Abstract Helium abundance and isotope variations have widespread application in groundwater-related studies. This stems from the inert nature of this noble gas and the fact that its two isotopes – helium-3 and helium-4 – have distinct origins and vary widely in different terrestrial reservoirs. These attributes allow He concentrations and $^{3}$He/$^{4}$He isotope ratios to be used to recognize and quantify the influence of a number of potential contributors to the total He budget of a groundwater sample. These are atmospheric components, such as air-equilibrated and air-entrained He, as well as terrigenic components, including in situ (aquifer) He, deep crustal and/or mantle He and tritogenic $^{3}$He. Each of these components can be exploited to reveal information on a number of topics, from groundwater chronology, through degassing of the Earth’s crust to the role of faults in the transfer of mantle-derived volatiles to the surface. In this review, we present a guide to how groundwater He is collected from aquifer systems and quantitatively measured in the laboratory. We then illustrate the approach of resolving the measured He characteristics into its component structures using assumptions of endmember compositions. This is followed by a discussion of the application of groundwater He to the types of topics mentioned above using case studies from aquifers in California and Australia. Finally, we present possible future research directions involving dissolved He in groundwater.

15.1 Introduction

Studies of the noble gas characteristics of groundwater have long been used to provide information about climatic conditions during periods of aquifer recharge (e.g. Mazor 1972; Andrews and Lee 1979). In this respect, the key attributes of the noble gases are their inert behavior coupled with their well defined solubility characteristics as a function of temperature and salinity. However, to fully exploit noble gases in this manner, groundwater residence times must also be known in order to place an absolute chronology against climatic variations. Ironically, the least useful noble gas for paleo-climate studies – helium, due to the relative insensitivity of its Henry’s Law coefficient to temperature change – is one of the most useful gases for providing chronological information, over both short and long timescales (e.g. Andrews and Lee 1979; Marine 1979; Torgersen 1980; Heaton and Vogel 1981). Thus, helium has often been considered as a stand-alone tracer to the other noble gases as it has found widespread application in groundwater-related research, mostly unrelated to climate studies. This is the approach adopted in this review – we emphasize the role of helium in groundwater – and direct the reader to other publications (e.g. Ballentine et al. 2002; Ballentine and Burnard 2002; Kipfer et al. 2002; Phillips and Castro 2003) which provide background on the utility of the other noble gases in groundwater.

We begin with an overview of the collection and measurement approaches commonly used to produce He data on groundwater samples. We provide details of field and laboratory techniques and protocols for the production of both precise and accurate He isotope and concentration data. By adopting reasonable estimates of potential endmember compositions which
contribute to observed (i.e., measured) values, we show how He variations can be resolved to yield quantitative information on the different sources comprising the He record. Such information can indeed be used to provide chronological information on the residence time of the groundwater since the time of recharge (i.e., since last equilibration with the atmosphere in the unsaturated zone). However, groundwater He data go far beyond this application, and we include discussion on other issues such as degassing fluxes from the crust and the influence of faults on the transfer of mantle-derived volatile to the atmosphere – topics which are amenable to study through exploiting He measurements of groundwater. We end with a section on future prospects of groundwater He studies, particularly in light of the increasing realization that groundwater He concentrations and its isotope composition can vary on both short and long timescales, and that documenting this variability has exciting potential for understanding fluid characteristics and movement through the crust especially in response to external perturbations, including seismic disturbances.

15.2 Materials and Methods

This section gives an overview of the procedures involved in producing helium data on groundwater samples. It includes a brief description of sample collection methods as well as laboratory procedures used to prepare He for isotopic and abundance measurement. It concludes with a note on data quality, nomenclature, and units.

15.2.1 Sample Collection

Collection of groundwaters for dissolved He analysis involves exploiting actively-pumping commercial (i.e., supply) wells, observation wells, natural springs or seeps. In all cases, the essential prerequisite during sampling is to avoid, or at least minimize, air contamination. In the case of wells, it is important that the well volume is purged prior to sampling so that only aquifer water is collected for analysis. This precaution involves sampling only after a given time period equivalent to purging approximately three volumes of the well. This safeguard is particularly important for observation wells where a pump has to be introduced to sample the groundwater. However, even for apparently continuously-pumping wells, caution must be exercised that sampling does not take place immediately following the start of a new pumping cycle as air can enter the well when the pumping cycle is interrupted or shut-off.

For natural springs and groundwater seeps, air contamination is avoided by inserting sampling tubing as far as possible into the “eye” of the spring, i.e., at the point where water leaves the ground. It must remain submerged and well below the surface level of the water for the entire sampling procedure. The tubing most commonly used is clear and flexible (e.g. PVC or PTFE – polytetrafluoroethylene), and its role is to transfer the groundwater into and out of the sampling vessel. In the case of wells, the same type of tubing can be connected to the well-head directly, usually via a sampling port, or to the outlet of the pump in the case of small, narrow-diameter pumps commonly used for observation wells. In all cases, prolonged flushing with the (water) sample of interest should remove, and can be seen to remove (in the case of transparent plastic tubing), any air bubbles which may have adhered to the sides of the tubing.

There are different types of sampling vessel which are used for the collection and storage of groundwaters for transfer back to the laboratory. The most common type is oxygen-free, annealed copper tubing, which is readily available at plumbers’ supply stores. A length of ~30 cm copper tube with a diameter of ~9–10 mm contains ~12 g water which is more than sufficient for He analysis. The copper tube is connected at each end with the plastic tubing and the system is flushed with the groundwater of interest. Water pressure flowing through the copper tubing can be reduced through innovative use of Y-connectors at the up-flow end of the copper – this can help with sealing of the copper tubes. Capturing the sample in the copper tubing can be achieved by use of two hinged knife-edged clamps (a.k.a. refrigeration clamps) which crimp the copper to form a tight seal – where pressure is maintained on the seal by the clamps, or through cold welding of the copper using specific field-portable welding tools. In the case of particularly gas-rich waters, a pressure release valve can be incorporated at the out-flow end of the plastic tubing to help ensure that any dissolved gases remain in solution.
The alternative type of vessel used in some cases for sample collection is a glass flask, which incorporates either one or two stopcock valves. A single stopcock vessel is evacuated to high vacuum and has a Y-inlet which facilitates flushing of the sample past the stopcock prior to opening the valve and capturing the sample. The other type of glass vessel has a stopcock at both ends and the water is flushed through the entire vessel before the stopcock valves are closed in turn. The essential feature of the glass sample vessels that ensures an accurate measurement of any dissolved helium is the type of glass employed. A number of commercially-available glasses (e.g. Corning-1720, Monax, AR-glass) have low He-permeability characteristics and provide secure sample containers over extended time periods (months to years). Pyrex and Duran glass vessels are not suitable for He work, even over short time periods (days to weeks), due to their high He diffusivity (Norton 1957) although they have been used successfully for gases other than He, including the heavier noble gases.

15.2.2 Sample Extraction and Preparation

Prior to measurement, helium must be purified and isolated from both the water phase and the other dissolved gases. This clean-up procedure usually takes place on a dedicated ultra-high vacuum (UHV) system to which the various sampling devices can be attached. Following opening of the seal or valve of the sample container, the water is captured in a bulb and any water vapor is condensed on a trap through the use of a slurry of dry ice and acetone (approximately -78°C). The remaining gases can be purified further through a combination of exposure of the gas phase to traps both with and without activated charcoal held at liquid nitrogen temperature (to condense CO₂ and Xe and adsorb Ar and Kr, respectively) and active gas reaction, using an active metal getter pump and/or hot titanium sponge. The remaining gas should be dominated by He and Ne. Depending upon the configuration of the line, the gas can be expanded into a glass breakseal for transfer to a mass spectrometer (e.g. Torgersen 1980; Stute et al. 1992; Kulongoski and Hilton 2002) or, if the preparation line is interfaced directly to the mass spectrometer preparation line, inlet directly for further processing before measurement (e.g. Andrews and Lee 1979; Stute et al. 1995; Beyerle et al. 2000; Furi et al. 2009; Stanley et al. 2009). Further processing usually involves cryogenic separation of He from Ne utilizing an activated charcoal trap attached externally to the cooling stage of a refrigeration unit using He as the coolant. Temperatures ~35 K or lower are usually sufficient to adsorb Ne completely onto the trap whilst He remains in the gas phase and thus ready for inlet into the measurement device.

