Tracing the migration of mantle CO$_2$ in gas fields and mineral water springs in south-east Australia using noble gas and stable isotopes

Rūta Karolytė$^1$$^*$, Gareth Johnson$^1$, Domokos Györe$^2$, Sascha Serno$^1$, Stephanie Flude$^1$, Finlay M. Stuart$^3$, Allan R. Chivas$^{3,4}$, Adrian Boyce$^2$ and Stuart M.V. Gilfillan$^1$

1 School of GeoSciences, University of Edinburgh, James Hutton Road, Edinburgh, EH9 3FE, UK
2 Isotope Geoscience Unit, Scottish Universities Environmental Research Centre (SUERC), East Kilbride, G75 0QF, UK
3 GeoQuEST Research Centre, School of Earth, Atmospheric and Life Sciences, University of Wollongong, Wollongong, NSW 2522, Australia
4 Department of Earth Sciences and Sprigg Geobiology Centre, The University of Adelaide SA 5005, Australia

$^a$Current address: Department of Earth Sciences, University of Oxford, 3 S Parks Rd, Oxford OX1 3AN, UK
$^*$Author for correspondence: ruta.karolyte@earth.ox.ac.uk

Keywords: Carbon Capture and Storage; geochemical tracing; noble gases; carbon isotopes; helium; mantle; CO$_2$ springs; solubility fractionation; Otway Basin.

Abstract

Geochemical monitoring of CO$_2$ storage requires understanding of both innate and introduced fluids in the crust as well as the subsurface processes that can change the geochemical fingerprint of CO$_2$ during injection, storage and any subsequent migration. Here, we analyse a natural analogue of CO$_2$ storage, migration and leakage to the atmosphere, using noble gas and stable isotopes to constrain the effect of these processes on the geochemical fingerprint of the CO$_2$. We present the most comprehensive evidence to date for mantle-sourced CO$_2$ in south-east Australia, including well gas and CO$_2$-rich mineral spring samples from the Otway Basin and Central Victorian Highlands (CVH). $^3$He/$^4$He ratios in well gases and CO$_2$ springs range from 1.21 to 3.07 R$_A$ and 1.23 – 3.65 R$_C$/R$_A$, respectively. We present chemical fractionation models to explain the observed range of $^3$He/$^4$He ratios, He, Ne, Ar, Kr, Xe concentrations and $\delta^{13}$C(CO$_2$) values in the springs and the well gases. The variability of $^3$He/$^4$He in the well gases is controlled by the gas residence time in the reservoir and...
associated radiogenic $^4$He accumulation. $^3$He/$^4$He in CO$_2$ springs decrease away from the main mantle fluid supply conduit. We identify one main pathway for CO$_2$ supply to the surface in the CVH, located near a major fault zone. Solubility fractionation during phase separation is proposed to explain the range in noble gas concentrations and $\delta^{13}$C(CO$_2$) values measured in the mineral spring samples. This process is also responsible for low $^3$He concentrations and associated high CO$_2$/$^3$He, which are commonly interpreted as evidence for mixing with crustal CO$_2$. The elevated CO$_2$/$^3$He can be explained solely by solubility fractionation without the need to invoke other CO$_2$ sources. The noble gases in the springs and well gases can be traced back to a single end-member which has suffered varying degrees of radiogenic helium accumulation and late stage degassing. This work shows that combined stable and noble gas isotopes in natural gases provide a robust tool for identifying the migration of injected CO$_2$ to the shallow subsurface.

1. Introduction

The development of geochemical tracing techniques to ascertain the origin and genetic link between natural gases trapped in subsurface reservoirs and those degassing at the surface is important to the safe and successful deployment of carbon capture and storage (CCS). Safe disposal of captured industrial CO$_2$ requires verification of the fate of the injected gas and reassurance that injected gas does not migrate to the surface (IPCC, 2005). To ensure this, CCS operators have to adhere to legislative guidelines and verify that injected CO$_2$ is securely contained within the reservoir formation (Dixon et al., 2015). While a variety of geophysical, geoelectric and thermal sensing monitoring techniques exist (Giese et al., 2009), the high sensitivity of geochemical monitoring techniques is useful for detecting seepage at low concentrations, verifying gas origin and tracing the interactions between different crustal fluids (Myers et al., 2013; Stalker and Myers, 2014; Roberts et al., 2017).

The noble gas isotopes have previously been applied in an engineered setting to assess CO$_2$ migration, dissolution and residual trapping in reservoir pore spaces at the Cranfield CO$_2$-EOR site field (Györe et al., 2015; Györe et al., 2017) and to study industrial underground natural gas storage in the Paris Basin (Jeandel et al., 2010). Noble gas tracers have been used to refute allegations of injected CO$_2$ leakage to the surface near the Weyburn-Midale CO$_2$ Monitoring and Storage Project (Gilfillan et al., 2017) and to identify fugitive gas migration to shallow aquifers caused by industrial hydraulic fracturing operations (Darrah et al., 2014). The techniques used in these industrial studies have been informed by preceding research of natural gas fields and springs (e.g. Ballentine and
Natural analogue studies remain a crucial gateway to developing geochemical tracing methods for the industrial sector, providing information about fluid migration and retention processes occurring over geological time scales (Baines and Worden, 2004; Haszeldine et al., 2005; Holland and Gilfillan, 2013).

Helium is an unrivalled indicator of crustal fluid migration in the subsurface because it is sensitive to changes in the balance between volatiles derived from the mantle and the crust. This is because the original helium composition of any subsurface fluid is not significantly modified by interaction with groundwater due to the low abundance of helium in the atmosphere (Ozima and Podosek, 2002). Hence, helium is particularly applicable to tracing gas migration through a water system in both natural and industrial fugitive gas migration monitoring settings. Here we draw from existing methodologies of helium use in tracing the migration of mantle fluids (Sano et al., 1990; Sakamoto et al., 1992), mixing of different fluid sources (O’Nions and Oxburgh, 1988; Sano and Marty, 1995) and dating natural gas and groundwater resources (Zhou and Ballentine, 2006; Liu et al., 2016) to provide a comprehensive account on the geochemical link between natural CO$_2$ gases, trapped in the subsurface and emanating in the shallow surface.

Noble gases are soluble in water and partition according to their relative solubilities during gas-water equilibration. This property has been utilised mainly in assessing reservoir-scale water-gas equilibration and gas migration or groundwater recharge conditions (Bosch and Mazor, 1988; Ballentine et al., 1996; Barry et al., 2016) and the presence of ‘excess air’ above the atmospheric solubility equilibrium (Aeschbach-Hertig et al., 2008; Kipfer et al., 2002). The former is largely based on atmospheric noble gas ratios, whilst the latter combines ratios with elemental concentrations. Atmospheric noble gas ratios in CO$_2$ springs are commonly similar to air saturated-water (ASW) and the utility of these noble gases is commonly overlooked. We discuss the use of noble gas concentration data in assessing the solubility fractionation effects of near-surface degassing and reconstructing the original noble gas composition for the purpose of tracing.

The physical and chemical processes contributing to and modifying the noble gas contents of CO$_2$ are explored using the data from three natural CO$_2$ fields in the Otway Basin of SE Australia and ten natural CO$_2$-rich springs in Victoria. We focus on identifying the origin of the gases and the genetic link between gases stored in reservoir traps and those emanating at the surface from the natural mineral springs.
Geological setting

2.1 Basin setting and location of CO\textsubscript{2} gas fields and springs

The Otway Basin developed along the southern Australian margin as a result of crustal extension due to sea floor spreading between Australia and Antarctica. The sedimentary section of the basin comprises Upper Jurassic – Lower Cretaceous Otway Group sediments (Bernecker and Moore, 2003). The present geometry of the basin is characterised by NW-SE trending normal faults, and was established during Jurassic to Cretaceous rifting and subsequent reactivation during a short-lived period of basin inversion in the Miocene (Cox et al., 1995; Teasdale et al., 2003).

The basement comprises Lachlan and Delamerian fold belts, separated by the Moyston lithospheric suture which extends to the Moho (Fig. 1a). Parallel N-S trending large-scale shear zones and reverse faults connect to the Moyston Fault at depth (Fig. 1d) (Cayley et al., 2011). The structure of the Otway Basin has been strongly controlled by the fabric of the underlying basement. Old basement structures have a significant rheology contrast along them and are more likely to undergo structural reactivation during a change in the stress regime (Hand and Sandiford, 1999). The Jurassic-Cretaceous extension was mainly accommodated along structural weaknesses of the basement, which created graben and half-graben structures favourable for fluid trapping. Hydrocarbons and CO\textsubscript{2} discoveries in the Otway Basin therefore tend to coincide with the location of deep basement faults (Bernecker and Moore, 2003).

The basin contains numerous accumulations of CO\textsubscript{2}, methane and other hydrocarbons in varying concentrations (Boult et al., 2004). The three gas fields investigated in this work contain CO\textsubscript{2} concentrations above 75 mol %, with the remainder of the gas content being primarily methane. The Caroline field is located in South Australia, near Mt Gambier and is a commercially explored CO\textsubscript{2} field which has a CO\textsubscript{2} concentration in excess of 98 %. At reservoir depth and temperature (2.5 km, 92 °C), CO\textsubscript{2} is in a supercritical fluid phase (Chivas et al., 1987). Boggy Creek and Buttress fields are located in the Port Campbell Embayment at the eastern side of the Otway Basin. Both fields contain mixtures of CO\textsubscript{2} and methane in the gas phase with no significant liquid hydrocarbon component (Boreham et al., 2011). Methane generation is dated to mid-Paleogene (Duddy, 1997), followed by a later-stage CO\textsubscript{2} emplacement (Boult et al., 2004; Watson et al., 2004; Lyon et al., 2005).

