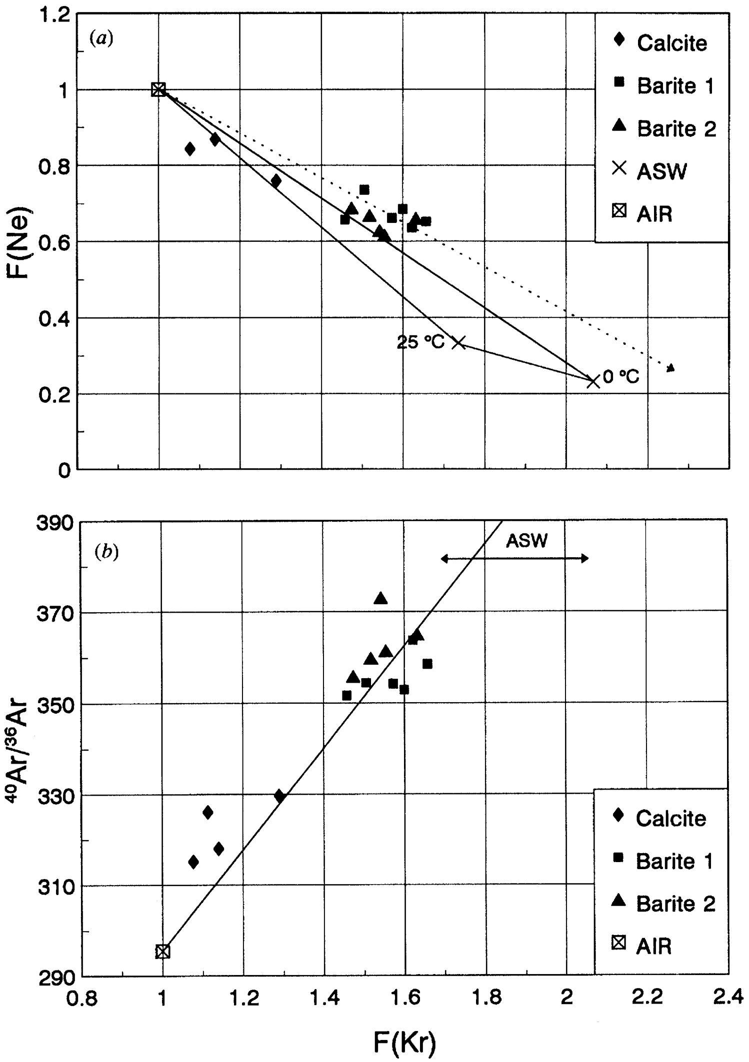

Figure 3. (*a*) Correlation between Ne/Ar and Kr/Ar ratios in trapped North Sea fluids, interpreted as resulting from a mixture of unfractionated air and an air saturated water component (ASW). (*b*) Correlation between $^{40}Ar/^{36}Ar$ and Kr/Ar indicates that the unfractionated air is free of radiogenic ^{40}Ar and probably a recent addition.

the Palo Duro Basin, Texas, were interpreted by Zaikowski *et al.* (1987) as resulting from saline recharge. Mass spectrometers are sufficiently sensitive to extend this type of observation to small amounts of palaeofluid trapped in inclusions but the extent to which elemental abundances are fractionated in the trapping process remains to be determined. Measurements of $^{36}Ar/Cl$ ratios (Kelley *et al.* 1986) in neutron irradiated samples, indicate abundance ratios corresponding roughly to air saturated brine in vein quartz from the South West England but an order of magnitude higher in fluorite from the North Pennines (Turner & Bannon 1992).

