

1 Tracing the migration of mantle CO₂ in gas fields and mineral water 2 springs in south-east Australia using noble gas and stable isotopes

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16 mantle; CO₂ springs; solubility fractionation; Otway Basin.

17 Abstract

18 Geochemical monitoring of CO₂ storage requires understanding of both innate and introduced fluids
19 in the crust as well as the subsurface processes that can change the geochemical fingerprint of CO₂
20 during injection, storage and any subsequent migration. Here, we analyse a natural analogue of CO₂
21 storage, migration and leakage to the atmosphere, using noble gas and stable isotopes to constrain
22 the effect of these processes on the geochemical fingerprint of the CO₂. We present the most
23 comprehensive evidence to date for mantle-sourced CO₂ in south-east Australia, including well gas
24 and CO₂-rich mineral spring samples from the Otway Basin and Central Victorian Highlands (CVH).
25 ³He/⁴He ratios in well gases and CO₂ springs range from 1.21 to 3.07 R_A and 1.23 – 3.65 R_C/R_A,
26 respectively. We present chemical fractionation models to explain the observed range of ³He/⁴He
27 ratios, He, Ne, Ar, Kr, Xe concentrations and δ¹³C(CO₂) values in the springs and the well gases. The
28 variability of ³He/⁴He in the well gases is controlled by the gas residence time in the reservoir and

29 associated radiogenic ^4He accumulation. $^3\text{He}/^4\text{He}$ in CO_2 springs decrease away from the main
30 mantle fluid supply conduit. We identify one main pathway for CO_2 supply to the surface in the CVH,
31 located near a major fault zone. Solubility fractionation during phase separation is proposed to
32 explain the range in noble gas concentrations and $\delta^{13}\text{C}(\text{CO}_2)$ values measured in the mineral spring
33 samples. This process is also responsible for low ^3He concentrations and associated high $\text{CO}_2/{}^3\text{He}$,
34 which are commonly interpreted as evidence for mixing with crustal CO_2 . The elevated $\text{CO}_2/{}^3\text{He}$ can
35 be explained solely by solubility fractionation without the need to invoke other CO_2 sources. The
36 noble gases in the springs and well gases can be traced back to a single end-member which has
37 suffered varying degrees of radiogenic helium accumulation and late stage degassing. This work
38 shows that combined stable and noble gas isotopes in natural gases provide a robust tool for
39 identifying the migration of injected CO_2 to the shallow subsurface.

40

41 1. Introduction

42 The development of geochemical tracing techniques to ascertain the origin and genetic link
43 between natural gases trapped in subsurface reservoirs and those degassing at the surface is
44 important to the safe and successful deployment of carbon capture and storage (CCS). Safe disposal
45 of captured industrial CO_2 requires verification of the fate of the injected gas and reassurance that
46 injected gas does not migrate to the surface (IPCC, 2005). To ensure this, CCS operators have to
47 adhere to legislative guidelines and verify that injected CO_2 is securely contained within the reservoir
48 formation (Dixon et al., 2015). While a variety of geophysical, geoelectric and thermal sensing
49 monitoring techniques exist (Giese et al., 2009), the high sensitivity of geochemical monitoring
50 techniques is useful for detecting seepage at low concentrations, verifying gas origin and tracing the
51 interactions between different crustal fluids (Myers et al., 2013; Stalker and Myers, 2014; Roberts et
52 al., 2017).

53 The noble gas isotopes have previously been applied in an engineered setting to assess CO_2
54 migration, dissolution and residual trapping in reservoir pore spaces at the Cranfield CO_2 -EOR site
55 field (Györe et al., 2015; Györe et al., 2017) and to study industrial underground natural gas storage
56 in the Paris Basin (Jeandel et al., 2010). Noble gas tracers have been used to refute allegations of
57 injected CO_2 leakage to the surface near the Weyburn-Midale CO_2 Monitoring and Storage Project
58 (Gilfillan et al., 2017) and to identify fugitive gas migration to shallow aquifers caused by industrial
59 hydraulic fracturing operations (Darrah et al., 2014). The techniques used in these industrial studies
60 have been informed by preceding research of natural gas fields and springs (e.g. Ballentine and

61 O’Nions, 1994; Gilfillan et al., 2014, 2009, 2008; Sherwood Lollar et al., 1997; Wilkinson et al., 2009).
62 Natural analogue studies remain a crucial gateway to developing geochemical tracing methods for
63 the industrial sector, providing information about fluid migration and retention processes occurring
64 over geological time scales (Baines and Worden, 2004; Haszeldine et al., 2005; Holland and Gilfillan,
65 2013).