CO\textsubscript{2}-rich mineral spring waters emanate at the ground surface within the extent and north of the basin. Over a hundred ambient temperature mineral springs are located in the Central Victorian Highlands (CVH) (Fig. 1b). Mineral water flows through a fracture-dominated aquifer consisting of Ordovician low-grade metasedimentary sequence and discharges into topographic lows such as...
streambeds. Many of the springs also release CO$_2$ and can be identified as degassing CO$_2$ bubble trails into creek beds or standing pools of water. Springs are clustered along the Muckleford Fault, which is a deep Proterozoic reverse fault extending down to the lower crust and connecting to the Moyston suture zone (Cayley et al., 2011) (Fig. 1d).

Mineral springs also emerge on the northern coast of Bellarine Peninsula, at Clifton Springs near Geelong, on the south-eastern edge of the Otway Basin (Fig. 1c). The central part of the Bellarine Peninsula has been uplifted in the late Miocene during the inversion of NE-SW trending normal faults (Coulson, 1933). The north coast of the peninsula is structurally controlled by the Curlew Monocline, underlain by a south dipping normal fault. The Curlew Monocline is parallel to the structural lineaments of the basement and could be associated with deeper basement faults (Dahlhaus, 2003). CO$_2$ springs emerge along the shoreline parallel to the fault.

The basement and the Otway Basin are overlain by the Newer Volcanic Province (NVP) extrusives that stretch from the CVH to the northern edges of the Port Campbell Embayment. The province is a well preserved intra-plate basaltic lava field with more than 400 eruptive centres (Boyce, 2013), active between 5 Ma and 4.5 ka (Cas et al., 2017). The last eruption dated at 4.5 ka, occurred at Mount Gambier, located near the Caroline CO$_2$ field (Robertson et al., 1996). Many of the oldest eruptive centres are found in the eastern side of the province and near the CVH (4.6 - 2.6 Ma) (Price et al., 1997), but no systematic pattern of eruption ages exists (Cas et al., 2017). There is no evidence for volcanic activity of this period in the Bellarine Peninsula where Clifton Springs are located, although The Older Volcanics (39 - 49 Ma) crop out in the area (Price et al., 1997). The cause of the recent volcanism is currently unresolved. Common theories include a mantle plume (Wellman and McDougall, 1974; Wellman, 1983), edge-driven isolated mantle convection (King and Anderson, 1998), batch-melting caused by fault reactivation (Lesti et al., 2008), or a combination of all these factors (Demidjuk et al., 2007; Davies and Rawlinson, 2014).

2.2 Previous noble gas studies of the gas fields and CO$_2$ springs

Despite the commercial exploration of CO$_2$ gas fields in the Otway Basin and springs in the CVH, studies of the CO$_2$ origins have been limited and the processes associated with the gas migration in the subsurface and to the surface are poorly understood. MORB and solar noble gas signatures have been identified in mantle xenolith samples from the Newer Volcanics (Matsumoto et al., 1997, 2002), primarily within CO$_2$-rich fluid inclusions (Matsumoto et al., 1998). Chivas et al. (1987) reported $^3$He/$^4$He values of up to 3.1 R$_A$ in the Caroline field and Caffee et al. (1999) identified the presence of primordial Xe in the field, providing evidence for a mantle source. Mantle helium has
also been reported in the Lavers-1 gas field in the Otway Basin (1.68 R/Ra) (Watson et al., 2004).

Preliminary $^{3}$He/$^{4}$He measurements of up to 3.1 R$_{a}$ have been reported in CO$_{2}$ springs at the CVH (Chivas et al., 1983) but no further study has been published. It has been suggested that the source of mantle volatiles in CO$_{2}$ springs is associated with the NVP (Lawrence, 1969), however no conclusive evidence currently exists other than geographic proximity to the eruptive centres. Prior to this work no geochemical study into the origin of the CO$_{2}$ degassing at the Bellarine Peninsula had been published.
Figure 1. Location map of the studied CO₂ gas fields and springs. a) Studied well gases are in two localities in the Otway Basin: Port Campbell Embayment and Mt Gambier. Clifton Springs are located on the eastern edge of the basin. The CVH CO₂ springs emerge from the Ordovician basement rocks in the CVH (Central Victorian Highlands). The Otway Basin and CVH are dissected by N-S trending faults. The NVP (Newer Volcanic Province) extends across both areas. b) Location of sampled CO₂ springs in CVH; many of the springs are located near the Muckleford Fault (see Table 1 for sample name abbreviations). c) Clifton Springs are located on the coast of Bellarine Peninsula, along the crest of the Curlewis.
Monocline. d) Sketch cross-section (not to scale) of A-A’ transect on Fig. 1a, showing the structural relationship between the basement and the basin. The Moyston and Mt Williams Faults extend to the Moho. Many of the basement faults (including The Muckelford fault at CVH) are inferred to be connected to the Moyston Fault at depth. Elements of the figure adapted from (Cartwright et al., 2002; Bernecker and Moore, 2003; Watson et al., 2003; Cayley et al., 2011; Cas et al., 2017).

2. Methods

2.1 Gas sampling

The reported samples are in two distinct groups: ‘well samples’ refer to produced gases collected from well heads. ‘Spring samples’ refer to sample collected at water pools and streams where CO₂ is naturally degassing. Gas samples from the natural gas fields in the Otway Basin were collected directly from producing well heads, using 9.5 mm diameter refrigeration grade copper tubing connected to a pressure regulator by plastic hosing. Bubbling gases from the springs were collected using an inverted plastic funnel placed over a bubbling vent, placed into the water column to form an air-tight seal, allowing gas to flow through plastic hose to the copper tube. Tubes were purged for 5 minutes and sealed using two steel clamps specifically manufactured for the purpose of creating a helium leak-tight cold weld seal (Holland and Gilfillan, 2013). Mineral spring water samples were collected via hand pumps, filtered through 0.45 µm pore-size filters and filled into Nalgene bottles. The temperature, pH and TDS of the water in shallow tube bores was measured in the field using a Hanna Instruments HI991300 Portable Waterproof temperature/pH/EC Meter with an accuracy of ± 0.5 °C, ± 0.01 pH and ± 1 µS/cm for temperature, pH and electrical conductivity respectively. TDS values were obtained from EC measurements using a conversion factor of 0.7 (Walton, 1989).

2.2 Laboratory procedures

All laboratory work was undertaken at the Scottish Universities Environmental Research Centre (SUERC). Copper tube samples were connected to an all-metal vacuum line, purified using VG Scienta ST22 titanium sublimation pump and ZrAl alloy getter. The isotopic composition of noble gases was measured using a MAP 215-50 mass spectrometer using techniques outlined in Györe et al. (2015). Bulk gas concentrations were measured using a Pfeiffer Vacuum QMS 200 quadrupole mass spectrometer and Hewlett Packard 5890 Series 11 Gas Chromatograph with uncertainties of ±1 %. Major gas concentrations are reported corrected for air. δ¹³(CO₂) values were determined using a VG Optima dual inlet isotope ratios mass spectrometer in dynamic mode using an internal standard (Dunbar et al., 2016). Values are reported relative to VPDB standard with uncertainties of ±0.2 ‰.
3. Results

A total of three well gas and ten spring samples were measured. Sample location, bulk gas composition, $\delta^{13}(\text{CO}_2)$ values, temperature, pH and TDS measurements are reported in Table 1. He, Ne and Ar isotope ratios, and He, Ne, Ar, Kr, Xe concentrations are reported in Table 2. The full suite of noble gases was measured in six of the CO$_2$ spring samples, while only He and Ne isotopes were measured in three well gas and four CO$_2$ spring samples.
Table 1. Details of the geographic location, bulk gas composition, $\delta^{13}$CO$_2$ values of 3 well gases and 10 CO$_2$ springs; pH, temperature and TDS measured in water from 10 mineral water bores.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Region</th>
<th>Latitude</th>
<th>Longitude</th>
<th>Bulk gas composition*</th>
<th>$\delta^{13}$C(CO$_2$)</th>
<th>Water from shallow bores</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>CO$_2$    CH$_4$   C$_2$H$_6$ C$_3$H$_8$ C$_4$H$_10$ N$_2$</td>
<td>VPDB</td>
<td>pH</td>
</tr>
<tr>
<td><strong>Well gases</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Caroline-1</td>
<td>CA</td>
<td>-37.9417</td>
<td>140.9083</td>
<td>99</td>
<td>0.9</td>
<td>0.01</td>
</tr>
<tr>
<td>Boggy Creek-1</td>
<td>BC</td>
<td>-38.5261</td>
<td>142.8245</td>
<td>87</td>
<td>10.0</td>
<td>0.1</td>
</tr>
<tr>
<td>Buttress-1</td>
<td>BU</td>
<td>-38.5167</td>
<td>142.8084</td>
<td>77</td>
<td>19.7</td>
<td>0.8</td>
</tr>
<tr>
<td><strong>CO$_2$ springs</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Taradale</td>
<td>TA</td>
<td>CVH</td>
<td>-37.1393</td>
<td>144.3500</td>
<td>&gt;99</td>
<td>–</td>
</tr>
<tr>
<td>Locarno</td>
<td>LO</td>
<td>CVH</td>
<td>-37.3113</td>
<td>144.1412</td>
<td>&gt;99</td>
<td>–</td>
</tr>
<tr>
<td>Deep Creek</td>
<td>DC</td>
<td>CVH</td>
<td>-37.3419</td>
<td>144.0733</td>
<td>&gt;99</td>
<td>–</td>
</tr>
<tr>
<td>Glenluce</td>
<td>GL</td>
<td>CVH</td>
<td>-37.1623</td>
<td>144.2225</td>
<td>&gt;99 0.1</td>
<td>–</td>
</tr>
<tr>
<td>Woolnoughs</td>
<td>WO</td>
<td>CVH</td>
<td>-37.2942</td>
<td>144.2065</td>
<td>&gt;99</td>
<td>–</td>
</tr>
<tr>
<td>Clifton Springs</td>
<td>CS</td>
<td>CVH</td>
<td>-38.1510</td>
<td>144.5659</td>
<td>&gt;99</td>
<td>–</td>
</tr>
<tr>
<td>Sutton</td>
<td>SU</td>
<td>CVH</td>
<td>-37.3480</td>
<td>144.1317</td>
<td>&gt;99</td>
<td>–</td>
</tr>
<tr>
<td>Argyle</td>
<td>AR</td>
<td>CVH</td>
<td>-37.3141</td>
<td>144.1553</td>
<td>&gt;99</td>
<td>–</td>
</tr>
<tr>
<td>Kyneton</td>
<td>KY</td>
<td>CVH</td>
<td>-37.2358</td>
<td>144.4200</td>
<td>&gt;99</td>
<td>–</td>
</tr>
<tr>
<td>Tipperary</td>
<td>TI</td>
<td>CVH</td>
<td>-37.3391</td>
<td>144.1186</td>
<td>&gt;99</td>
<td>–</td>
</tr>
</tbody>
</table>