15.2.3 Instrumentation

Most He isotope and He concentration data are produced using magnetic sector noble gas mass spectrometers, incorporating Nier-type ion sources (which use high-sensitivity electron bombardment for ionization) and a sufficiently large radius flight tube (often with extended geometry) to achieve a resolution of 600 or more without undue restriction on the source slit width. In this way, it is possible to completely separate ⁴He⁺ from the interfering HD⁺-T⁺ doublet at mass 3 and thus record accurate ³He/⁴He ratios. With magnetic sector mass spectrometers of lower resolution, a correction is usually applied for the tailing effect of the HD⁺ peak into the ³He⁺ measurement position. Given the large difference between the relative abundance of ³He and ⁴He in most groundwaters (around six orders of magnitude if ³He/⁴He ratios are air-like), magnetic sector machines must employ a multiplier device for the small ³He⁺ ion beams while ⁴He⁺ can be measured using a conventional Faraday cup collector.

An alternative means of producing He data is to use quadrupole mass spectrometers (a.k.a. residual gas analyzers) which employ a potential field distribution between source and detector to allow transmittance of selected e/m ratios and deflect others to ground. With this type of device, the mass resolution is severely compromised (compared to sector machines) so that it is not possible to separate ³He⁺ from interfering species at mass 3: therefore, quadrupole mass spectrometers are useful for measuring ⁴He abundances only and ³He/⁴He ratio information must be gained elsewhere. It is important to note that these instruments do have sufficient resolution to separate peaks at adjacent
masses (e.g., mass 3 and mass 4) so are frequently used to measure the $^{3}\text{He}/^{4}\text{He}$ ratio of gases which have been spiked with a known amount of the minor isotope, $^{3}\text{He}$. In this way, accurate information on sample $^{3}\text{He}$ abundances can be gained by the isotope dilution technique which overwhelms natural variations in $^{3}\text{He}$ (and any HD-T) with spike-derived $^{3}\text{He}$ (e.g., Poole et al. 1997; Kulongoski and Hilton 2002; Hamme and Emerson 2004; Sano and Takahata 2005). Original (sample) $^{3}\text{He}/^{4}\text{He}$ information is not recoverable by this technique.

### 15.2.4 Measurement Protocols and Standards

Once helium has been purified, the usual measurement protocol upon inlet into the mass spectrometer involves either simultaneous collection of the species of interest, i.e., $^{3}\text{He}$ and $^{4}\text{He}$, or peak jumping whereby masses are measured in sequential fashion by adjustment of a controlling parameter (e.g., magnetic field) allowing greater time to be spent on smaller ion beams, i.e., $^{3}\text{He}$. Instrument configuration will determine which mode of measurement is possible. In the case of quadrupole-based instruments, peak jumping (a.k.a. mass scanning) is the only possible mode. Data collected on peaks of interest are normally extrapolated to the time of sample inlet in an attempt to minimize discrimination effects caused by differences in ionization efficiencies of various species and/or mass-dependent collector biases. This approach allows the extrapolated $^{3}\text{He}/^{4}\text{He}$ ratio or $^{4}\text{He}$ abundance to be determined.

An essential prerequisite for the production of accurate $^{3}\text{He}/^{4}\text{He}$ and $^{4}\text{He}$ abundance data is the preparation of standards which are used to calibrate and optimize instrument performance as well as standardize raw sample results. In the first instance, peak shape and peak resolution issues can be resolved through use of standards as well as ensuring that machine sensitivity is adequate for the measurements to be undertaken. Secondly, sample measurements need to be quoted relative to a standard of known isotopic composition and $^{4}\text{He}$ abundance. In the case of magnetic sector instruments which employ different types of detectors, determining the relative detector gain is an inherent challenge. This is particularly acute for helium isotope measurements because of the necessity of using a multiplier detector for $^{3}\text{He}$, and a Faraday cup for $^{4}\text{He}$. In this case, the measured $^{3}\text{He}/^{4}\text{He}$ ratio is a purely arbitrary value and specific to the device used and dependent upon source and/or detector conditions operating at the time of measurement. However, knowledge of the multiplier gain is unnecessary as long as measured $^{3}\text{He}/^{4}\text{He}$ values are compared to a standard of known $^{4}\text{He}$ isotopic composition. Air, collected under known conditions of temperature, pressure and relative humidity, is often the standard of choice given its well known (present-day) $^{3}\text{He}/^{4}\text{He}$ ratio ($1.399 \pm 0.013 \times 10^{-6}$; Mamyrin et al. 1970) and $^{4}\text{He}$ abundance ($5.24 \pm 0.05$ ppm volume fraction dry air; Ozima and Podosek 1983). Thus, by measuring aliquots of air $^{4}\text{He}$, similar in size to samples and prepared under identical laboratory conditions, and taking account of any variations in collector linearity, it is possible to normalize sample $^{3}\text{He}/^{4}\text{He}$ and $^{4}\text{He}$ abundances to that of the standard giving a measure of the relative enrichment/depletion of $^{3}\text{He}$ relative to $^{4}\text{He}$, or just $^{4}\text{He}$, compared to the standard. For example, sample $^{3}\text{He}/^{4}\text{He}$ ratios (R) are routinely quoted relative to the air $^{3}\text{He}/^{4}\text{He}$ ratio (R$_{A}$) with the absolute value known only through multiplying by the $^{3}\text{He}/^{4}\text{He}$ of air ($1.4 \times 10^{-6}$). Thus, if the sample $^{3}\text{He}/^{4}\text{He}$ is given as 0.1R$_{A}$, its absolute value is $1.4 \times 10^{-7}$.

### 15.2.5 Data Quality, Nomenclature, and Units

Helium data – isotope ratios and abundances – should be quoted with realistic estimates of the uncertainty on the measurements. The factors that constitute the quoted uncertainty include the measurement statistics on individual measurements of sample and normalizing standard $^{3}\text{He}/^{4}\text{He}$ ratios (primarily a measure of the uncertainty on the $^{3}\text{He}$ measurement), the reproducibility of standard measurements ($^{3}\text{He}/^{4}\text{He}$ and $^{4}\text{He}$ abundance) over the course of the measurement run, and blank contributions. The latter is rarely an issue in groundwater studies provided sufficient volumes of water are used for He extraction (i.e., $> \sim 10$ cm$^{3}$). Other effects that could contribute to the uncertainty include the linearity of detector response – measurements on standards and samples should be made on approximately the same amounts of
He – and whether He and Ne were separated prior to measurement. Although hardly an issue with the most recent data, there are reports in the older literature (e.g. Rison and Craig 1983) cautioning that the presence of Ne can have an effect on measured $^3$He/$^4$He ratios.