66 Helium is an unrivalled indicator of crustal fluid migration in the subsurface because it is
67 sensitive to changes in the balance between volatiles derived from the mantle and the crust. This is
68 because the original helium composition of any subsurface fluid is not significantly modified by
69 interaction with groundwater due to the low abundance of helium in the atmosphere (Ozima and
70 Podosek, 2002). Hence, helium is particularly applicable to tracing gas migration through a water
71 system in both natural and industrial fugitive gas migration monitoring settings. Here we draw from
72 existing methodologies of helium use in tracing the migration of mantle fluids (Sano et al., 1990;
73 Sakamoto et al., 1992), mixing of different fluid sources (O’Nions and Oxburgh, 1988; Sano and
74 Marty, 1995) and dating natural gas and groundwater resources (Zhou and Ballentine, 2006; Liu et
75 al., 2016) to provide a comprehensive account on the geochemical link between natural CO₂ gases,
76 trapped in the subsurface and emanating in the shallow surface.

77 Noble gases are soluble in water and partition according to their relative solubilities during
78 gas-water equilibration. This property has been utilised mainly in assessing reservoir-scale water-gas
79 equilibration and gas migration or groundwater recharge conditions (Bosch and Mazor, 1988;
80 Ballentine et al., 1996; Barry et al., 2016) and the presence of ‘excess air’ above the atmospheric
81 solubility equilibrium (Aeschbach-Hertig et al., 2008; Kipfer et al., 2002). The former is largely based
82 on atmospheric noble gas ratios, whilst the latter combines ratios with elemental concentrations.
83 Atmospheric noble gas ratios in CO₂ springs are commonly similar to air saturated-water (ASW) and
84 the utility of these noble gases is commonly overlooked. We discuss the use of noble gas
85 concentration data in assessing the solubility fractionation effects of near-surface degassing and
86 reconstructing the original noble gas composition for the purpose of tracing.

87 The physical and chemical processes contributing to and modifying the noble gas contents of
88 CO₂ are explored using the data from three natural CO₂ fields in the Otway Basin of SE Australia and
89 ten natural CO₂-rich springs in Victoria. We focus on identifying the origin of the gases and the
90 genetic link between gases stored in reservoir traps and those emanating at the surface from the
91 natural mineral springs.

92 2 Geological setting

93 2.1 Basin setting and location of CO₂ gas fields and springs

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

100 The basement comprises Lachlan and Delamerian fold belts, separated by the Moyston
101 lithospheric suture which extends to the Moho (Fig. 1a). Parallel N-S trending large-scale shear zones
102 and reverse faults connect to the Moyston Fault at depth (Fig. 1d) (Cayley et al., 2011). The structure
103 of the Otway Basin has been strongly controlled by the fabric of the underlying basement. Old
104 basement structures have a significant rheology contrast along them and are more likely to undergo
105 structural reactivation during a change in the stress regime (Hand and Sandiford, 1999). The Jurassic-
106 Cretaceous extension was mainly accommodated along structural weaknesses of the basement,
107 which created graben and half-graben structures favourable for fluid trapping. Hydrocarbons and
108 CO₂ discoveries in the Otway Basin therefore tend to coincide with the location of deep basement
109 faults (Bernecker and Moore, 2003).