* Bulk gas composition for Caroline-1 from Chivas et al. (1987), Boggy Creek-1 from Akbari (1992)

* from Cartwright et al. (2002)
Table 2. Noble gas concentrations and isotopic ratios for 3 well gas samples and 10 CO₂ springs.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>³He/⁴He (Rc/RA)</th>
<th>²¹Ne/²²Ne</th>
<th>²¹Ne/²²Ne</th>
<th>⁴⁰Ar/³⁶Ar</th>
<th>⁴He x 10⁶</th>
<th>²⁰Ne x 10⁵</th>
<th>⁴⁰Ar x 10⁵</th>
<th>⁸⁴Kr x 10⁵</th>
<th>¹³²Xe x 10⁹</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Well gases</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Caroline-1</td>
<td>3.07 (0.12)</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td></td>
<td>96.0 (5.0)</td>
<td>2.2 (0.1)</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Boggy Creek-1</td>
<td>1.21 (0.01)</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td></td>
<td>384.4 (18.6)</td>
<td>124.1 (5.3)</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Buttress-1</td>
<td>1.25 (0.01)</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td></td>
<td>478.8 (23.2)</td>
<td>15.4 (0.7)</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td><strong>CO₂ springs</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Taradale</td>
<td>1.23 (0.03)</td>
<td>9.73 (0.06)</td>
<td>0.030 (0.001)</td>
<td>314 (1)</td>
<td>0.195 (0.008)</td>
<td>4.0 (0.2)</td>
<td>34.3 (1.5)</td>
<td>5.3 (0.2)</td>
<td>8.2 (0.3)</td>
</tr>
<tr>
<td>Locarno</td>
<td>3.14 (0.09)</td>
<td>9.68 (0.05)</td>
<td>0.030 (0.001)</td>
<td>303 (1)</td>
<td>0.191 (0.003)</td>
<td>5.7 (0.2)</td>
<td>59.1 (2.5)</td>
<td>7.8 (0.3)</td>
<td>10.4 (0.43)</td>
</tr>
<tr>
<td>Deep Creek</td>
<td>2.45 (0.07)</td>
<td>9.92 (0.05)</td>
<td>0.029 (0.001)</td>
<td>301 (5)</td>
<td>0.190 (0.003)</td>
<td>8.9 (0.4)</td>
<td>132.3 (5.6)</td>
<td>22.8 (0.8)</td>
<td>39.5 (1.6)</td>
</tr>
<tr>
<td>Glenluce</td>
<td>1.57 (0.07)</td>
<td>9.71 (0.05)</td>
<td>0.028 (0.000)</td>
<td>308 (1)</td>
<td>0.189 (0.003)</td>
<td>163.0 (6.0)</td>
<td>1372 (58)</td>
<td>94.4 (3.5)</td>
<td>63.1 (2.6)</td>
</tr>
<tr>
<td>Woolnoughs</td>
<td>1.71 (0.07)</td>
<td>9.78 (0.06)</td>
<td>0.030 (0.001)</td>
<td>299 (1)</td>
<td>0.190 (0.003)</td>
<td>0.97 (0.04)</td>
<td>1781 (3.7)</td>
<td>86.0 (3.2)</td>
<td>79.9 (3.3)</td>
</tr>
<tr>
<td>Clifton Springs</td>
<td>1.97 (0.06)</td>
<td>9.73 (0.06)</td>
<td>0.029 (0.001)</td>
<td>323 (1)</td>
<td>0.191 (0.003)</td>
<td>42.0 (2.0)</td>
<td>128.8 (5.5)</td>
<td>22.9 (0.8)</td>
<td>29.8 (1.2)</td>
</tr>
<tr>
<td>Sutton</td>
<td>3.14 (0.03)</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>1.61 (0.05)</td>
<td>42.5 (1.5)</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Argyle</td>
<td>3.65 (0.08)</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>87.9 (2.6)</td>
<td>5502 (196)</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Kyneton</td>
<td>1.24* (0.04)</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>4.9 (0.1)</td>
<td>13834 (493)</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Tipperary</td>
<td>2.70 (0.05)</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>0.48 (0.01)</td>
<td>438.3 (8.9)</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

Concentrations are in cm³(STP)/cm³. Standard conditions are 0 °C at 1 bar.

Errors are 1σ standard deviation.

* ³He/⁴He reported uncorrected for atmospheric component due to air contamination.
3.1. Bulk gas concentrations, $\delta^{13}(\text{CO}_2)$ and water measurements

The concentration of CO$_2$ in the Buttress field is 77 % with the remainder of gas predominately constituting of CH$_4$ (19.7 %), N$_2$ (1.9 %) and traces of higher hydrocarbons (0.8 % C$_2$H$_6$, 1.1 % C$_3$H$_8$).

Bulk gas compositions for the other two well gases are taken from the literature. CO$_2$ concentration in the adjacent Boggy Creek field is slightly higher (87%) (Akbari, 1992). The Caroline field has the highest CO$_2$ concentrations of 99 % with traces of CH$_4$, N$_2$ and C$_2$H$_6$ (Chivas et al., 1987). All mineral spring gas samples were measured to be above 99 % CO$_2$ with the remainder of gas composed of noble gases. Glenluce is the only spring showing trace amounts of CH$_4$ (0.1 %). The $\delta^{13}(\text{CO}_2)$ values of the gas samples range from -9.4 to -6 ‰ in springs, and -7.6 to -4.1 ‰ in the well gases. The temperature of the water samples varies from 15.1 – 20.9 °C, pH ranges from 5.6 to 6.3 in CVH springs and 5.5 in Clifton Springs. Total dissolved solids (TDS) values range from 0.63 to 2.85 g/L.

3.2. Noble gas results

$^{3}\text{He}/^{4}\text{He}$ ratios are reported normalised to the value of air (where 1 R$_A$ is the atmospheric ratio of $1 \times 10^{-6}$). $^{3}\text{He}/^{4}\text{He}$ R$_c/R_A$ are corrected for $^{4}\text{He}$ derived from the atmospheric component, using the $^{4}\text{He}/^{20}\text{Ne}$ value of the sample following the methodology in Craig (1978). It is assumed that all $^{20}\text{Ne}$ is derived from ASW and the $^{4}\text{He}/^{20}\text{Ne}$ value of ASW at 20 °C is 0.27 (Kipfer et al., 2002).

$^{4}\text{He}/^{20}\text{Ne}$ ratios of the well gases are 4-5 orders of magnitude above the ASW value (3097-44656) and range between 0.35 and 326 in the spring samples. $^{3}\text{He}/^{4}\text{He}$ R$_c/R_A$ values differ significantly from the measured $^{3}\text{He}/^{4}\text{He}$ ratios in spring samples with $^{4}\text{He}/^{20}\text{Ne}$ ratios <10 (Woolnoughs and Tipperary). Kyneton is the only sample with significant atmospheric contamination ($^{4}\text{He}/^{20}\text{Ne}$ = 0.35) which would make the correction erroneous (Sano et al., 2006) therefore its $^{3}\text{He}/^{4}\text{He}$ value is reported uncorrected (1.24 R$_A$). The $^{3}\text{He}/^{4}\text{He}$ ratios of the remaining spring samples range from 1.23 to 3.65 R$_c/R_A$. $^{3}\text{He}/^{4}\text{He}$ ratios of well gases from the Port Campbell region are 1.21 and 1.25 R$_c$. The sample collected from the Caroline CO$_2$ field in South Australia exhibits a higher value of 3.07 R$_c$, in agreement with previous measurements (Chivas et al., 1987). All samples are compatible with two-component mixing in a $^{3}\text{He}/^{4}\text{He}$ vs $^{4}\text{He}/^{20}\text{Ne}$ plot, where variable $^{3}\text{He}/^{4}\text{He}$ end-members mix with ASW (Fig. 2).