Recent precise analyses using our spiked system have been made on a wide range of samples, including secondary barite and calcite veins from North Sea oil cores (Burnard *et al.* 1992), calcite and sulphides from several different types of ore deposit

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(Ford *et al.* 1992), modern cave speleothem (Ayliffe *et al.* 1992), modern sulphide deposits from the sea floor (Turner & Stuart 1992; Stuart *et al.* 1992), ophiolites, and deep crustal fluids trapped in igneous and metamorphic rocks. The data in figure 3*a* is typical of the results obtained for basinal fluids, in this case brines trapped during the formation of late (Tertiary) diagenetic fault related veins at depths of around 2 km in the North Sea oil field. Figure 3*a* shows F-values for neon and krypton in ASW at temperatures between 0 and 25 °C. None of the measurements correspond to a simple ASW component, but lie close to (but not on) mixing lines between unfractionated air and ASW. Unfractionated air dominates the gas release from calcite. A correlation between $^{40}\mathrm{Ar}/^{36}\mathrm{Ar}$ and F(Kr), figure 3*b*, suggests that radiogenic $^{40}\mathrm{Ar}$ is absent in the air component and therefore that it represents recently trapped air, probably acquired since the sample was recovered. In contrast the ASW component contains a well defined proportion of radiogenic $^{40}\mathrm{Ar}$. Extrapolating the correlation in figure 3*b* to the ASW field indicates $^{40}\mathrm{Ar}/^{36}\mathrm{Ar} \approx 390$, a value typical of deep circulating ground waters (Andrews *et al.* 1987). F-value correlations involving xenon show Xe enhancements up to a factor of 2 over ASW in the barite. Xe enhancements have been interpreted as resulting from fluid interactions with sediments containing large amounts of adsorbed Xe (Andrews *et al.* 1987). An alternative explanation which cannot be ruled out is preferential adsorption of modern xenon (Bohlke & Irwin 1992).

Absolute concentrations of noble gases in inclusion fluids may be determined by measuring the pressure rise when inclusions are opened by crushing or laser decrepitation (Burnard *et al.* 1992). The measurements are straightforward for $\mathrm{CO_2}$ rich inclusions but for aqueous systems are difficult to interpret. High apparent concentrations have been observed in a wide range of samples which may be an artefact caused by the adsorption of water on mineral surfaces, newly created during crushing, or fractionation of noble gases and water during the trapping process. It will be necessary to understand the trapping process in more detail before concentration measurements on inclusion fluids can be used in a comparable way to those on modern groundwater.

In summary, an ASW signature in the F-values in inclusion fluids is an indicator of a source at the Earth's surface. However fractionation effects in noble gas ratios, and between noble gases and water appear, at present, to preclude using noble gases to determine palaeo-recharge temperatures or to distinguish meteoric from saline recharge.

5. Mantle noble gases in inclusion fluids

The presence of mantle helium in groundwaters can be used to infer fluxes of other mantle derived-volatile species as well as providing direct information on the influence of tectonics on these fluxes. There are no major difficulties in extending these measurements to inclusion fluids, but three practical problems influence their interpretation; diffusive loss of helium, the effect of multiple generations of inclusions, and *in situ* production of $^3\mathrm{He}$ and $^4\mathrm{He}$.

The clearest evidence for leakage occurs in inclusions in quartz. Absolute concentrations of helium and He/Ar ratios are an order to magnitude lower in quartz than in coexisting fluorite from veins in the North Pennine ore field (Stuart & Turner 1992). Thus while quartz is an ideal mineral for microthermometric fluid inclusion studies, it is essentially worthless as a source of helium analyses. In contrast, fluorite, calcite, barite and various sulphides appear able to retain helium for long periods.