110 The basin contains numerous accumulations of CO₂, methane and other hydrocarbons in
111 varying concentrations (Boult et al., 2004). The three gas fields investigated in this work contain CO₂
112 concentrations above 75 mol %, with the remainder of the gas content being primarily methane. The
113 Caroline field is located in South Australia, near Mt Gambier and is a commercially explored CO₂ field
114 which has a CO₂ concentration in excess of 98 %. At reservoir depth and temperature (2.5 km, 92 °C),
115 CO₂ is in a supercritical fluid phase (Chivas et al., 1987). Boggy Creek and Buttress fields are located
116 in the Port Campbell Embayment at the eastern side of the Otway Basin. Both fields contain
117 mixtures of CO₂ and methane in the gas phase with no significant liquid hydrocarbon component
118 (Boreham et al., 2011). Methane generation is dated to mid-Paleogene (Duddy, 1997), followed by a
119 later-stage CO₂ emplacement (Boult et al., 2004; Watson et al., 2004; Lyon et al., 2005).

120 CO₂-rich mineral spring waters emanate at the ground surface within the extent and north of
121 the basin. Over a hundred ambient temperature mineral springs are located in the Central Victorian
122 Highlands (CVH) (Fig. 1b). Mineral water flows through a fracture-dominated aquifer consisting of
123 Ordovician low-grade metasedimentary sequence and discharges into topographic lows such as

124 streambeds. Many of the springs also release CO₂ and can be identified as degassing CO₂ bubble
125 trails into creek beds or standing pools of water. Springs are clustered along the Muckleford Fault,
126 which is a deep Proterozoic reverse fault extending down to the lower crust and connecting to the
127 Moyston suture zone (Cayley et al., 2011) (Fig. 1d).

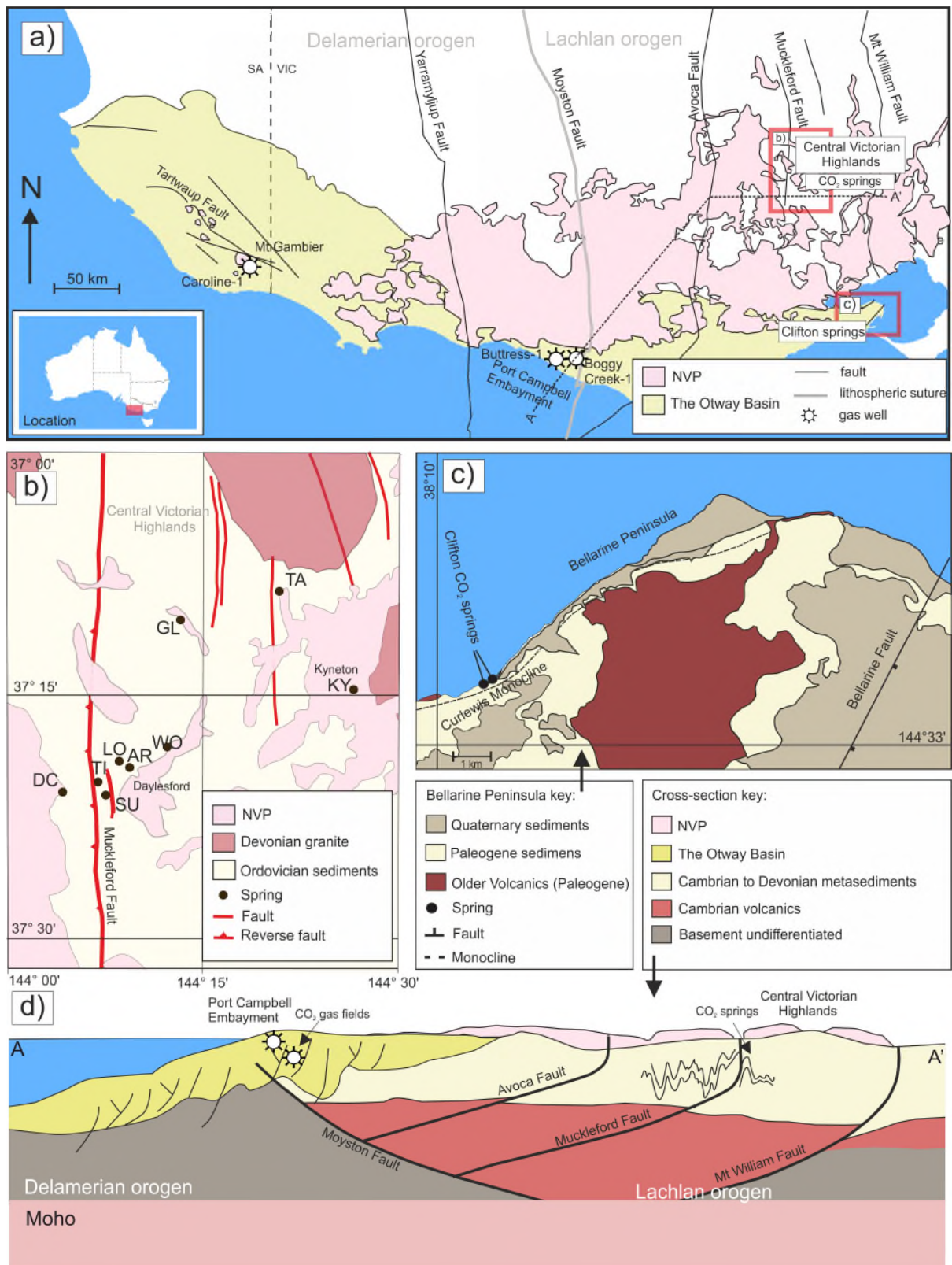
128 Mineral springs also emerge on the northern coast of Bellarine Peninsula, at Clifton Springs
129 near Geelong, on the south-eastern edge of the Otway Basin (Fig. 1c). The central part of the
130 Bellarine Peninsula has been uplifted in the late Miocene during the inversion of NE-SW trending
131 normal faults (Coulson, 1933). The north coast of the peninsula is structurally controlled by the
132 Curlewis Monocline, underlain by a south dipping normal fault. The Curlewis Monocline is parallel to
133 the structural lineaments of the basement and could be associated with deeper basement faults
134 (Dahlhaus, 2003). CO₂ springs emerge along the shoreline parallel to the fault.