CO$_2$/$^{3}\text{He}$ ratios of the well gases are within or below the Mid-Ocean Ridge Basalt (MORB) range of $1 \times 10^9$ to $1 \times 10^{10}$ (Marty and Jambon, 1987). This is quite distinct from the higher CO$_2$/$^{3}\text{He}$ values predicted for near $^{3}\text{He}$-free carbonates (O’Nions and Oxburgh, 1988; Sherwood Lollar et al., 1997). CO$_2$ concentrations in the spring samples are uniform, whilst CO$_2$/$^{3}\text{He}$ ratios vary over two orders of magnitude, $2.26 \times 10^9$ and $6.5 \times 10^{11}$, across the typical mantle and crustal values (Fig. 3).
Figure 2. $^3$He/$^4$He $R_A$ plotted against $^4$He/$^{20}$Ne ratios of springs and well gases. Solid lines depict binary mixing between ASW and the highest regional end-member (Argyle, 3.65 $R_A$), Caroline field and a crustal end-member (0.02 $R_A$). Black tick marks show percentage of helium from Caroline end-member in the mixture. Few springs fall close to the mixing line with the Caroline field, the remaining samples have variable amounts of crustal component. The errors are smaller than the symbols. Abbreviations of sample names are given in Table 1.
Figure 3. CO$_2$/He ratios plotted against CO$_2$ concentrations for the well gases (yellow circles) and CO$_2$ springs (black circles). The shaded area shows the range of CO$_2$/He values in the mantle (Marty and Jambon, 1987) and crustal (O’Nions and Oxburgh, 1988) sourced volatiles. Well gas samples are within the mantle range but with positive correlation between CO$_2$/He ratios and CO$_2$ concentrations. CO$_2$ concentrations are uniform in the spring samples, however CO$_2$/He ratios are wide-ranging across the typical mantle and crustal values. Vertical errors are smaller than symbols. Abbreviations of sample names are given in Table 1.

Neon, argon, krypton and xenon concentrations were measured in six CO$_2$ spring samples (Taradale, Locarno, Deep Creek, Glenluce, Woolnoughs and Clifton Springs) (Table 2). $^{20}$Ne/$^{22}$Ne ratios of the spring samples range between 9.68 ± 0.05 and 9.92 ± 0.05, close the air value of 9.8 (Eberhardt et al., 1965). $^{40}$Ar/$^{36}$Ar ratios range from 299 ± 1 to 323 ± 1, slightly above the value of air (298.5) (Lee et al., 2006). In contrast to relatively uniform and air-like isotope ratios, noble gas concentrations are highly variable. $^{20}$Ne concentrations vary over three orders of magnitude ($3.43 \pm 0.15 \times 10^{-8}$ to $1.4 \pm 0.1 \times 10^{-5}$); $^{40}$Ar concentrations vary from $5.3 \pm 0.2 \times 10^{-5}$ to $9.44 \pm 0.43 \times 10^{-4}$. $^{84}$Kr and $^{132}$Xe concentrations range from $8.2 \pm 0.3 \times 10^{-9}$ to $7.9 \pm 3 \times 10^{-8}$ and $6.5 \pm 0.3 \times 10^{-10}$ to $3.6 \pm 0.2 \times 10^{-9}$, respectively.

4. Discussion – link between the CO$_2$ source in the reservoirs and springs

4.1. He-CO$_2$ abundance system

The trends in He-CO$_2$ abundance of well gases and CO$_2$ springs can be distinguished using a ternary diagram after Giggenbach et al. (1993). This allows depiction of the relative ratios between CO$_2$-He-He rather than absolute concentrations (Fig. 4). The MORB end-member (Marty and Jambon, 1987) is displayed for reference with a straight mixing line showing addition of radiogenic $^4$He. Caroline, Buttress, and Boggy Creek well gases as well as Argyle and Glenluce springs fall on a mixing line between MORB and crustal end-members. The rest of the springs lie on the mixing trajectory with low He/high CO$_2$ end-member (the CO$_2$ apex of the plot).

Based on the observed trends, two main processes can be identified. Addition of radiogenic $^4$He to the MORB-type component lowers the $^3$He/$^4$He, decreases CO$_2$/He and does not affect CO$_2$/He ratio (the trend towards the $^4$He apex of the graph). All CO$_2$ well gas and spring samples exhibit variation in $^3$He/$^4$He ratios due to radiogenic $^4$He addition. Subsequently, either helium loss or CO$_2$ addition increases both CO$_2$/He and CO$_2$/He but does not affect the $^3$He/$^4$He ratios. The second
process affects the majority of the springs (excluding Glenluce and Argyle) but none of the well gas samples (trajectory towards the CO$_2$ apex of the plot).

To evaluate this two-step process in the following discussion, we select two samples to use as initial end-members. Argyle spring is representative of the regional high-mantle end-member, least affected by radiogenic $^4$He addition (exhibiting the highest measured $^3$He/$^4$He ratio 3.65 of $R_c/R_A$, $[^4\text{He}]=8.8 \pm 0.3 \times 10^{-5}$ cm$^3$(STP)/cm$^3$). The highest He concentrations were measured in Glenluce sample ($^3$He/$^4$He 1.57 $R_c/R_A$, $[^4\text{He}]=1.6 \pm 0.1 \times 10^{-4}$ cm$^3$(STP)/cm$^3$), which is the least affected by secondary He loss or CO$_2$ addition.

The $^3$He/$^4$He ratio can be modified by dilution with non-CO$_2$ gas (usually methane) with a different He isotopic signature (Sherwood Lollar et al., 1994), radiogenic $^4$He accumulation in situ (Newell et al., 2015; Liu et al., 2016) or He stripping from formation water during gas migration through lithological units enriched in $^4$He (Sano et al., 1990; Sakamoto et al., 1992). The resulting $^3$He/$^4$He ratio can then be overprinted by addition of CO$_2$ from a different source (O’Nions and Oxburgh, 1988) or phase fractionation during degassing (Matthews et al., 1987). If the well gases and CO$_2$ springs share a common source, then these processes can be accounted for and gas composition can be traced back to a single initial end-member.
Figure 4. Ternary diagram (after Giggenbach et al., 1993) showing the relationship between the concentrations of CO$_2$, $^3$He, $^4$He expressed as their ratios. MORB value used for reference is 8 ±1 RA (Marty and Jambon, 1987). The dashed lines show mixing between different components. The two clear trends are: 1) Radiogenic $^4$He addition, which shifts gas composition to the right apex of the ternary plot, 2) CO$_2$ addition or He loss trend towards the top apex of the plot. Port Campbell well gases fall on the mixing line between MORB and crustal end-member. Spring samples fall on He loss/CO$_2$ addition trendline.

Abbreviations of sample names are given in Table 1.

4.2 Radiogenic $^4$He addition

$^4$He is produced by the alpha decay of uranium and thorium in the crust. These elements are primarily concentrated in accessory minerals such as zircon and apatite, which release helium at a constant rate above the blocking temperature of the mineral (Tolstikhin et al., 2017). Similarly, $^3$He is produced by thermal neutron capture by $^6$Li, which can be approximated based on Li content of the crust (Ballentine and Burnard, 2002). However, this contribution is minimal relative to the amount of...
He released from mantle fluids and can be considered to be negligible in the context of in-situ crustal helium accumulation. After production, radiogenic helium is either trapped in the pore spaces in-situ or mobilised by any migrating water or gas phase present in the subsurface and then transported elsewhere. If a natural gas trap exists in-situ, helium will preferentially accumulate in the gas phase due to its low solubility in water.

4.2.1. Radiogenic $^4\text{He}$ accumulation in-situ

The initial $^3\text{He}/^4\text{He}$ ratio of mantle-sourced gas can be reduced by direct accumulation of $^4\text{He}$ produced in the crust, or by mixing with $^4\text{He}$-rich methane. The former would be applicable to CO$_2$ springs, the latter to well gases containing CO$_2$ and CH$_4$ mixtures. In both cases, the final $^4\text{He}$ concentrations are controlled by the rate of $^4\text{He}$ production in the crust. The contents of radiogenic $^4\text{He}$ accumulated in-situ in a natural gas trap can therefore be considered as a function of time since the initial emplacement of the gas in the trap, given a known crustal helium production rate (Liu et al., 2016). Under this assumption, we can estimate the residence time required for the observed $^3\text{He}/^4\text{He}$ ratios in both the well gases and the springs.