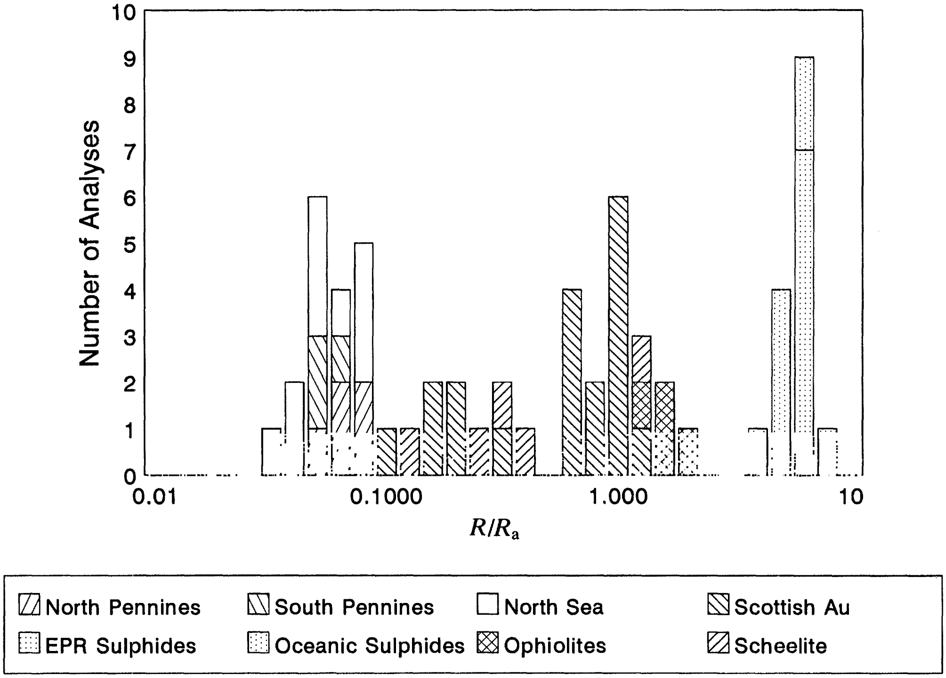

Figure 4. $^3He/^4He$ ratios (expressed as ratios relative to the atmospheric value, R_a) in trapped fluids from a variety of geological settings.

The effects of multiple generations of fluid inclusions can be limited by careful sample selection and evaluated by the intelligent use of isotope mixing diagrams. The use of lasers to analyse ^3He from individual inclusion does not seem feasible. A 100 µm inclusion of sea water from a hydrothermal vent would contain only a few thousand atoms of ^3He, which is comparable with detection limits.

In situ production may occur in the inclusion fluids themselves or within the mineral lattice followed by recoil or diffusion into the inclusions. Crushing may also lead to release of lattice gases produced *in situ*. The importance or otherwise of *in situ* gases can be determined in separate heating experiments or estimated if U and Th contents are known. During repeated crushing gas is evolved from smaller inclusions and the presence of *in situ* lattice gases can be recognized by a systematic increase in the ratio of radiogenic and nucleogenic isotopes to ASW gases (Stuart *et al.* 1993).

Figure 4 illustrates $^3He/^4He$ determinations on inclusion fluids from a wide variety of crustal environments. R/R_a values from late stage calcite and barite veins from the North Sea oil fields and from fluorite veins from the MVT mineralization of the North and South Pennine ore fields are in the range 0.05–0.08, dominated by crustal helium. The North Sea analyses are comparable with those of Hooker *et al.* (1985) made on well gases which were probably trapped at times similar to the fluids we have analysed. The low R/R_a values were attributed to the long time difference between crustal stretching during the Jurassic and the major period of oil and gas formation in the Tertiary. The Pennine ore fluids are low temperature high salinity brines which probably originated as connate water.

At the opposite end of the scale oceanic sulphides show R/R_a values comparable to MORB and to vent fluids. The EPR (East Pacific Rise) sulphides are black smoker sulphide minerals from 21° N which have sampled vent fluids directly (Turner &

Stuart 1992). Those labelled Oceanic sulphides are from a massive sulphide deposit from a sediment-covered ridge (Stuart *et al.* 1993) where the lower ^{3}He/^{4}He ratios reflect the addition of radiogenic He in the pore fluids. The ratio of mantle helium to ASW gases in these samples provides a direct measure of the effects of sea water mixing. Ancient ocean floor sulphides also retain a record of the mantle gases trapped during their formation, a fact illustrated by the analyses of sulphides from the Troodos ophiolite.