As stated previously, $^3$He/$^4$He ratios (R) are usually quoted relative to air ($R_A$). Occasionally, however, $^3$He/$^4$He data are reported as absolute values (e.g. $1 \times 10^{-7}$). It should be clear from the previous discussion that such values involve selection of the air $^3$He/$^4$He value – it is worthwhile checking that the air value adopted is explicitly stated to reassure the user when comparing such data to other data quoted in the more conventional manner. We also point out that there are a number of ways that He concentrations are reported. The concentration of He in a groundwater should be reported in stated units (atoms, moles or cm$^3$ STP) per unit mass (usually gram) of water. For example, the concentration of $^4$He in groundwater could be reported as $4.2 \times 10^{-6}$ cm$^3$ STP g$^{-1}$ H$_2$O. Prefixes such as “n” (nano-) – in the form ncm$^3$ STP – are potentially confusing but are frequently seen: they imply units of $10^{-9}$ cm$^3$ STP.

Finally, we note that in addition to He concentration, it is usual to report the Ne concentration in the same sample – in the following section it will become clear why the Ne measurement is so important. Neon concentrations are usually given as either a stand-alone concentration (e.g. atoms Ne g$^{-1}$ H$_2$O) or as a He/Ne ratio. In the former case, it is worthwhile to check that it is the total Ne concentration that is quoted as opposed to the $^{20}$Ne concentration – the major isotope of Ne and one usually selected for measurement. In the latter case of reporting Ne as a He/Ne ratio, it should be explicit in the data table if the value is the absolute ratio or the air-normalized value, i.e., the sample He/Ne ratio divided by the same ratio in air (air He/Ne = 0.288, (Weiss 1971)). Given the means of producing such data by mass spectrometric instrumentation, it is likely to be the latter.

15.3 Applications of Helium Isotopes

Helium is a useful and well-exploited tracer in groundwater-related studies because of its unique isotopic characteristics and inert nature. Helium concentrations in groundwater often exceed the expected solubility equilibrium values as a result of radiogenic production and release of He from aquifer material into associated pore waters. By measuring the abundance of in situ produced He, it is possible to determine the residence time of the groundwater in the aquifer, over both short and long timescales (Andrews and Lee 1979; Marine 1979; Torgersen 1980; Kipfer et al. 2002).

Complications to He-derived chronologies arise with the introduction of He into the groundwater from extraneous sources. Contributions to the extraneous He content can include (a) release of stored He from aquifer material, either by weathering (Torgersen 1980) or diffusion (Solomon et al. 1996), (b) diffusion of He out of confining strata (Andrews and Lee 1979), (c) a basal flux of He from the deeper crust (Heaton 1984; Torgersen and Clarke 1985; Torgersen and Clarke 1987; Torgersen 2010), and/or (d) a mantle He flux usually associated with faults, volcanic activity, crustal extension, or magmatic intrusion (Torgersen 1993; Kennedy et al. 1997; Kulongsoksi et al. 2005; Sano and Nakajima 2008; Pik and Marty 2009). In all these cases, He can migrate into the aquifer resulting in observed He excesses. In turn, this can lead to overestimation of groundwater residence times (ages).

Means of resolving and quantifying the extraneous sources of helium rely upon careful scrutiny of the helium isotope and concentration record together with associated properties of the aquifer matrix. The weathering and/or diffusive release of He from aquitards and aquifer minerals generally occurs within ~50 Ma (Solomon et al. 1996), such that sediments >50 Ma will no longer be a significant source of extraneous helium. The basal He flux ($J_0$) may be identified and quantified if the age structure of the groundwater in the aquifer has been established by alternative techniques (e.g. $^{14}$C, $^{36}$Cl, or hydrodynamically calculated residence times) (e.g. Andrews and Lee 1979; Torgersen and Clarke 1985; Lehmann et al. 2003; Kulongsoksi et al. 2008). The subsurface addition of He ($^3$He or $^4$He) will change the $^3$He/$^4$He ratio from that of air-equilibrated water ~1 $R_{eq}$ (where $R_{eq} = ^3$He/$^4$He of air-equilibrated water = ~1.4 $\times$ 10$^{-6}$; Clarke et al. 1976), thereby providing a means to identify the source of the extraneous He (e.g. Clarke et al. 1969; Tolstikhin 1975). In the case of mantle helium, its contribution may be identified and quantified based on measured $^3$He/$^4$He ratios and observed shifts from established crustal production rates (e.g. O’Nions and Oxburgh 1983; Kennedy et al. 1997;
Kulongoski et al. 2003). Consequently, helium isotope ratios have found utility in many areas of contemporary research associated with the occurrence of mantle volatiles in groundwater, including quantifying mantle volatiles fluxes, identifying transport mechanisms, and tracing extant tectonic processes (e.g. Oxburgh et al. 1986; O’Nions and Oxburgh 1988; Torgersen 1993; Kennedy et al. 1997; Kulongoski et al. 2005; Kennedy and Van Soest 2007; Crossey et al. 2009).

15.3.1 Helium Components

In order to effectively use helium as a tracer in groundwater systems, it is first necessary to distinguish the various sources of helium which comprise the total dissolved He content of a water sample. The measured sample He concentration may represent superimposition of several He components, which, upon resolution, can provide insight into the origin of the various He contributions to the system. As described by Kulongoski et al. (2008), the sources of $^3$He and $^4$He include terrigenic sources, such as in situ production ($He_{is}$) from the decay of U, Th, and Li in the aquifer material, a mantle flux ($He_{m}$), a deep crustal flux ($He_{dc}$), and tritiogenic helium-3 ($^3He_t$) from the decay of tritium in groundwater. Atmospheric sources include air-equilibrated helium ($He_{eq}$) and dissolved-air bubbles ($He_a$). The He mass-balance equation describing total He dissolved in groundwater (Torgersen 1980; Stute et al. 1992; Castro et al. 2000) resolves the measured $^3$He/$^4$He ratio of the sample ($R_s$) into its components:

$$R_s = \frac{^3He_s}{^4He_s} = \frac{^3He_{eq} + ^3He_a + ^3He_{in} + ^3He_{dc} + ^3He_{m} + ^3He_t}{^4He_{eq} + ^4He_a + ^4He_{in} + ^4He_{dc} + ^4He_{m}}$$

(15.1)

In this equation, $^3He_s$ and $^4He_s$ are the helium-3 and helium-4 concentrations measured in a groundwater sample.

The different sources of He have distinct $^3$He/$^4$He ratios. End-member $^3$He/$^4$He ratio values include air: $R_A = -1.4 \times 10^{-6}$ (Clarke et al. 1976), mantle: $R_m = 1.1 \times 10^{-5} = 8 R_A$ (Graham 2002), and in situ and deep crustal sources: $R_{is} \sim R_{dc} \sim 3 \times 10^{-8} = 0.02 R_A$ (Mamyrin and Tolstikhin 1984). These endmembers are used to distinguish between and resolve the various components that comprise the measured $^3$He/$^4$He ratio of a sample.

15.3.1.1 Atmospheric Helium Components in Groundwater

The atmospheric He components include $He_{eq}$ and $He_a$. The contribution of atmospheric He components to the total (measured) He in a groundwater sample may be calculated using the measured concentrations of Ne, He, and the He/Ne ratio of each sample, along with an estimate of the recharge temperature. The recharge temperature can be derived from the concentration of the noble gases other than He (e.g. Mazor 1972; Stute et al. 1992; Weyhenmeyer et al. 2000; Kipfer et al. 2002; Kulongoski et al. 2009) or from the average temperature measured at the recharge area covering the period of groundwater recharge (e.g. Stute and Schlosser 1993; Kulongoski et al. 2005; Kulongoski et al. 2008).