The $^4\text{He}$ production rate (Craig and Lupton, 1976) and $^4\text{He}$ concentration in the pore fluid increases at the rate of $J_{^4\text{He}}$ (Torgersen, 1980):

$$^4P = 0.2355 \times 10^{-12} \times [\text{U}] \times (1 + 0.123 \times [\text{Th}]/[\text{U}] - 4)$$

$$J_{^4\text{He}} = ^4P \times \rho \times (1 - \phi)/\phi)$$

Where:

$[\text{U}], [\text{Th}]$ – concentrations in ppm

$^4P$ – crustal $^4\text{He}$ production rate in cm$^3$ STP/g yr

$J_{^4\text{He}}$ – $^4\text{He}$ production rate cm$^3$ STP/yr

$\rho$ – density of the crust in g/cm$^3$

$\phi$ – porosity of the rocks as a fraction

Assuming $^4\text{He}$ has been accumulating in mantle-sourced CO$_2$ with a known initial composition, the final $^3\text{He}/^4\text{He}$ ratio is expressed as a function of time modified from Newell et al. (2015):
$^{3}\text{He} / ^{4}\text{He}(t) = F \times ^{3}\text{He}_m / (J_{\text{He}} \times t + ^{4}\text{He}_m)$

(3)

Where:

$F$ – fraction of mantle-sourced gas in the reservoir

$H e_m$ – helium concentration of the mantle-source end-member

t – time in years

The final result is independent of the timing of CO$_2$ emplacement as it records the total $^4\text{He}$ accumulated since the start of the gas trap filling, so in the case of CO$_2$/methane mixture, the recorded age will be that of the methane emplacement. Argyle spring concentrations are taken as representative of the initial mantle-sourced end-member, based on the highest measured $^3\text{He} / ^4\text{He}$ ratio (3.65 $R_c / R_A$). This ratio is significantly lower than SCLM or MORB values, but we assume this to be representative of the end-member at the time of emplacement. Similar value is measured in the Caroline field which has likely been emplaced at a similar time to Mount Gambier eruptions dated at 5 ka (Roberston et al., 1996), so we assume this to be a regional feature and that some radiogenic $^4\text{He}$ accumulation occurred within the melt before the gas emplacement.

Assuming an average reservoir porosity of 25% (Watson et al., 2003), average crustal $^{238}\text{U}$ and $^{232}\text{Th}$ concentrations of 2.8 and 10.7 mg/kg and average crustal density of 2.5 g/cm$^3$ (Rudnick and Fountain, 1995) the estimated age of filling of the Boggy Creek field is 32 Ma (Fig 5). Assuming ± 5% and ± 10% uncertainty in porosity and $^{238}\text{U}$ and $^{232}\text{Th}$ concentrations respectively, the accumulation age could vary between 22 and 45 Ma (showed in shaded area in Fig 5). The model only considers $^4\text{He}$ accumulated in-situ and does not account for other $^4\text{He}$ sources in the total budget which could include: the initial $^4\text{He}$ contents in the gas phase acquired from the source rock, helium stripped from water during the two stages of methane and CO$_2$ migration in the reservoir and any external $^4\text{He}$ flux, caused by heat release associated with regional tectonic events or volcanism. The model also assumes all radiogenic $^4\text{He}$ produced in the crust is released into the pore water. Contribution from any of the outlined processes would act to decrease the modelled range, so the calculated accumulation age range can therefore be taken as a maximum estimate.

Methane in Port Campbell traps is associated with the last hydrocarbon generation stage that commenced during the mid-Paleogene (Duddy, 1997; Boreham et al., 2004), which closely matches the range of accumulation ages calculated. The $^4\text{He} / ^4\text{He}$ ratios observed within the Boggy Creek and Buttress fields can plausibly be explained by an Argyle-type end-member mixing with methane containing radiogenic $^4\text{He}$, confirming the binary mixing with methane trend depicted in Figure 4.
Figure 5. \(^3\)He/\(^4\)He ratio vs time since gas emplacement calculated for the composition of the Boggy Creek-1 sample. To achieve the current \(^3\)He/\(^4\)He ratio measured in Boggy Creek (1.21 Ra), Argyle-type CO\(_2\) (3.65 Ra) would have to mix with methane that has been emplaced at 32 Ma. Shaded area shows uncertainty.

The same calculation can be applied to the CO\(_2\) springs. The \(^{238}\)U-\(^{232}\)Th contents are assumed to be the same; the porosity of a fracture-dominated metasedimentary aquifer is estimated to be lower (10 ± 5 %). To reduce the initial \(^3\)He/\(^4\)He ratios of 3.65 to the lowest measured value of 1.23 Ra, it would take 9 Ma years on average and between 4-15 Ma within the uncertainty of the parameters. To account for the range of observed \(^3\)He/\(^4\)He ratios, this scenario requires emplacement of separate gas pockets for each individual spring at different times between 9 Ma and present and retention within the crust before the onset of the recent migration to the surface.

Multiple gas injection events could be associated with discrete episodes of seismic or volcanic activity, although the latter is unlikely because the volcanic cones are far fewer than the individual mineral springs (>100) (Shugg, 2009), and given the predominately monogenetic eruptive character of the NVP extrusives (Boyce, 2013) volcanic activity is unlikely to produce so many different gas pulses. Irrespective of the gas emplacement mechanism, the heavily folded and fractured Ordovician metasedimentary sequence is unlikely to act as an effective gas trap for millions of years. In-situ \(^4\)He accumulation in CO\(_2\) springs is therefore an unlikely process to account for the observed variation in \(^3\)He/\(^4\)He ratios.

4.2.2. Radiogenic \(^4\)He stripping from enriched pore-water

An alternative model to in-situ generation is modification of magmatic \(^3\)He/\(^4\)He ratios by dilution of mantle He by interaction with radiogenic helium-rich basement fluids during lateral
movement of the CO₂. Stagnant fluids in basement rocks with high U/Th concentrations are enriched
in radiogenic ⁴He well above ASW levels with ³He/⁴He ratios in the crustal range (0.02 Rₘ) (Bottomley
et al., 1984; Weinlich et al., 1999; Holland et al., 2013; Warr et al., 2018). Isolated stagnant pockets
of these fluids within the Cambrian – Ordovician basement sequence are a likely source of ⁴He for
the migrating mantle CO₂. In this case, the process is still governed by the helium production rate in
the crust (similar to the in-situ ⁴He accumulation discussed above), but the controlling factor is
distance migrated through the basement rather than time.

Samples with higher ³He/⁴He ratios are located geographically closer to each other and the
Muckleford fault zone. Under the assumption that one of these major fault zones could provide a
pathway for mantle CO₂ ascent to the surface, we can infer that the spring with the highest
measured ³He/⁴He ratio (Argyle, 3.65 Rₘ) would be the closest to the main conduit. Figure 6a shows
the relationship between the ³He/⁴He ratios and the radial distance of sample location to the Argyle
spring. Kyneton spring is excluded from this because of its contamination with an atmospheric
component. The observed ³He/⁴He ratios consistently decrease with increasing distance from the
inferred conduit, suggesting mantle CO₂ is being progressively diluted with a crustal component with
increasing distance migrated through the basement.

The mechanism of interaction with these fluids depends on whether CO₂ migrates in the gas phase
or dissolved in water. In case of the former, the governing factor is differences in solubility as helium
is strongly partitioned from the fluid to the migrating gas phase. If CO₂ migrates dissolved in water,
the mixing with the crustal fluids can be described by a mechanical dispersion model (Sano et al.,
1990). Assuming that mantle fluids are supplied through a single conduit at a constant rate under
steady-state homogeneous and isotropic conditions under an equal hydrostatic pressure, ³He/⁴He is
calculated as a function of the radial distance to the conduit (r) following the approach detailed in
Sano et al. (1990) of deriving the location-specific helium dispersion constant (α) by fitting a least
squares function to the measured ³He/⁴He and radial distance data points.

\[
\frac{³He}{⁴He}(r) = \left( \frac{³Pr^2 + \alpha ³He_m}{⁴Pr^2 + \alpha ⁴He_m} \right)
\]

Where:

\( r \) – radial distance from the main gas conduit

\( \alpha \) – helium dispersion constant, dependent on the pore network geometry

\( P \) – crustal helium production rate in atoms/cm³s, calculated under the same crustal density and U,

Th content assumptions as in the ⁴He accumulation model.
Similar decreases in $^3$He/$^4$He ratios with increasing distance from a central volcanic cone has been observed in various active volcanoes (Marty and Jambon, 1987; Williams et al., 1987; Sano et al., 1990; Sakamoto et al., 1992). The calculated hydrodynamic dispersion coefficient (methods in Sano et al., 1990) is 0.035 cm$^2$/s, which compares well with the estimates in the original model (0.09 and 0.055 cm$^2$/s).

The overall average rate of $^3$He/$^4$He decrease in 4 volcanic locations reviewed by Sakamoto et al. (1992) varied between 0.3 to 0.5 Ra/km. The average rate of $^3$He/$^4$He decrease in CVH is 0.1 Ra/km, potentially reflecting fluid migration via more efficient fracture networks and conduits in a faulted sequence relative to the previously investigated volcanic and volcanoclastic sequences. Fractured aquifers have lower tortuosity relative to porous ones, which results in shorter effective travel distance for the same total flow path distance (Clennell, 1997) and therefore lower rate of interaction with radiogenic basement fluids per distance travelled.