Two suites of samples with intermediate values of R/R_a, in the range 0.2–2, identify tectonic settings with a clear mantle involvement. The samples labelled Scottish Au are sulphide minerals from Au–Ag–Zn deposits from the Caledonian province in Scotland. The mineralization is thought to have involved fluids associated with extensive subduction related magmatism which occurred during the closure of the Iapatus ocean to the south. The helium data are consistent with such models and the relative proportion of mantle, crustal and ASW gases provides a means of inferring relative contributions of different fluids to the mineralization process. The scheelite samples in figure 4 represent analyses of individual zones of a large scheelite ($CaWO_4$) crystal from the 88 Ma Dae Hwa W–Mo deposit, S. Korea. A significant mantle component is evident in the He isotope data despite the close relationship between the mineralization and granite emplacement (Stuart *et al.* 1993). The coincidence of silicic magmatism and mantle-derived ^{3}He in contemporary (Kennedy *et al.* 1987), as well as ancient crustal fluids indicates a clear link between mantle and crustal melting.

6. Radiogenic helium and argon

Radiogenic ^{4}He and ^{40}Ar are released from crustal rocks by thermal diffusion and chemical leaching into ground water and hydrothermal fluids. Thermal release may be continuous provided the ambient crustal temperatures are above the blocking temperatures for helium and/or argon. In some areas (Torgersen & Clarke 1985) there is evidence that, on a regional scale and especially for helium, this steady flux roughly matches the crustal production rate (see review by O'Nions & Oxburgh 1988). On the other hand episodic release is expected in areas in areas of intense regional metamorphism or igneous melting, leading to very high ^{40}Ar/^{36}Ar ratios (Turner & Bannon 1992; Stuart *et al.* 1993).

The interpretation of radiogenic isotope concentrations and ratios is dependent on the detailed geological setting, but some generalizations can be made. In regions where large-scale metamorphism or melting is not occurring, the concentrations of radiogenic isotopes provide a measure of the residence times of the fluids or alternatively of their fluxes through the crust. In general residence times increase and fluxes decrease with crustal depth so that ratios of radiogenic to atmospheric gases increase with depth (Andrews 1985). Furthermore the ^{4}He/^{40}Ar ratio is expected to be equal to the production ratio (*ca.* 5 for average crust of Taylor & McLennan (1985)) where both gases are being quantitatively released but may be higher in situations where helium is preferentially released. This is most likely to occur at relatively low temperatures where diffusive escape of helium can occur but argon is retained in the mineral lattice (O'Nions & Balantine, this symposium; Zartman *et al.* 1961).

Examples of radiogenic gases in the North Sea vein material and from the Pennines MVT ore deposits are shown in figures 5 and 6. Figure 5 indicates that both

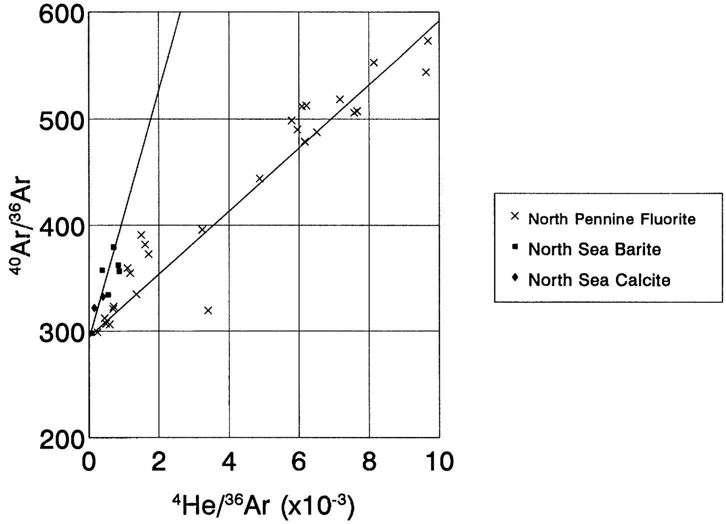

Figure 5. Correlations between ^{40}Ar/^{36}Ar and ^{4}He/^{36}Ar resulting from the addition of radiogenic ^{40}Ar and ^{4}He to dissolved atmospheric argon and helium.