The amount of air-entrained He in each groundwater sample may be calculated assuming that the dissolved Ne of a sample ($Ne_s$) represents the sum of the Ne from air-equilibration ($Ne_{eq}$) and from air-bubble entrainment ($Ne_a$), and that there is no fractionation in the resulting air-entrained He/Ne ratio (Torgersen 1980). The Ne content resulting from air-equilibration can be calculated from knowledge of the temperature at recharge, and is subtracted from the measured Ne concentration to give the amount of Ne due to air-bubble entrainment. The $Ne_a$ is then used to calculate the amount of air-entrained He ($He_a$), using the known ratio of He to Ne ratio of air ($He_a/Ne_a = 0.288$) (Weiss 1971).

He and Ne oversaturation in groundwater, i.e., relative to air-equilibrated water at a given temperature, may reflect overpressure effects during groundwater infiltration and/or rapid fluctuations in the water table (e.g. Stute and Talma 1998; Beyerle et al. 2003; Kulongoski et al. 2004). This latter possibility is thought to result from large and rapid fluctuations in the water table of shallow aquifers during flood events, resulting in dissolution of trapped air bubbles in the unsaturated zone by increased water pressure (e.g. Kulongoski et al. 2003; Ingram et al. 2007; Kulongoski et al. 2009).
15.3.1.2 Excess (Terrigenic) Helium: Radiogenic, Deep Crustal, Tritiogenic, and Mantle Components in Groundwater

The sum of the in situ produced, deep crustal, tritiogenic, and mantle He components is often referred to as “excess” or “terrigenic” helium (He\text{ex}). Note that although tritium has an atmospheric source, it decays to $^3$He ($^3\text{H}$ \text{t}_{1/2} = 12.32 years) within the groundwater system so the daughter product is included as a terrigenic component. The contribution of each of these components to the total He can be determined using measured $^4$He concentrations and assumed $^3$He/$^4$He ratios which are characteristic of the different sources (endmembers). First, however, excess helium-3 ($^3$He\text{ex}) and helium-4 ($^4$He\text{ex}) are calculated by subtracting the concentrations of He due to air equilibration ($^4$He\text{eq}) and air-bubble entrainment ($^4$He\text{a}) from the measured He concentration of the sample ($^4$He\text{s}):

$$^4\text{He}_{\text{ex}} = ^4\text{He}_\text{s} - ^4\text{He}_\text{eq} - ^4\text{He}_\text{a}$$  (15.2)

Similarly, $^3$He\text{ex} is calculated using $^4$He\text{eq} and $^4$He\text{a} concentrations multiplied by the $^3$He/$^4$He ratios characteristic of the different sources (endmembers):

$$^3\text{He}_{\text{ex}} = (^3\text{He}_\text{s} \times R_s) - (^3\text{He}_\text{eq} \times R_{\text{eq}}) - (^3\text{He}_\text{a} \times R_a)$$  (15.3)

Equations (15.2) and (15.3) can be combined to yield $R_{\text{ex}}$ which represents the excess $^3$He\text{ex}/$^4$He\text{ex} ratio.

15.3.2 Resolution of Helium Components

The total dissolved He of a sample may be separated into its various components by transforming the He mass-balance equation (15.1) (e.g. Torgersen 1980; Stute et al. 1992):

$$\frac{^3\text{He}_\text{s} - ^3\text{He}_\text{a}}{^3\text{He}_\text{eq} + ^3\text{He}_\text{is} + ^3\text{He}_\text{dc} + ^3\text{He}_\text{m} + ^3\text{He}_t} = \frac{^4\text{He}_\text{eq} + ^4\text{He}_\text{is} + ^4\text{He}_\text{dc} + ^4\text{He}_\text{m}}{^4\text{He}_\text{ex}}$$  (15.4)

$$R_{\text{ex}} = \frac{^4\text{He}_\text{is} \times R_{\text{is}} + ^4\text{He}_\text{dc} \times R_{\text{dc}} + ^4\text{He}_\text{m} \times R_{\text{m}}}{^4\text{He}_\text{is} + ^4\text{He}_\text{dc} + ^4\text{He}_\text{m}}$$  (15.6)

$$= \frac{^4\text{He}_\text{is} \times R_{\text{is}} + ^4\text{He}_\text{dc} \times R_{\text{dc}} + ^4\text{He}_\text{m} \times R_{\text{m}} + ^3\text{He}_t}{^4\text{He}_\text{ex}}$$  (15.7)

Substituting (15.7) into (15.5), gives the linear equation ($Y = mX + b$):

$$^3\text{He}_\text{s} - ^3\text{He}_\text{a} \times ^3\text{He}_\text{eq} = \left( R_{\text{eq}} - R_{\text{ex}} + \frac{^3\text{He}_t}{^3\text{He}_\text{eq}} \right) \times \frac{^4\text{He}_\text{eq} - ^4\text{He}_\text{a}}{X} + R_{\text{ex}}$$  (15.8)

In (15.8), $Y$ is the measured $^3$He/$^4$He ratio corrected for air-bubble entrainment ($R_c$), $X$ is the fraction of $^4$He in water resulting from air equilibration with respect to the total $^4$He in the sample, corrected for air-bubble entrainment, and $b = R_{\text{ex}}$ is the isotopic ratio of non-atmospheric excess-He (e.g. Weise and Moser 1987; Castro et al. 2000).

In order to identify the addition of extraneous He in a given suite of groundwater samples, it is useful to plot $Y$ vs. $X$ (as defined above) for each groundwater sample. This helium-isotope-evolution plot presents the evolution of the groundwater systems from recharge conditions, where, after correction for air-bubble entrainment, all of the dissolved He is from air-equilibration [$^4\text{He}_\text{eq}/(^4\text{He}_\text{s} - ^4\text{He}_\text{a}) \approx 1$], to conditions dominated by crustal and/or mantle contributions, in which air-equilibrated He is a small fraction of the total He [$^4\text{He}_\text{eq}/(^4\text{He}_\text{s} - ^4\text{He}_\text{a}) < 0.05$]. This $Y$ vs. $X$ plot is used to estimate: (1) $R_{\text{ex}}$ (the $Y$-axis intercept) which is the isotopic ratio of non-atmospheric excess-He (including deep crustal and mantle fluxes), and (2) the possible contribution of
tritiogenic $^3\text{He}$ (related to the gradient “m”) which is diagnostic of groundwater recharged since 1953.

A linear regression of the dataset provides the excess-helium ratio ($R_{\text{ex}}$), which is the Y-intercept. The gradient (m) of the regression line represents the decay of tritium and subsequent production of $^3\text{He}$ in the groundwater samples. When using this plot, it is a useful reference to include the evolutionary trajectory representing the addition of radiogenic He (with the $^3\text{He}/^4\text{He}$ ratio of $\sim 0.02 \text{ R_A}$) to air-saturated water (ASW). If samples plot along the radiogenic He-ASW trajectory, this indicates that the flux of He into such groundwater systems is dominated by radiogenic “crustal” $^4\text{He}$ production, which is typical of stable continental platforms (e.g. Torgersen and Clarke 1985; Torgersen and Clarke 1987; Ballentine et al. 2002; Kulongoski et al. 2008). If samples plot above the radiogenic He-ASW trajectory, then additional $^3\text{He}$ has been added to the groundwater, and may be explained by: (1) a contribution of $^3\text{He}$ from anomalous concentrations of lithium in crustal materials and production of $^3\text{He}$ via the $^6\text{Li}(n, \alpha)^3\text{H}(\beta^-)^3\text{He}$ reaction, (2) mixing of older groundwater with young (nuclear-bomb produced) tritiated water, and/or (3) a contribution from a mantle-derived He flux (Table 15.1).