135 The basement and the Otway Basin are overlain by the Newer Volcanic Province (NVP)
136 extrusives that stretch from the CVH to the northern edges of the Port Campbell Embayment. The
137 province is a well preserved intra-plate basaltic lava field with more than 400 eruptive centres
138 (Boyce, 2013), active between 5 Ma and 4.5 ka (Cas et al., 2017). The last eruption dated at 4.5 ka,
139 occurred at Mount Gambier, located near the Caroline CO₂ field (Robertson et al., 1996). Many of
140 the oldest eruptive centres are found in the eastern side of the province and near the CVH (4.6 - 2.6
141 Ma) (Price et al., 1997), but no systematic pattern of eruption ages exists (Cas et al., 2017). There is
142 no evidence for volcanic activity of this period in the Bellarine Peninsula where Clifton Springs are
143 located, although The Older Volcanics (39 - 49 Ma) crop out in the area (Price et al., 1997). The cause
144 of the recent volcanism is currently unresolved. Common theories include a mantle plume (Wellman
145 and McDougall, 1974; Wellman, 1983), edge-driven isolated mantle convection (King and Anderson,
146 1998), batch-melting caused by fault reactivation (Lesti et al., 2008), or a combination of all these
147 factors (Demidjuk et al., 2007; Davies and Rawlinson, 2014).

148 2.2 Previous noble gas studies of the gas fields and CO₂ springs

149 Despite the commercial exploration of CO₂ gas fields in the Otway Basin and springs in the
150 CVH, studies of the CO₂ origins have been limited and the processes associated with the gas
151 migration in the subsurface and to the surface are poorly understood. MORB and solar noble gas
152 signatures have been identified in mantle xenolith samples from the Newer Volcanics (Matsumoto et
153 al., 1997, 2002), primarily within CO₂-rich fluid inclusions (Matsumoto et al., 1998). Chivas et al.
154 (1987) reported ³He/⁴He values of up to 3.1 R_A in the Caroline field and Caffee et al. (1999) identified
155 the presence of primordial Xe in the field, providing evidence for a mantle source. Mantle helium has

156 also been reported in the Lavers-1 gas field in the Otway Basin (1.68 R/R_A) (Watson et al., 2004).
157 Preliminary ³He/⁴He measurements of up to 3.1 R_A have been reported in CO₂ springs at the CVH
158 (Chivas et al., 1983) but no further study has been published. It has been suggested that the source
159 of mantle volatiles in CO₂ springs is associated with the NVP (Lawrence, 1969), however no
160 conclusive evidence currently exists other than geographic proximity to the eruptive centres. Prior to
161 this work no geochemical study into the origin of the CO₂ degassing at the Bellarine Peninsula had
162 been published.