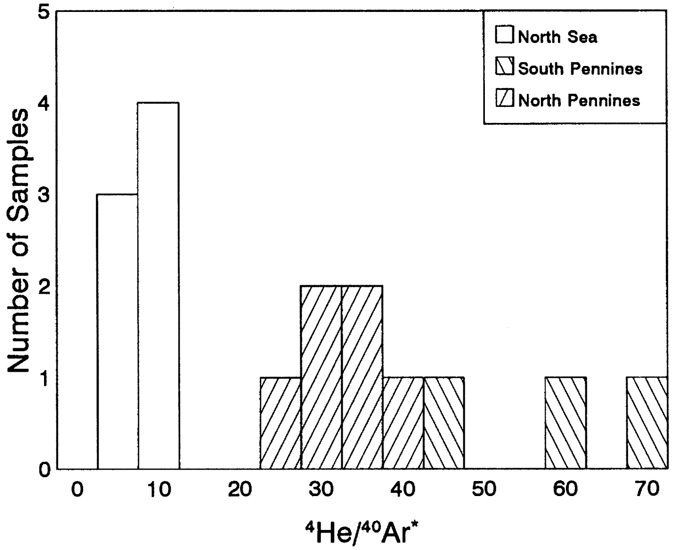

Figure 6. Histogram of radiogenic ^{4}He/^{40}Ar ratios. Those in the Pennine ore fluids exceed production ratios by large factors, suggesting that the gas is released from crustal sediments by diffusive loss at comparatively low temperature. Ratios in the North Sea fluids are closer to the production ratio.

are mixtures of air (ASW) argon (^{4}He/^{36}Ar ≈ 0 and ^{40}Ar/^{36}Ar ≈ 296), and radiogenic ^{4}He and ^{40}Ar. The principal differences are in ^{4}He/^{40} for the radiogenic component and the relative proportions of radiogenic and atmospheric components, ^{4}He/^{36}Ar. A histogram of the measured ^{4}He/^{40}Ar ratios in figure 6 demonstrates that the North Sea fluids contain the two isotopes in proportions close to the production ratio. In contrast ^{4}He/^{40}Ar for the Pennine samples are up to an order of magnitude higher. On the grounds that ^{4}He is released by diffusion at lower temperatures than ^{40}Ar, Ford *et al.* (1992) interpreted these high ratios as indicating the predominance of low temperature interactions of the basinal brines responsible for the mineralization. This inference is consistent with the low homogenization temperatures determined in the fluid inclusions. As a corollary the data indicates that the fluids contain little contribution of radiogenic gases from deeper in the crust, where higher temperatures would lead to a greater contribution from radiogenic ^{40}Ar. In contrast the much lower ratios observed in the North Sea oil reservoir samples, implies either a significant contribution from depths where diffusive loss of argon occurs or a significant contribution from diagenetic dissolution of K-rich minerals such as feldspar and clay minerals.

^{4}He/^{36}Ar and ^{40}Ar/^{36}Ar can be used to infer approximate concentrations of radiogenic ^{4}He and ^{40}Ar on the assumption that the concentration of ^{36}Ar is that of air saturated water, $[^{36}\mathrm{Ar}]_{\mathrm{ASW}}$, approximately 10^{-6} cm^3 STP g^{-1}. ^{4}He production and movement is related to groundwater movement according to the expression:

$$\nabla\cdot[(^4\mathrm{He}/^{36}\mathrm{Ar})\cdot\boldsymbol{\Phi}(\mathrm{H_2O})] = P_4/[^{36}\mathrm{Ar}]_{\mathrm{ASW}} - \partial/\partial t(^4\mathrm{He}/^{36}\mathrm{Ar}), \tag{1}$$

where $\boldsymbol{\Phi}(\mathrm{H_2O})$ is the flux of water and P_4 the production rate of ^{4}He per unit volume.

One of the simplest interpretations of ^{4}He concentrations assumes that ^{4}He is acquired locally from the rocks through which the fluids pass. The concentration is then related to the time, T, for which the fluids have been accumulating radiogenic gases. Assuming 100% release of ^{4}He from the rocks, T is given by:

$$T = (^4\mathrm{He}/^{36}\mathrm{Ar})\,p[^{36}\mathrm{Ar}]_{\mathrm{ASW}}/P_4, \tag{2}$$

where p is the porosity. The production rate of ^{4}He in average continental crust is around 10^{-12} cm^3 STP cm^{-3} a^{-1} and for approximate calculations equation (2) simplifies to

$$T \approx (^4\mathrm{He}/^{36}\mathrm{Ar})\,p\ \mathrm{Ma}. \tag{3}$$

^{4}He/^{36}Ar values for the North Sea barite are in the range 300–600, which combined with porosities of around 0.15 and ignoring possible contributions from *in situ* decay since trapping, indicates accumulation ages from 45 to 90 Ma. These are less than, but of the same order as, the age of the basin at the time of oil formation and in so far as they are representative argue for only limited recharge of the basin fluids.