One or all of these sources of extraneous $^3\text{He}$, however, may be discounted on the basis of aquifer composition or regional geology. The production of $^3\text{He}$ from the reaction involving thermal neutron capture by lithium ($^6\text{Li}(n, \alpha)^3\text{H}(\beta^-)^3\text{He}$) within the aquifer is negligible if the lithium concentration in the aquifer is low (Andrews 1985). Groundwater that recharged prior to extensive nuclear weapons testing in the 1960s will not contain excess $^3\text{He}$ from the decay of nuclear bomb-derived $^3\text{H}$. Indeed, relatively young, nuclear-bomb tritiated water with elevated $^3\text{He}/^4\text{He}$ ratios would plot towards the right-hand-side of the helium-isotope-evolution plot (i.e., $^4\text{He}_{\text{eq}}/(^4\text{He}_{\text{eq}}-^4\text{He}_\text{a}) \rightarrow 1$). If the sample $^3\text{He}/^4\text{He}$ ratio ($R_a$) reflects radiogenic helium, i.e., no extraneous $^3\text{He}$ is measured, then a mantle-derived He contribution may be discounted.

15.3.2.1 Case Studies: Uluru Basin, Australia and Mojave Desert, USA

An example of the use of the helium-isotope-evolution plot is shown in Fig. 15.1, where helium results from groundwater samples from the Uluru Basin, Northern Territory, Australia (Kulongoski et al. 2008) and the Eastern Morongo Basin, California, USA (Kulongoski et al. 2005) are plotted together. As a reference, the evolutionary trajectory representing the addition of radiogenic helium (0.02 R_A) to air saturated water (ASW) (line labeled “a”) is also included, as is a line representing the addition of 10% mantle helium and $^3\text{He}$ from the decay of 4.8 TU of tritium (line labeled “d”).

A linear regression of the Uluru Basin dataset (red squares) gives the equation $Y = 17.5X + 0.07$ ($r^2 = 0.99$) and is labeled as line “b”. The intercept (of line “b”) with the Y-axis is $0.07 \times 10^{-7}$ (0.005 R_A), which is consistent with in situ radiogenic production of He. The Uluru groundwater samples consistently plot along the radiogenic He-ASW trajectory line “a”, from which we conclude that $^3\text{He}_\text{em}$, $^3\text{He}_\text{et}$, and $^3\text{He}_\text{is}$ contribute negligible amounts of helium-3 to the Uluru Basin groundwater system, and the Uluru groundwater basin is dominated by production of radiogenic “crustal” He. Uluru Basin $R_{\text{ex}}$ values are also consistent with the He production ratio of between 2.2 and 3.3 $\times 10^{-8}$ (0.016–0.024 R_A) calculated by Torgersen and Clarke (1987) for the Hooray Sandstone in eastern Australia. The gradient ($m = 17.5$) of line “b” reflects the complete decay of approximately 1.8 tritium units (TU) (1 TU = 1 atom of T in $10^{18}$ atoms of H; upon decay, 1 TU yields $2.5 \times 10^{-15}$ cm$^3$ STP $^3\text{He}$ g$^{-1}$ H$_2$O); this represents the background tritium value in the Uluru Basin.

In contrast, all of the Eastern Morongo Basin (EMB) samples (blue circles) plot above the radiogenic He–ASW trajectory (line “a”). A linear regression of the EMB data produces the following equation $Y = 11.8X + 4.4$, ($r^2 = 0.76$), and is labeled line “c” in Fig. 15.1. Significantly, the intercept of line “c” with the Y-axis occurs at 0.32 R_A. This value ($R_{\text{ex}}$) is considerably greater than expected for in situ radiogenic production of helium. As stated above, there are three possibilities to explain the observation of the apparently high value of the $^3\text{He}/^4\text{He}$ excess: (1) a contribution of $^3\text{He}$ from the $^6\text{Li}(n, \alpha)^3\text{H}(\beta^-)^3\text{He}$ reaction in crustal materials, (2) mixing of older groundwater with younger nuclear-bomb tritiated water, and/or (3) a contribution from a mantle-derived helium flux.

The production of $^3\text{He}$ from the reaction involving thermal neutron capture by lithium ($^6\text{Li}(n, \alpha)^3\text{H}(\beta^-)^3\text{He}$) may be dismissed due to the unrealistically
large concentrations of lithium (>850 ppm Li) which would be necessary in aquifer rock to produce the observed $^{3}$He/$^{4}$He ratio (0.32 $R_A$). Assuming a lithium content of ~50 ppm, an upper limit for a typical sedimentary lithology (Andrews 1985; Ballentine and Burnard 2002), the calculated $^{3}$He/$^{4}$He production ratio in the rock would be $2.59 \times 10^{-8}$ or 0.02 $R_A$ (Kulongoski et al. 2003).

For groundwater residence times >50 years, no excess nuclear-bomb tritium is expected. The groundwaters sampled in this study have helium and/or $^{14}$C-derived residence times significantly greater than 50 years. The gradient of the linear-regression of EMB data, 11.8, is consistent with complete decay of 4.8 tritium units (TU); this represents the background tritium value in the EMB. If the background tritium value is taken as 4.8 TU, this would produce $1.2 \times 10^{-14}$ cm$^3$ STP $^{3}$He g$^{-1}$ H$_2$O. For EMB ground-water samples older than 50 years, $^{3}$He concentrations are significantly higher, ranging from 2 to $1,150 \times 10^{-14}$ cm$^3$ STP $^{3}$He g$^{-1}$ H$_2$O (Table 15.1); therefore, the decay of nuclear “bomb” produced tritium should represent a negligible contribution to the total measured $^{3}$He.

By default, we conclude that the high $R_{ex}$ in the EMB groundwaters results from an influx of mantle-derived helium-3 ($^{3}$Hem). Using the regression value of 0.32 $R_A$ we can estimate that the average contribution of mantle He is 4.6% of the total helium, assuming a simple binary mixture of mantle ($R_m \sim 8 R_A$) and crustal ($R_{dc} \sim 0.02 R_A$) components. Although the sub-continental lithospheric mantle have a lower end-member composition (e.g. 6 $R_A$; Dunai and Porcelli 2002), this would make a small difference only to the calculated fraction of mantle-derived He in any given sample.
15.3.3 Excess Helium and the Utility of Helium Isotopes in Groundwaters

In this section, we report on the utility of He studies of groundwater systems. The list is by no means exhaustive but is meant to illustrate recent applications of He geochemistry to issues of groundwater chronology, crustal degassing, and the role of faulting in loss of mantle-derived volatiles to the atmosphere. The approach is predicated on successfully resolving observed He isotope and abundance variations into component structures, as discussed above.

15.3.3.1 Radiogenic Helium Produced In Situ: Chronological Applications

Radiogenic helium is produced by $\alpha$-decay of U- and Th-series nuclides in crustal minerals, and accumulates in groundwater. The accumulation rate ($^{4}$He$_{sol}$) of radiogenic $^{4}$He in groundwater can be quantified based on the U and Th content and the porosity of the aquifer (e.g. Andrews and Lee 1979; Torgersen 1980; Stute et al. 1992; Castro et al. 2000):

$$^{4}\text{He}_{sol} = \rho \times \Lambda \times \left\{ 1.19 \times 10^{-13} [U] + 2.88 \times 10^{-14} [\text{Th}]\right\} \times \frac{(1 - \phi)}{\phi} \quad (15.9)$$

In (15.9) $^{4}$He$_{sol}$ is the rate of $^{4}$He accumulation (the $^{4}$He solution rate in cm$^3$ STP g$^{-1}$ H$_2$O a$^{-1}$); $\Lambda$ is the fraction of He produced in the rock that is released into the water phase – this is assumed to be unity (Andrews and Lee 1979); and $\rho$ is the bulk density of the aquifer material. The $^{4}$He production rates from U and Th decay are $1.19 \times 10^{-13}$ cm$^3$ STP $^{4}$He $\mu$g$^{-1}$ a$^{-1}$ and $2.88 \times 10^{-14}$ cm$^3$ STP $^{4}$He $\mu$g$^{-1}$ a$^{-1}$, respectively (Andrews and Lee 1979). The U and Th concentrations ([U] and [Th]) in the aquifer material (ppm) and the fractional effective porosity ($\phi$) of the aquifer material are measured parameters.