Springs with the highest $^3$He/$^4$He ratios are clustered near the N-S trending Muckleford Fault and a smaller parallel fault striking along Lake Daylesford (Fig 6b). Previous studies have shown that clusters of NVP volcanic vents are commonly aligned parallel to nearby basement faults throughout the province (van Otterloo et al., 2013; Cas et al., 2017). Mantle xenoliths were found in the vicinity of the faults, suggesting fast mantle upwelling rates through the lithosphere were prevalent during periods of magmatic activity (van Otterloo et al., 2014). While further work is required to provide geomechanical and structural geological evidence for current fluid migration along the fault zones in the CVH, the spatial distribution of $^3$He/$^4$He ratios suggests that these basement lineaments potentially play an important role in the currently active mantle-CO$_2$ ascent to the surface.
Figure 6 a). Plot of $^3$He/$^4$He $R_c/R_A$ values relative to the distance from the Argyle spring (highest $^3$He/$^4$He ratio), inferred to be closest to the conduit. $^3$He/$^4$He ratios decrease with increasing radial distance. The solid line is $^3$He/$^4$He dispersion with distance model calculated based on Sano et al. (1990). b) Geographical distribution of CO$_2$ springs. Springs with the highest $^3$He/$^4$He ratios are clustered close to N-S trending basement-scale Muckelford thrust fault and parallel smaller fault near Lake Daylesford. Shaded areas show $^3$He/$^4$He ratio ranges which decrease with increasing distance from the Argyle spring. Kyneton spring is excluded due to atmospheric contamination. Abbreviations of sample names are given in Table 1.
4.3. Evaluating models to account for CO₂/³He and δ¹³C(CO₂) variation

The combination of CO₂, helium and δ¹³C(CO₂) values is commonly used to identify the presence of mantle volatiles. This is because CO₂/³He ratios have been well constrained for mantle-derived melts, fluids and volatiles, with an average MORB value accepted as $1.5 \pm 0.5 \times 10^9$ (Sano and Marty, 1995; Marty and Tolstikhin, 1998). ³He is not produced in significant amounts in the crust, so low ³He/⁴He ratios and associated CO₂/³He ratios between $10^{10} – 10^{15}$ are typically associated with a crustal CO₂ source (O’Nions and Oxburgh, 1988). The CO₂/³He ratios observed in ten CO₂ samples from the Victorian mineral springs vary over two orders of magnitude ($2.8 \times 10^9$ to $6.5 \times 10^{11}$), encompassing the range typical of mantle and crust end-members. A trend in increasing CO₂/³He ratios is therefore commonly associated with admixture of crustal CO₂ and/or degassing in open system (e.g. Crossey et al., 2009; Newell et al., 2015; Ruzié et al., 2013), defined by Rayleigh fractionation. Here, we test both of these possibilities.

Crustal end-members can have a wide range of CO₂/³He ratios but a narrow range of ³He/⁴He ratios (0.01 – 0.07 R_A) (Ozima and Podosek, 2002). Figure 7 shows CO₂/³He values plotted against ³He/⁴He R_A ratios with binary mixing curves representing mantle (8 R_A) source and various crustal components. Significantly, samples with high CO₂/³He ratios do not necessarily show lower ³He/⁴He ratios, as would be expected in the case of mixing with ³He-poor crustal CO₂ source and trend perpendicular to the calculated mixing lines. To explain the range of measured CO₂/³He ratios, variable amounts of mixing with a wide range of different crustal reservoirs (CO₂/³He – $10^{10}$ - $10^{14}$) would need to be invoked, which is unlikely in the setting where bedrock lithology is uniform across the area.

Crustal CO₂ addition can be further assessed by combining He data with δ¹³C(CO₂) values (Sano and Marty, 1995). The range of δ¹³C(CO₂) values measured in the springs (-9.4 to -6‰) partly overlap the typical mantle range (-7 to -4‰) (Wycherley et al., 1999). However, increasing CO₂/³He ratios do not consistently correlate with δ¹³C(CO₂) change towards carbonate or organic end-members (Fig. 8). Instead, a vertical trend exists, which would require mixing with an end-member with constant proportions of both organic and carbonate-sourced CO₂. To explain the highest observed CO₂/³He ratios, 99 % of non-mantle (crustal/organic mixture) CO₂ addition is required. Such significant amounts of crustal CO₂ sourced by dissolution of bedrock minerals would liberate cations contained in the dissolving minerals and increase the TDS values of the water. Figure 9 shows that there is no clear positive correlation between the CO₂/³He ratios in the volatiles and TDS values in their associated waters. Alternatively, CO₂ and helium loss during open system degassing can be evaluated using Rayleigh fractionation modelling. Figure 8 also shows a calculated open system
Rayleigh fractionation line, assuming average pH of 6.1 and 15 °C temperature. The calculated fractionation factor between He/CO\textsubscript{2} is 0.012; the enrichment factor $\ln 10^3 \alpha_{\delta ^{13}C(CO_2)}$(aq)/(CO\textsubscript{2})\textsubscript{g} is 2.2‰. Open system degassing under measured conditions would result in a similar fractionation in CO\textsubscript{2}/\textsuperscript{3}He ratio but a significantly more extensive than observed fractionation of $\delta ^{13}C(CO_2)$ values. We therefore conclude that degassing under open system conditions is not supported by the data.

Previous geochemical modelling work showed that CO\textsubscript{2} does not cause significant amounts of bedrock mineral dissolution in the Ordovician aquifer (Karolytė et al., 2017) and there is no geological evidence for addition of large amounts of crustal CO\textsubscript{2} from other sources (e.g. carbonate metamorphism). The possibility of significant amounts of organic CO\textsubscript{2} addition is also ruled out, because the observed trend on Figure 8 cannot be explained by addition of organic CO\textsubscript{2} in the absence of the crustal component. Based on the combined evidence from $\delta ^{13}C(CO_2)$-He, CO\textsubscript{2} abundance and TDS contents of the mineral waters, we conclude that there is no significant crustal CO\textsubscript{2} addition to the mantle volatiles sampled at the CVH and Clifton Springs. CO\textsubscript{2} loss during degassing under open system conditions is also not supported by the data.

![Figure 7](image_url)

Figure 7. Binary mixing plot between MORB (red triangle) ($^4\text{He}/^3\text{He} 8 R_A$, CO\textsubscript{2}/$^3\text{He} 1.5 \times 10^9$) and various crustal end-members (CO\textsubscript{2}/$^3\text{He} 10^{13}-10^{14}$). The springs form a near-horizontal trendline and do not follow any of the mixing lines, suggesting that mixing does not control the variation in CO\textsubscript{2}/$^3\text{He}$ values. All error bars are smaller than the printed symbols.
Figure 8. $\text{CO}_2/\text{He}$ ratios vs $\delta^{13}\text{C}(\text{CO}_2)$ values for gas samples in relation to mixing between the mantle, carbonate and organic $\text{CO}_2$ end-members based on Sano and Marty (1995). Caroline, Boggy Creek and Buttress well gases fall within the mantle range. Spring samples do not show a coherent trend towards either an organic or carbonate $\text{CO}_2$ end member. The observed trend would require $>99\%$ contribution of a component with constant proportions of both organic and carbonate-sourced $\text{CO}_2$. Green line shows Rayleigh fractionation during degassing under average measured pH and temperature, open circles indicate percentage of gas left. The data do not fall on either the mixing or open system degassing curves (discussed in text). Abbreviations of sample names are given in Table 1.
Figure 9. \( \text{CO}_2/\text{He} \) vs TDS measured in water, sampled via hand pumps from tube bores. \( \text{CO}_2/\text{He} \) values are not correlated with TDS. A positive correlation would be expected if crustal CO\(_2\) were added as a result of bedrock mineral dissolution.

Alternatively to mixing with different CO\(_2\) sources, the variability of \( \delta^{13}\text{C}(\text{CO}_2) \) values (-9.4 to -6‰) can be explained by degassing in separate individual systems under a range of different pH and temperature conditions. Equilibrium fractionation between \( \delta^{13}\text{C}(\text{CO}_2) \) in aqueous and gaseous phases is controlled by the temperature and the relative amounts of HCO\(_3\)- and H\(_2\)CO\(_3\), which are pH-dependent. If H\(_2\)CO\(_3\) is the dominant dissolved inorganic carbon (DIC) species, degassing CO\(_2\) is slightly enriched in \(^{13}\text{C}\). Conversely, when HCO\(_3\)- dominates the system, degassing CO\(_2\) is relatively depleted in \(^{13}\text{C}\) (Deines et al., 1974). The pH values measured in mineral water bores range from 5.5 to 6.1 and temperatures are 15 – 21 °C. In this particular range of conditions, the ratio of HCO\(_3\) to H\(_2\)CO\(_3\) in DIC varies significantly. The resulting calculated equilibrium enrichment factors between DIC and gaseous CO\(_2\) range from -3.4 to -0.43‰. Degassing under different DIC speciation conditions therefore can fully account for the observed 3.4‰ variability in \( \delta^{13}\text{C}(\text{CO}_2) \) values of the spring gases.

The trends observed in our data are not unique to this study. \( \text{CO}_2/\text{He} \) ratios ranging between \( 10^9 \) to \( 10^{14} \) combined with \( \delta^{13}\text{C}(\text{CO}_2) \) values without an obvious trend towards organic or carbonate end-member is a common observation, commonly interpreted as a result of simple mantle and crustal end-member mixing (Aka et al., 2001; Crosse, et al., 2009; Mao et al., 2009). Other workers recognised that simple mixing is not a conclusive interpretation (Italiano et al., 2014) and suggested contribution of a solubility fractionation process (Matthews et al., 1987; Hilton, 2009; Newell et al., 2015). Where open system Rayleigh fractionation is proposed, it is commonly not conclusively supported by evidence from \( \delta^{13}\text{C}(\text{CO}_2) \) values (Ruzié et al., 2013; Bräuer et al., 2016). In the following...
section, we explore how this trend can alternatively be explained by fractionation during a two-step process of dissolution and degassing.