A more realistic interpretation of radiogenic gas concentrations in long-lived crustal fluids assumes that they are not generated locally but are brought in by advection and mixing from greater depth (Torgersen & Clarke 1895; Torgersen *et al.* 1988). In this case ^{4}He/^{36}Ar can be used to relate the flux of radiogenic ^{4}He, $\boldsymbol{\Phi}(^4\mathrm{He})$, to that of water:

$$\boldsymbol{\Phi}(^4\mathrm{He}) = (^4\mathrm{He}/^{36}\mathrm{Ar})\,[^{36}\mathrm{Ar}]_{\mathrm{ASW}}\,\boldsymbol{\Phi}(\mathrm{H_2O}). \tag{4}$$

The detailed application of (4) depends on assumptions regarding the flux of ^{4}He and the flow pattern. If it is assumed that the average vertical flux of ^{4}He is equal to the areal production rate then expression (4) applied over a suitably large area (one in which the net horizontal flow is small in comparison to the total vertical flow) can be used to provide an estimate of the mean outward flux of water. The value of the production rate per unit surface area of continental crust is around 3×10^{-6} cm^3 STP cm^{-2} a^{-1}. Substituting this for $\boldsymbol{\Phi}(^4\mathrm{He})$ in expression (4) leads to the approximate result:

$$\boldsymbol{\Phi}(\mathrm{H_2O}) \approx 3/(^4\mathrm{He}/^{36}\mathrm{Ar})\,\mathrm{g\,cm^{-2}\,a^{-1}}. \tag{5}$$

Substituting ^{4}He/^{36}Ar 300–600 leads to $\boldsymbol{\Phi}(\mathrm{H_2O}) \approx 5\times10^{-3}$–$10^{-2}$ g cm^{-2} a^{-1}, which over a period of 100 Ma would correspond to a vertical column of water some

5–10 km in height. For a given $^4He/^{36}Ar$ ratio then the assumption that the fluids are carrying helium from the full depth of continental crust clearly requires much larger fluxes of water than is necessary on the assumption of local production. The order of magnitude higher $^4He/^{36}Ar$ ratios observed in the North Pennine fluids may be taken to indicate correspondingly longer residence times or lower fluxes of water.

Enhanced ^4He and ^{40}Ar fluxes and preferential release of ^4He could be produced from the subsidence and heating of old sediments containing radiogenic gases in detrital minerals. The ^4He flux which would arise from the downward passage of sediments composed of minerals of age T at a rate dz/dt through an isotherm at which ^4He is released from minerals is given by

$$\boldsymbol{\Phi}(^4\mathrm{He}) = \frac{\mathrm{d}z}{\mathrm{d}t} P_4 T. \qquad (6)$$

This flux would equal the mean crustal production if the subsidence rate were equal to the thickness of the crust divided by T. For example in 100 Ma old sediments this would require an (exceptionally high) subsidence rate of 0.3 km a^{-1}.

The interpretation of the significance the three sources of noble gas isotopes in inclusion fluids (surface waters, mantle and crust) is clearly a powerful tool, particularly when coupled with a detailed knowledge of the local geological and tectonic setting. The illustrations above have been based on relatively few analyses from each location but point the way to more definitive interpretations based on in-depth regional studies on samples from a wide range of depth and locations.

7. Analysis of kilo-atom quantities of xenon by resonance ionization

Resonance ionization mass spectrometry is a technique whereby a tuned high intensity laser beam is used to resonantly excite and then ionise atoms of a specific element. Its main features are that it is element specific, thereby reducing interferences, and has the potential for very high ionization efficiencies. Resonance ionisation of the light noble gases is not yet possible because of the high excitation energies required but it is in use for krypton (Thonnard *et al.* 1984) and xenon (Gilmour *et al.* 1991, 1992) and extends the sensitivity for the analysis of these gases by two orders of magnitude, approaching single atom detection limits.