If the accumulation of excess He ($^{4}$He$_{ex}$) in groundwater can be attributed solely to in situ production, then the He age of the groundwater may be estimated by dividing the excess $^{4}$He ($^{4}$He$_{ex}$) by the solution rate ($^{4}$He$_{sol}$) (e.g. Andrews and Lee 1979; Marine 1979). However, we caution that excess He may also be introduced to groundwater reservoirs from a basal flux, in which case it is necessary to account for this He flux in order to calculate realistic groundwater ages (Heaton 1984; Torgersen and Clarke 1985). This topic is considered next. However, we note that in addition to its utility for calibrating He residence times, the flux of He from either continental or mantle degassing also may be used to model constraints on the chemical and thermal evolution of the Earth (e.g. O’Nions...
and Oxburgh 1988), and/or examine the transport mechanism of volatiles through the crust (e.g. Torgersen 1993; Kulongoski et al. 2003; 2005).

15.3.3.2 Deep Crustal Helium: Crustal Fluxes

If a basal flux contributes He to a groundwater system, it may be quantified if the groundwater age is known by an independent method (e.g. C-14 chronology). Conversely, the He groundwater age may be determined if the basal flux is known. The corrected groundwater residence time ($\tau_{corr}$) can be calculated from the following equation (e.g. Heaton 1984; Torgersen and Clarke 1985):

$$\tau_{corr} = \frac{4\text{He}_{ex}}{\frac{J_0}{\phi z_0 \rho_w} + 4\text{He}_{sol}}$$ (15.10)

In (15.10), $4\text{He}_{ex}$ has units of cm$^3$ STP He g$^{-1}$ H$_2$O, $J_0$ (cm$^3$ STP He cm$^{-2}$ a$^{-1}$) is the basal flux, $\phi$ is the effective fractional porosity of the aquifer, $z_0$ is the depth (cm) at which this flux enters the aquifer, and $\rho_w$ is the density of water ($\sim$1 g cm$^{-3}$). In many cases, $z_0$ may be estimated as the distance from the middle of the perforations in the well casing to the interface between the aquifer and the basement formation (Kulongoski et al. 2003; 2005).

In order to determine the basal flux of He ($J_0$) and improve the sensitivity of the $^4$He chronometer, it is useful to plot the $^4$He residence times (age) vs. ages derived by alternative methods (such as $^{14}$C, $^{36}$Cl, or hydrologically derived age). Different values of the basal flux are assumed in order to search for concordance between $^4$He and other age-dating techniques. Values of $3 \times 10^{-8}$ cm$^3$ STP cm$^{-2}$ a$^{-1}$ represent a low basal flux of He, in comparison with fluxes recorded from various aquifers worldwide (see Table 15.1). Groundwater chronometry studies typically investigate aquifers with simple flow systems in which groundwater residence time increases along a confined flow path. Calibration of the flow systems may be made by comparing $^4$He and $^{14}$C or $^{36}$Cl-derived ages.

Observations of high He concentrations in the basal layer of aquifers (e.g. the Great Artesian Basin; Torgersen and Clarke 1985), coupled with numerical models of groundwater flow incorporating advective mass transport (Bethke et al. 1999), indicate that the distribution of helium in aquifer systems must also have vertical structure, owing to the basal He flux, in addition to horizontal “plug-piston” flow (Zhao et al. 1998). Introduction of the basal flux may occur by diffusion from crystalline basement followed by entrainment and upward migration, particularly as the discharge region is approached (Bethke et al. 2000).

Case Study: Alice Springs, Australia

The following example shows how He can be utilized for groundwater dating purposes. Helium residence times (ages) were calculated for a suite of samples from Alice Springs, Australia assuming $\phi = 0.15$, $\rho = 2.6$ g cm$^{-3}$, $[U] = 1.7$ ppm, $[\text{Th}] = 6.1$ ppm (15.9), and $\text{He}_{sol} = 3.93 \times 10^{-12}$ cm$^3$ STP He g$^{-1}$ H$_2$O a$^{-1}$ (Kulongoski et al. 2008). In Fig. 15.2, we plot calculated mean ages derived from $^4$He, $^{14}$C and $^{36}$Cl for a range of basal fluxes of $^4$He, from zero to $3 \times 10^{-8}$ (units of cm$^3$ STP He cm$^{-2}$ a$^{-1}$). The straight lines (1:1 reference line) would indicate concordance in ages between the various chronometers.

The He ages of the youngest Alice Springs samples show concordance between $^4$He, $^{14}$C, $^{36}$Cl derived ages when zero or low $J_0$ values ($0-3 \times 10^{-8}$ units of cm$^3$ STP He cm$^{-2}$ a$^{-1}$) are adopted (Fig. 15.2). This observation agrees with findings by other workers that relatively young groundwaters (<50 ka) are dominated by in situ He production, rather than a basal flux (e.g. Torgersen and Clarke 1985). However, a larger basal He flux ($3 \times 10^{-8}$ cm$^3$ STP He cm$^{-2}$ a$^{-1}$) would be required for the $^4$He ages of the older groundwaters to approximate the $^{14}$C ages. $^{36}$Cl-derived ages do not require a larger basal flux for agreement with $^4$He ages, suggesting that they may also overestimate groundwater ages. The presence of a basal flux in the majority of the groundwater samples suggests that these aquifers accumulate He from a diffusive process rather than from a localized (deep) source, such as faults. It would appear that the stable cratonic continental platform of central Australia, therefore, may limit any trans-crustal flux or mantle-derived volatiles into aquifers of the region.

15.3.3.3 Tritiogenic Helium-3: Chronological Applications

The use of tritium ($^3$H), combined with its daughter isotope, helium-3 ($^3$He$_t$), to study groundwater flow
was first proposed by Tolstikhin and Kamenskiy (1969). However, widespread adoption of the $^3$H–$^3$He method occurred only following the analytical advance of measuring $^3$H by the $^3$He in-grow method (Clarke et al. 1976). Early studies of marine and lacustrine systems made use of this technique (e.g. Jenkins and Clarke 1976; Kipfer et al. 2002; Schlosser and Winckler 2002). A decade later, the calculation of groundwater residence times (ages) using $^3$H–$^3$He dating was made possible when the fraction of $^3$He derived directly from tritium decay ($^3$He$_t$) could be successfully resolved from other sources (e.g. Takaoka and Mizutani 1987; Poreda et al. 1988; Schlosser et al. 1988; Schlosser et al. 1989). Determination of water residence times in lakes and groundwater by $^3$H–$^3$He dating is now used extensively to study transport and mixing processes.

The $^3$H–$^3$He method provides a quantitative determination of groundwater residence time based on the accumulation of the inert gas $^3$He$_t$, the $\beta$-decay product of tritium decay. As mentioned previously, tritium ($^3$H) is a short-lived radioactive isotope of hydrogen with a half-life of 12.32 years. $^3$H is produced naturally in the atmosphere from the interaction of cosmogenic radiation with nitrogen (Craig and Lal 1961), by above-ground nuclear explosions, and by the operation of nuclear reactors. Following the release of large amounts of tritium into the atmosphere from nuclear-bomb testing in the 1950s and 1960s, the International Atomic Energy Agency (IAEA) implemented a global monitoring program of tritium in precipitation, with the result that tritium has been used extensively as a tracer in hydrology studies (International Atomic Energy Association 1983; 1986; Hong et al. 2011).