### 4.4 Noble gas abundance modification by solubility in water

The variation observed in $^3$He concentrations in the mineral spring samples is also replicated in $^4$He and other noble gases. Figure 10 shows the distribution of noble gas concentrations in all studied springs. Importantly, the variance in observed gas concentrations decreases with element mass (Fig. 10), indicating a solubility-controlled process. If mantle CO$_2$ is transported to the surface in solution, this process can be modelled as dissolution and subsequent degassing.

#### Figure 10. Noble gas concentrations of CO$_2$ spring samples in cm$^3$ (STP)/cm$^3$. The variation in concentrations decreases with increasing molecular mass. Solid black line shows the concentrations measured in Glenluce spring, which has the highest helium concentrations and least fractionated CO$_2$/$^3$He ratios.

During the equilibration between gas and water, noble gases are partitioned between the phases according to their solubility coefficient, as defined by Henry’s Law:

$$C_{i,w} = \frac{C_{i,g}}{K_i}$$

Where C is concentration, subscripts g and w denote gas and water phases and $K_i$ is dimensionless Henry’s constant for noble gas i. $K_i$ is temperature, pressure and salinity dependent (Kipfer et al., 2002). The final concentrations in both phases depend on the volumetric gas/water ratio. The equilibrium concentrations in the water ($C_{i,w}^{eq}$) are expressed as (Zartman et al., 1961):
\[ C_{i,w}^{eq} = C_{i,t} \times F_w \]  
(6)

\[ F_w = \frac{C_{i,w}V_w}{C_{i,w}V_w + C_{i,g}V_g} \]  
(7)

Where \( V \) is volume, \( C_{i,t} \) is the total noble gas budget, and \( F_w \) is the fraction of noble gases in the water. Combining equations 5-7, \( C_{i,w}^{eq} \) is:

\[ C_{i,w}^{eq} = C_t \times \left( 1 + \frac{V_g}{V_w} K_i \right)^{-1} \]  
(8)

After the equilibration step, the water and the gas source separate and ascend to the surface independently. The gases collected at the surface of stream beds are assumed to have been transported in solution. During degassing at the surface, the noble gases are partitioned between the phases again. The final measured gas concentrations are:

\[ C_{i,g}^f = C_{i,w}^{eq} \times \left( 1 + \left( \frac{V_g}{V_w} \right)^{-1} \frac{1}{K_i} \right)^{-1} \]  
(9)

For the purpose of investigating a shallow degassing process, equilibration with fresh water at atmospheric pressure and 20 °C temperature is assumed. Henry’s constants and activity coefficients for water conditions were calculated from empirical equations from Crovetto et al. (1982) for Ne, Ar, Kr and Xe and Smith (1985) for He, following the methodology in Ballentine and Burnard (2002). Henry’s constant for CO\(_2\) is calculated using empirical equations from Crovetto (1991). Assuming the density of fresh water (0.996 cm\(^3\)/g) (Weast et al., 1988), concentrations in ASW are converted from cm\(^3\)/g to cm\(^3\)/cm\(^3\) for Figure 11.

The highest helium concentrations and lowest CO\(_2\)/He ratio were measured in the Glenluce spring. We therefore assume that Glenluce is the least solubility fractionated end-member. For the purpose of the model, we make a simplifying assumption that the Glenluce sample represents the total amount of CO\(_2\) and noble gases from both the mantle and ASW sources (\( C_t \)). This end-member equilibrates with a volume of water which, in theory, is noble gas free. When \( \frac{V_g}{V_w} \to 0 \), \( F_w \to 1 \), all gases are dissolved in water. All gas contents are transferred into the water phase \( C_{i,w}^{eq} \) and the ratios are equal to the initial ones. When \( \frac{V_g}{V_w} \to \infty \) and \( F_w \to 0 \), only a small fraction of noble gas contents are dissolved in water. In this case, the ratios are the most fractionated and the concentrations in water are low. After the equilibration, the water separates from the gas source, migrates to the surface and degasses. We make a simplifying assumption that the water degasses entirely \( \frac{V_g}{V_w} \to \infty \), all dissolved gases are transferred into the gas phase and therefore the final measured \( C_{i,g}^f \to C_{i,w}^{eq} \).
Figure 11 shows CO$_2$/He ratios, $^3$He concentrations relative to $^4$He, $^{20}$Ne, $^{40}$Ar, $^{84}$Kr and $^{132}$Xe and the calculated solubility curves $C_{tg}$. The data points fall on the modelled line and is clearly distinguishable from mixing with ASW, which is more enriched in all atmospheric noble gases. Air and ASW components are potentially introduced by inclusion of small amounts of air and water into the copper tube during sampling and are the most significant in Kyneton, Tipperary and Woolnoughs samples. Tipperary and Woolnoughs springs include a combination of ASW and air components, which is obvious in different element pair plots (Fig. 11 c,d,e,f) and less apparent in $^3$He vs $^4$He (Fig. 11b) because air and ASW have similar $^3$He/$^4$He ratios. Figure 11b also clearly shows that the original concentrations in Kyneton spring have been overprinted by admixture of air, most likely during sample collection and clearly identified in the $^4$He/$^{20}$Ne ratios. The ASW component is more evident in the heavier atmospheric noble gases in the Deep Creek sample (Fig. 11 ,d,e,f).

With the exceptions discussed above, all other samples plot close to the modelled solubility fractionation line. The maximum extent of fractionation between CO$_2$ and He is limited by the ratio of Henry’s constants $K_{CO_2}/K_{He}$ (Fig. 11a). The calculated $\frac{V_g}{V_w}$ ratios and progressive loss of noble gas concentrations with decreasing F are consistent across all noble gas elemental pairs. When $\frac{V_g}{V_w}$ is unity, 47% of the total CO$_2$ is dissolved but only 1% of helium. The resulting CO$_2$/$^3$He ratio is 1.4 x $10^{11}$, which is the highest in the sample group, excluding the previously discussed samples which are contaminated with air. This means that dissolution in water under equal gas/water ratios explains the maximum observed fractionation of CO$_2$/$^3$He values. According to the model, the minimum $\frac{V_g}{V_w}$ ratio required to dissolve the entire sample without fractionating the CO$_2$/$^3$He is 0.0005, or 2000 times more water than gas.
Figure 11. $\text{CO}_2$/He ratios (a) and $^4\text{He}$ concentrations relative to $^4\text{He}$ (b), $^{20}\text{Ne}$ (c), $^{40}\text{Ar}$ (d), $^{84}\text{Kr}$ (e) and $^{132}\text{Xe}$ (f) in cm$^3$(STP)/cm$^3$. The solid blue line shows the concentrations in the gas phase after a two-step dissolution.
and degassing. First, water equilibrates with gas under different gas/water ratios. Second, the water of that composition degasses entirely. Tick marks show gas/water ratios during the dissolution stage. Dashed lines show mixing with ASW at 20 °C; dotted line shows mixing with air. Some deviations from the modelled line occur due to mixing with ASW and/or air. a) The extent of CO$_2$/He fractionation during dissolution is limited by $K_{CO2}/K_{He}$. All samples fall within this range except for Ti and WO. c) shows that this is because Ti and WO have a contribution between ASW and air components, plotting between these end-members. This is consistently replicated for Woolnoughs spring in c) d) and e). Ar, Kr and Xe concentrations of CS, DC, LO and TA springs are within the limits of mixing with ASW and calculated model line. Abbreviations of sample names are given in Table 1.

The model results are not a strict interpretation of the geological system, but rather an indication of how the water controls the noble gas budget. The samples with high noble gas concentrations and mantle CO$_2$/$^3$He ratios might alternatively be interpreted to represent the residual gas cap migrating the gas phase after the equilibration with water or having had minimal interaction with the water. However, in cases where gas migrates dissolved in water and degasses at the surface, equilibration in equal volumes of gas and water is needed to fractionate the CO$_2$/$^3$He ratios by two orders of magnitude. This is a significant consideration for the use of CO$_2$/$^3$He ratios in interpretation of gas provenance in gases equilibrating with water.

Figure 12 shows a theoretical fractionation model of mantle-derived CO$_2$ under the same ambient atmospheric conditions as the previous model. A sample with the starting concentrations of [CO$_2$] = 0.99 and [He] = 1.2 x 10$^{-12}$ cm$^3$STP/cm$^3$ is dissolved in water under different gas/water ratios. The figure shows how the decreasing fraction of moles relative to the starting value, transferred to the water and gas phases during the two-stage process, translates to CO$_2$/$^3$He ratios. When the gas/water ratio is low during the dissolution step, all gasses are dissolved into the water phase and the ratio is unchanged. As the gas/water ratio decreases, overall less gas is transferred into the water phase, but the water becomes more enriched in CO$_2$ relative to helium. The second step considers degassing after the equilibration, when the remaining non-dissolved gas is removed from the system and the water degasses under three scenarios ($V_g/V_w \rightarrow 0$, 0.25 and 1). This effectively shows that in a multi-step dissolution and degassing process, the CO$_2$/$^3$He ratio is entirely dependent on the gas/water ratios and the extent of fractionation is limited by the ratio of Henry’s constants $K_{CO2}/K_{He}$. In practice, the process is relevant to the point where the gas concentrations are above those in ASW and the signal is not entirely diluted. Where CO$_2$ is the main carrier gas, this effect may not be intuitively obvious, because the measured CO$_2$ concentrations are always > 99 % and the observed variation is the $^3$He concentrations.
Figure 12. Theoretical model of two step dissolution and degassing of mantle CO$_2$ and the effect on the CO$_2$/He ratio. $F$ is the fraction of moles in the modelled phase relative to the starting value. Symbols with arrows indicate $\frac{V_g}{V_w}$ ratios approaching infinity and zero, black dots mark specific calculated ratios. The solid black line shows the water phase during dissolution stage (step 1). The dashed lines show the resulting gas phase after degassing of the water phase under three different scenarios ($\frac{V_g}{V_w}$ -0, 0.25, 1) (step 2). The maximum fractionation of CO$_2$/He is limited by the relative ratio of $K_{CO2}/K_{He}$.