The instrument in use in Manchester is based on the scheme of Chen *et al.* (1980) and uses a wavelength of 249.6 nm. Laser pulses are focused into the ion source of a low volume ultra high vacuum time-of-flight mass spectrometer and ionise all the xenon atoms in a 0.25 mm^3 volume in the source. The sample xenon is concentrated into this small volume by condensing it onto a 1 mm^2 cold spot and then releasing it into the ionizing laser beam by a second low power heating laser pulsed 1 μs ahead of the main laser.

The instrument, referred to as RELAX (refrigerator enhanced laser analyser for xenon), is capable of detecting individual xenon atoms but is currently limited by blanks to sample sizes of a few thousand atoms of the major isotopes. The rapid analysis time, combined with gas extraction by laser ablation, assist in minimizing the blanks. Figure 7 illustrates some preliminary data. The plot shows the presence of ^{238}U fission xenon in a single mineral grain from the Doddabetta charnockite, Nilgiris, South India. The most extreme point, in which the $^{136}Xe/^{132}Xe$ ratio is three times the atmospheric value, corresponds to a total sample of fission ^{136}Xe of only 26000 atoms.

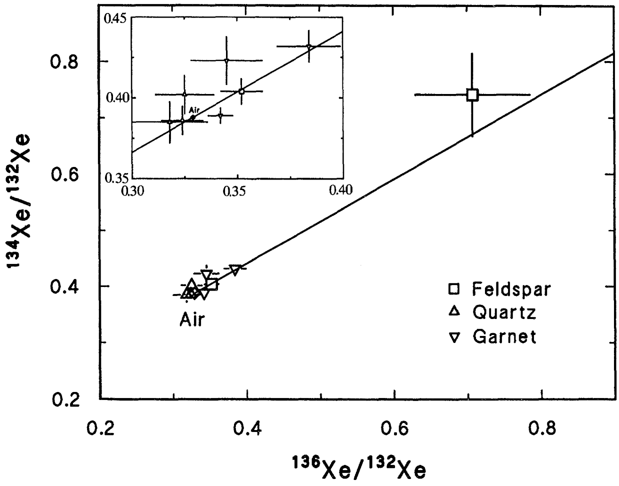

Figure 7. Mixing line between air and ^{238}U fission xenon in individual mineral grains analysed by resonance ionization mass spectrometry. The ^{136}Xe fission content of the feldspar is only 26000 atoms.

A number of processes lead to the production of xenon isotopes, including fission, neutron absorption by Ba, I and Te and cosmic ray spallation of Ba. Cosmic ray production rates for ^{126}Xe in barite are of the order of 10 atoms a^{-1} g^{-1}. Blank levels for this low abundance isotope are correspondingly low, i.e. a few 10s of atoms, and cosmic ray dating of barite should be possible. Mantle xenon with its characteristic ^{129}Xe anomaly and fission signature have been detected in individual olivine and clinopyroxene phenocrysts in ocean island basalts. It is clear that in the near future several applications to sedimentary rocks will be possible.

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Discussion

M. GRUSZCZYNSKI. The Zechstein fluids give δ^{18}O values up to +18 permil but Professor Turner's values of +26 permil indicate an influence of hydrothermal fluids.

G. TURNER. The quartz mineral value is +26 permil but the fluid value indicated by this is +7 permil.

A. HALLIDAY. Does *in situ* production of ^{4}He from U cause problems?

G. TURNER. The *in situ* contribution appears to increase as crushing continues in high U minerals and may originate in the crystal lattice. Its importance may be judged from the amount of gas released by fusion. This effect has not been seen in sulphides.

A. HALLIDAY. Quartz is leaky for He but did Professor Turner imply that fluorite, barite and calcite are not?

G. TURNER. Fluorite is better than quartz but it may still leak. The concentration of ^{4}He is typically an order of magnitude higher in fluorite than in quartz.