Fig. 15.2 Alice Springs $^4$He vs. $^{14}$C and $^{36}$Cl/Cl groundwater residence times. Plots of corrected $^4$He Alice Springs groundwater residence times (porosity $\phi = 0.2$) vs. $^{14}$C derived and $^{36}$Cl/Cl derived residence times, for three basal fluxes ($J_o = 0, 3 \times 10^{-8},$ and $30 \times 10^{-8}$ cm$^3$ STP He cm$^{-2}$ a$^{-1}$). Un-shaded areas represent the windows of applicability for $^{14}$C (a, c, e) and $^{36}$Cl/Cl (b, d, f). From Kulongoski et al. (2008)
As tritium forms an intrinsic part of a water molecule within a groundwater system, the daughter product ($^3$Het) remains dissolved in solution following decay of the parent. Thus, the tritium-helium clock starts when $^3$Het begins accumulating from the decay of $^3$H. The time that the water has resided in the aquifer can be calculated by determining $^3$Het. This technique, based on the ratio $^3$H/$^3$Het, is more precise than using tritium alone because it does not depend on the tritium input function or the atmospheric tritium content at the time of recharge. Instead, the $^3$H–$^3$He method is based on the assumption that groundwater is a closed system, and the $^3$Het/$^3$H ratio increases predictably as a function of time. Thus, the calculated $^3$H–$^3$He age only depends upon the initial $^3$H activity and measurement of its daughter product $^3$Het, which must be resolved from the total $^3$He dissolved in groundwater (Takaoka and Mizutani 1987; Poreda et al. 1988; Schlosser et al. 1988; Schlosser et al. 1989).

15.3.3.4 Mantle-Derived Helium: Identification, Quantification, and Geologic Significance

The contribution of mantle-derived He to the total He in a groundwater sample may be identified by resolving the measured He concentration into its various components, and then quantified by assuming a binary mantle-crust mixture with end-member compositions (mantle = 8 RA, crust = 0.02 RA). In this way, it is possible to compute the absolute concentrations of He ($^4$He and $^3$He) contributed by each end-member. The crustal and mantle helium contributions can provide information about the evolution of the groundwater since recharge as well as associated geological processes.

High $^3$He/$^4$He ratios (i.e., values greater than crustal production ratios), indicative of a mantle-derived input of He, are often found in close proximity to specific geological features such as volcanic systems and major faults, or associated with regions of high heat flow such as regions of crustal extension or where there is magmatic activity. In such cases, mantle-derived $^3$He measured in groundwater may be used to explore mantle-crust interaction processes including mechanisms of volatile transfer into and through the crust (Table 15.1). For example, Kennedy et al. (1997) showed that high $^3$He/$^4$He ratios (up to ~4 RA) in groundwater proximal to the San Andreas Fault (SAF) in California could be used to estimate the transport rate of mantle fluids through the crust. By assuming that measured values reflect the dilution of mantle helium ($R_m = 8$ RA) with crustal (radiogenic) helium ($R_{dc} = 0.02$ RA), they calculated that an upward flow rate of 1–10 mm year$^{-1}$ is necessary to maintain observed ratios assuming steady-state production and release of crustal He. This range was considered a lower limit, since hydrodynamic dispersion, the effects of mixing between fault fluids and radiogenic crustal fluids, or episodic flow events were not taken into account. For a crustal thickness of 30 km, and a flow rate of 10 mm year$^{-1}$, it would require nearly 3 Ma for mantle fluids to reach the surface. Over the same time period, He would be expected to move only ~1 m by diffusion through bulk granite ($D_{He} = 5 \times 10^{-7} \text{ m}^2 \text{ a}^{-1}$; (Ballentine and Burnard 2002)) or ~300 m by diffusion through groundwater ($D_{He} = 0.03 \text{ m}^2 \text{ a}^{-1}$; (Ballentine and Burnard 2002)), thus emphasizing the important role of advection in the transport of mantle helium through the crust.

Adveective flow of (deep) crustal fluids containing mantle-derived He, particularly in the vicinity of faults, implies that the Eastern California Shear Zone (ECSZ) extends to considerable depths, possibility into the lowermost crust. Episodic fracturing and subsequent fluid flow is a likely mechanism to enable the transfer of mantle volatiles through the brittle-ductile boundary – estimated at a depth between 10 and 15 km for typical crustal thermal gradients – and towards the surface (Nur and Walder 1990; Rice 1992; Kennedy et al. 1997). On the other hand, if faults in the ECSZ are limited to relatively shallow depths, by a mid-crustal decollement for example (e.g. Webb and Kanamori 1985; Jones et al. 1994), then their role would be to transport volatiles from the decollement to the surface. In this case, faults would act as conduits, and fault activity would regulate the release of accumulated $^3$He$_m$ (and $^4$He$_{dc}$) into the shallow crust.

Case Study: The Influence of Faults and Seismic Activity in the East Morongo Basin (EMB)

In this section, we review the role of faults – their surface distribution and activity – in controlling the
distribution of $^{3}\text{He}_m$ and $^{4}\text{He}_{dc}$ concentrations in groundwaters of the Eastern Morongo Basin (EMB) (Kulongoski et al. 2005).

The presence of faults, particularly if they lead to greater permeability in the fault zone, should act to channel He fluxes to the surface. If this is the case, then wells in close proximity to faults should have groundwater with associated high $^{3}\text{He}_m$ (and $^{4}\text{He}_{dc}$) fluxes as a result of relatively rapid transport of helium and other mantle and/or deep-crustal derived volatiles via the fault zone. In the EMB, wells located near the Emerson, Elkins, and Lavic Lake-Bullion Faults have relatively high $^{3}\text{He}_m$ concentrations; however, wells sampled near the Hidalgo-Surprise Springs Fault Zone (Fig. 3), show no evidence of high concentrations of $^{3}\text{He}_m$. This leads to the conclusion that the presence of faults alone does not necessarily lead to enhanced transport of deep crustal and mantle fluids.

Intermittent fault activity or episodic fault rupture (Nur and Walder 1990) may be a contributory factor why $^{3}\text{He}_m$ fluxes vary between sites either close to one another or close to faults. In this scenario, pore fluid pressure in the fault zone could increase until it reaches the level of the least compressive stress in the crust, whereby it would induce hydraulic fracturing and fluid release: this would then be followed by a drop in pore pressure and resealing of the system (Nur and Walder 1990). Local hydro-fracturing, induced by fluid pressure increases (e.g. from porosity reduction, dehydration, vertical fluid fluxes), could create local inter-connected networks allowing fluid flow (Miller and Nur 2000). Such localized networks may explain variations in observed $^{3}\text{He}_m$ accumulation and mantle flux rates throughout the EMB. It should be noted that significant time periods (Ma) are necessary for advective transport of $^{3}\text{He}_m$ from the mantle to the shallow crust; therefore, it is unlikely that an individual rupture event would result in instantaneously high $^{3}\text{He}_m$ groundwater concentrations, unless these faults directly tapped a shallow reservoir containing $^{3}\text{He}_m$ (Sano 1986; Gulec et al. 2002). However, the cumulative activity (slip) along faults may facilitate transfer and transport of volatiles from the mantle to the crust over geologic time scales, resulting in a heterogeneous distribution of $^{3}\text{He}_m$, as observed in the EMB. In this respect, it is informative to consider the recent seismic record for the EMB region.

Recent seismic activity in the EMB includes the rupture of the Emerson Fault during the 1992 Landers earthquake, and rupture of the Lavic Lake-Bullion Fault (LLBF) during the 1999 Hector Mine earthquake. Significantly, the highest concentrations of $^{3}\text{He}_m$ are observed at sites near the terminus of the 1999 rupture of the LLBF and in wells near the Emerson Fault (Fig. 15.3). These observations are consistent with the model of episodic hydrofracture-induced flow enhancing the transfer of mantle volatiles to the shallow crust.