4.4.1. Summary

The geological interpretation of the proposed solubility fractionation model requires two stages of phase separation - dissolution followed by degassing. Mantle CO$_2$ equilibrates with individual aquifers under different gas/water ratios. Following this, CO$_2$-saturated water and the remaining gas separate and ascend independently, driven by the differences in buoyancy force. Continuous seepage of dry CO$_2$ (up to 6000 ppm) has been identified in the localised fractures of the Ordovician sandstone outcropping near the Tipperary spring (Roberts et al., 2019), confirming the decoupled CO$_2$ and water migration. Water migrates to the surface through individual conduits, forming individual mineral water bodies and eventually springs. This model is consistent with the $\delta^{13}$C(CO$_2$) data, explained by degassing under measured temperature and pH conditions with each spring acting as a separate system. This appears to be a plausible interpretation of the CVH mineral springs, which show high variability in dissolved carbon and cation contents, indicating restricted individual aquifers for separate springs (Cartwright et al., 2002; Weaver et al., 2006). Mineral water degasses at the surface and all noble gases and CO$_2$ are assumed to be stripped from the water phase. The
final measured noble gas budgets are strongly controlled by the initial stage of equilibrating with water.

4.5 Model summary and application to CO₂ tracing

This case study of south-east Australian CO₂ gas reservoirs and natural springs provides a framework for investigating genetic link between CO₂ stored in reservoirs and migrating into shallow aquifers. Our findings suggest that the combined helium, CO₂ abundance and δ¹³C(CO₂) system allows to distinguish between key processes that modify the initial geochemical composition: admixture of crustal or organic sourced CO₂, mixing with non-CO₂ crustal gases and fractionation between water and gas phases in either open or closed system. Helium isotopic signature is a particular strength for source identification in CO₂ spring samples because it can be corrected for atmospheric component. In contrast, neon and argon isotope ratios are likely to be close to the values of air.

A useful way to think about the addition of radiogenic ⁴He by addition of non-CO₂ radiogenic component is to model it as a function of either time or distance. The ⁴He dating approach presented here allows constraint of the residence time needed to accumulate ⁴He and use this to discriminate between alternative interpretations based on their feasibility in the geological context. While a more comprehensive modelling technique might be needed if an accurate age is the objective of the study (Zhou and Ballentine, 2006; Liu et al., 2016), this method confirmed in-situ ⁴He accumulation as a viable process in the studied well gases but not in CO₂ springs. The spatial distribution of ³He/⁴He ratios in the springs indicated that the distance from the main conduit is a more important factor in CO₂ springs. This is controlled by the interaction with ⁴He-enriched stagnant basement fluids and can be modelled as fluid dispersion or a solubility process, depending if CO₂ is assumed to migrate dissolved in water or in a gas phase. In case of the former, our data are in good agreement with similar observations in volcanic settings (Sano et al., 1990). The latter is also viable and would produce a similar pattern.

Radiogenic ⁴He can also be added by mixing with a crustal CO₂ source. In this case, decreasing ³He/⁴He ratios should correlate with an increase in CO₂/³He and either a negative or positive shift in δ¹³C(CO₂) values, following a trajectory of mixing lines. Alternatively, it is possible that ⁴He addition is decoupled from a secondary phase separation process controlling δ¹³C(CO₂) values and CO₂/³He ratios. In this case, no clear correlation between and CO₂/³He and ³He/⁴He is expected. If the system is characterised by progressive gas loss in an open system, generally a significant progressive enrichment of δ¹³C(CO₂) values is expected in non-geothermal temperatures.
Alternatively, the sample suite may effectively represent a series of individual systems, where water and gas equilibrate under different gas/water ratios. In this case, no particular trend is anticipated. The variation of $\delta^{13}$C(CO$_2$) values can instead be controlled by the phase separation at different pH and temperature conditions. Temperature and pH readings of waters should always be taken to account for this effect. All noble and major gas concentrations and their relative ratios, including CO$_2$/He are modified by dissolution in water and/or degassing, while elemental ratios are not expected to change. This can be tested by modelling fractionation under different gas/water ratios, which should be consistent across all element pairs. Importantly, we show how solubility models can be tested by incorporating Ne, Ar, Kr and Xe concentration data, which are often not interpreted in natural spring studies because of the air-like isotopic ratios. While CO$_2$/He is expected to be easily modified, $^3$He/$^4$He ratio is not altered by phase partitioning and is a reliable indicator of gas provenance.

5. Conclusions

$^3$He/$^4$He and CO$_2$/He ratios in well gas and CO$_2$ spring samples in the Otway Basin and the Central Victorian Highlands show unambiguous evidence for a predominantly mantle origin for the CO$_2$ stored in the gas fields and actively migrating to the surface at the springs. The main processes modifying noble gas geochemical signatures are crustal $^4$He addition and noble gas elemental fractionation between the water and gas phases.

$^3$He/$^4$He ratios in well gases vary due to mixing with methane, which has crustal helium contents directly dependent on gas residence time in the reservoir. The $^3$He/$^4$He ratio variation in CO$_2$ springs is controlled by interaction with $^4$He-enriched basement pore fluids and is directly dependent on the radial distance to the gas supply conduit. The observed decline in $^3$He/$^4$He ratios with distance suggests that CO$_2$ is supplied from a single conduit in the area around Argyle spring. $^3$He/$^4$He ratios are the highest in samples clustered near the Muckleford Fault and smaller parallel faults in its vicinity, suggesting that one of these basement lineaments could be acting as a pathway for mantle CO$_2$ to reach the shallow subsurface.

The variability of noble gas abundance patterns observed in the CO$_2$ springs can be explained by solubility fractionation during equilibration with groundwater. If gas is dissolved in water, transported and exsolved at the surface, a two-step dissolution and degassing process can be considered. If gases ascend to the surface dissolved in water, original CO$_2$/He ratios are unlikely to be preserved. In CVH springs, CO$_2$/He ratios in the range of $10^{11} - 10^{12}$ correlate with decreasing
concentrations of all noble gases and can be explained by variation of gas/water ratios during
dissolution in water. Gas/water ratios up to 1 during the dissolution stage can explain the maximum
observed fractionation in CO$_2$/$^3$He ratios. The $\delta^{13}$C(CO$_2$) values are controlled by dissolution and
degassing at pH range of 5.8 - 6.3. This internally consistent model explains the abundance and
isotopic signature in He, Ne, Ar, Kr, Xe and $\delta^{13}$C(CO$_2$).

Taking these processes into account, noble gas compositions observed in well gases in Port
Campbell, Mount Gambier, as well as CO$_2$ springs in CVH and Clifton Springs are traced back to a
single end member of $^3$He/$^4$He of 3.07 - 3.65 R$_A$, proving a common source. This implies a uniform
regional gas composition in the Otway basin and CVH.

Importantly, we present evidence that $^3$He loss resulting in high CO$_2$/$^3$He ratios, commonly
associated with crustal CO$_2$ addition, can be explained without the need to invoke mixing with
crustal CO$_2$, which is especially important in the absence of a clear mixing trend in $\delta^{13}$C(CO$_2$) values.
Hence, CO$_2$/$^3$He values should be compared to the concentrations of other noble gases and used
with caution when assessing the origin of CO$_2$ degassing at surface springs.

The techniques outlined in this paper can be used to identify the origin of CO$_2$ seeps at the
surface and their connectivity to reservoir gases. Hence, they can be applied to CO$_2$ sequestration or
other industrial fugitive gas monitoring settings, such as surrounding shale gas operations. Helium-
CO$_2$ abundance relationship can be used to determine the gas connectivity as long as the industrial
gas has a different initial He isotope ratio to the ASW end-member. The genetic link between
separate CO$_2$ seeps can be tested by applying solubility fractionation modelling to account for
changes in noble gas concentrations caused by interaction with water. Noble gases are particularly
sensitive tracers to small-scale gas migration and should be considered for surface monitoring of any
industrial site where emission of fugitive gas is possible.

Acknowledgments

This work was supported by an EPSRC PhD studentship in partnership with CO2CRC and
Badley Geoscience Ltd. G. Johnson and S. Gilfillan were partially supported by both UKCCSRC and
Scottish Carbon Capture and Storage (SCCS), S. Serno was funded by the UK Carbon Capture and
Storage Research Centre (UKCCSRC) Call 2 grant. S. Flude was supported by by EPSRC grant
#EP/K036033/1. We thank the field operators – BOC, Air Liquide and CO2CRC for permission to
sample the gas reservoirs. Craig Vivian and Peter Dumsey are thanked for support while sampling in
the field. We thank Terry Donnelly and Marta Zurakowska at SUERC for assistance in obtaining stable
isotope and noble gas measurements of gas samples. Ian Cartwright is thanked for providing background data on the Daylesford springs.
References


Sakamoto M., Sano Y. and Wakita H. (1992) $^{3}$He/$^{4}$He ratio distribution in and around the Hakone


Wycherley H., Fleet A. and Shaw H. (1999) Some observations on the origins of large volumes of