Groundwaters in the EMB that contain relatively high concentrations of $^{3}\text{He}_m$ are also observed to have high concentrations of crustal (radiogenic) helium ($^{4}\text{He}_{dc}$). The relation between high $^{4}\text{He}_{dc}$ and $^{3}\text{He}_m$ concentrations suggests a similar transport mechanism for the two components through the crust (Ballentine et al. 1991), and may be attributed to increased permeability through the active fault zone. Transmission of mantle and deep crustal fluid/gas through fault zones by episodic fracturing would then represent a plausible mechanism for enhanced helium transport through the crust (Kulongoski et al. 2005).

### 15.4 Future Prospects

It is becoming increasingly clear that the presence of crustal faulting plays an important role in the transfer of mantle-derived He, and other volatiles through the crust (see discussion in Hilton (2007)). Faults serve as high permeability conduits for fluids as they traverse the crust-mantle transition zone. In turn, this implies that such fluids must exist at extremely high pressures – in order to maintain open pathways during volatile transport. As discussed above, little is known concerning the nature of the flow regime – be it continuous or episodic – so it is difficult to relate spatial variability of groundwater $\text{He}_m$ or $\text{He}_{dc}$ signals to the location of high permeability zones such as faults. Recent studies have sought to address this issue by adapting or developing instrumentation to collect groundwater and other fluid samples over prolonged time periods to assess temporal variability in the He isotope and abundance record.
15.4.1 Submarine Studies Using Fluid Flow Meters

The Extrovert Cliffs site in Monterey Bay, California is situated close to several active strike-slip faults, including the Monterey and San Gregorio fault zones, and has many cold seeps located at ~1,000 m depth below sea level. By adapting instrumentation designed to measure diffuse fluid fluxes on the seafloor (Tryon et al. 2001), Furi et al. (2009) were able to capture dissolved gases in emanating cold seep fluids over deployment intervals up to 3 weeks.

As illustrated in Fig. 15.4, the measured helium and neon concentrations ($^{4}\text{He}_m$ and $^{20}\text{Ne}_m$) were found to show remarkable fluctuations, on time-scales of only a few hours. In addition, the isotopic composition of the dissolved He also varied. For example, measured and terrigenic (crust + mantle) $^{3}\text{He}/^{4}\text{He}$ ratios increased from 1.2 to 1.5 $R_A$ within just 2.5 h (e.g. at $t = 455$ h). A maximum increase from 0.9 to 1.75 $R_A$ is observed in the data record with the lower time-resolution (at $t = 517$ h). As discussed by Furi et al. (2009), temporal variations in dissolved gas characteristics (isotopes and concentrations) can be influenced by interaction with a hydrocarbon phase within the aquifer. In spite of this complicating process, it was still possible to resolve the He signal into component structures associated with air-equilibration, excess-air entrainment, and terrigenic fluxes (both crustal and mantle-derived). Indeed, the mantle He contribution is mostly 20–30% (up to 2.3 $R_A$), with a short duration spike of 60% mantle He.

Fig. 15.3 Concentration of excess $^{3}\text{He}$ measured in Eastern Morongo Basin, California groundwater samples. Also shown is the gravimetric depth to basement in grey-shading, regional faults, and region of high thermal anomaly, from Kulongoski et al. (2005)
Significantly, the correlation of high \(^3\)He/\(^4\)He ratios with a transient pulse in the flow rate at Extrovert Cliff (Fig. 15.4e) indicates that the release of mantle-derived fluids is episodic and cannot be explained solely by hydrostatic pressure changes due to the variable tidal load (Fig. 15.4f). In this respect, the controlling factor is likely episodic fracturing in the San Gregorio or Monterey Bay fault zones. This is consistent with the notion of continuous ascent of mantle-derived fluids through the crust, increasing pore fluid pressure until it overcomes the least principal stress, resulting in hydrofracturing and release of fluids (e.g. Nur and Walder 1990).

15.4.2 On-Land Studies: SPARTAH Instrumentation

Barry et al. (2009) reported a new approach to sampling groundwater from land-based groundwater and...
geothermal wells through development of a new instrument for the continuous collection of water samples over prolonged periods, up to ~6 months. The instrument is dubbed SPARTAH (Syringe Pump Apparatus for the Retrieval and Temporal Analysis of Helium). Motivation for the development of SPARTAH came, in part, through He monitoring studies in seismically-active regions of the crust (e.g. Hilton 1996; De Leeuw et al. 2010) whereby collection of samples took place at regular frequencies of ~3 months. However, in some instances (e.g. Italiano et al. 2001), variations in the monitored He record could occur at comparable or shorter frequencies and so would be missed by adoption of a fixed (and regular) sampling regimen.

The SPARTAH device consists of an off-the-shelf programmable syringe pump equipped with a high-power stepper motor capable of extremely accurate and low withdrawal rates (between 0.0001 mL/h and 220 mL/min). The pump is operated in withdrawal mode whereby fluid is accurately and smoothly drawn into the syringe at a user-defined rate. Well water is drawn into the coils at a constant rate set by the syringe pump, and is independent of the pumping rate of the well. The only stipulation is that the well operates continuously so that air is not entrained into the coils. At any time during a deployment, the tubing can be isolated by closing shut-off valves, and disengaged (for transfer to the laboratory) or replaced to extend the duration of sampling.

SPARTAH was successfully tested at two locations: Selfoss, Iceland and San Bernardino, California (Fig. 15.5). These test deployments demonstrated that well fluids could be drawn smoothly, accurately, and continuously into the Cu-tubing and be time-stamped through user-determined operating parameters. As discussed by Barry et al. (2009), the use of SPARTAH has the potential to revolutionize studies relying on time-series records of dissolved He variations. It has a number of advantages over periodic sampling. Briefly, these include long, maintenance-free deployment times (6 months or more) with continuous sampling, user defined sample resolutions (i.e., sections of coil representing a fixed number of hours or days can be selected for analytical work), and accurate time-stamping of water aliquots due to constant withdrawal rates. Finally, it should be noted that the use of SPARTAH is not restricted to He or any other dissolved gas. The Cu-tubing can be sectioned and processed for various trace elements, stable isotopes or

![Graph](image-url)

**Fig. 15.5** Helium isotope variations captured in the SPARTAH Cu-coils at Selfoss, Iceland (1-week deployment) and San Bernardino, California (1-month deployment). *Note: helium is mainly mantle-derived in Selfoss but is predominantly crustal in origin at San Bernardino. Individual error bars are given at the 2σ level. The mean $^3$He/$^4$He values for Selfoss (black) and San Bernardino (red) are illustrated by dashed lines (Barry et al. 2009).**
any other intrinsic water property of interest. Thus, innovative analytical processing could lead to contemporary records of different tracers, enabling assessments of relative sensitivities to external perturbations. Deployment of SPARTAH at strategically-placed locations can lead to more detailed and accurate assessments of the responses of He and other geochemical parameters to external forcing factors, such as earthquakes.

Acknowledgements We thank Mark Baskaran for the invitation to contribute this review chapter. We acknowledge funding from the National Science Foundation, U.S. Geological Survey, and Scripps Institution of Oceanography.

References

Clarke WB, Beg MA, Craig H (1969) Evidence for primordial He (super 3) in the earth. EOS, Transactions, American Geophysical Union 50:222


Tolstikhin IN (1975) Helium isotopes in the Earth’s interior and in the atmosphere; a degassing model of the Earth. Earth Planet Sci Lett 26:88–96

304 J.T. Kulongoski and D.R. Hilton