163
 164 **Figure 1.** Location map of the studied CO₂ gas fields and springs. **a)** Studied well gases are in two localities in the Otway
 165 Basin: Port Campbell Embayment and Mt Gambier. Clifton Springs are located on the eastern edge of the basin. The CVH
 166 CO₂ springs emerge from the Ordovician basement rocks in the CVH (Central Victorian Highlands). The Otway Basin and
 167 CVH are dissected by N-S trending faults. The NVP (Newer Volcanic Province) extends across both areas. **b)** Location of
 168 sampled CO₂ springs in CVH; many of the springs are located near the Muckleford Fault (see Table 1 for sample name
 169 abbreviations). **c)** Clifton Springs are located on the coast of Bellarine Peninsula, along the crest of the Curlew's

170 **Monocline. d) Sketch cross-section (not to scale) of A-A' transect on Fig. 1a, showing the structural relationship between**
171 **the basement and the basin. The Moyston and Mt Williams Faults extend to the Moho. Many of the basement faults**
172 **(including The Muckelford fault at CVH) are inferred to be connected to the Moyston Fault at depth. Elements of the**
173 **figure adapted from** (Cartwright et al., 2002; Bernecker and Moore, 2003; Watson et al., 2003; Cayley et al., 2011; Cas et
174 al., 2017).

175 2. Methods

176 2.1 Gas sampling

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

192 2.2 Laboratory procedures

193 All laboratory work was undertaken at the Scottish Universities Environmental Research
194 Centre (SUERC). Copper tube samples were connected to an all-metal vacuum line, purified using VG
195 Scienta ST22 titanium sublimation pump and ZrAl alloy getter. The isotopic composition of noble
196 gases was measured using a MAP 215-50 mass spectrometer using techniques outlined in Györe et
197 al. (2015). Bulk gas concentrations were measured using a Pfeiffer Vacuum QMS 200 quadrupole
198 mass spectrometer and Hewlett Packard 5890 Series 11 Gas Chromatograph with uncertainties of ±1
199 %. Major gas concentrations are reported corrected for air. δ¹³(CO₂) values were determined using a
200 VG Optima dual inlet isotope ratios mass spectrometer in dynamic mode using an internal standard
201 (Dunbar et al., 2016). Values are reported relative to VPDB standard with uncertainties of ±0.2 ‰.

202 3. Results

203 A total of three well gas and ten spring samples were measured. Sample location, bulk gas
204 composition, $\delta^{13}(\text{CO}_2)$ values, temperature, pH and TDS measurements are reported in Table 1. He,
205 Ne and Ar isotope ratios, and He, Ne, Ar, Kr, Xe concentrations are reported in Table 2. The full suite
206 of noble gases was measured in six of the CO_2 spring samples, while only He and Ne isotopes were
207 measured in three well gas and four CO_2 spring samples.

208 **Table 1. Details of the geographic location, bulk gas composition, $\delta^{13}\text{C}(\text{CO}_2)$ values of 3 well gases and 10 CO_2 springs; pH, temperature and TDS measured in water from**
 209 **10 mineral water bores.**

Sample name	Label	Location			Bulk gas composition*							$\delta^{13}\text{C}(\text{CO}_2)$	Water from shallow bores		
		Region	Latitude	Longitude	CO_2	CH_4	C_2H_6	C_3H_8	C_4H_{10}	N_2	VPDB	pH	T °C	TDS g/L	
<i>Well gases</i>															
Caroline-1	CA	Mount Gambier, SA	-37.9417	140.9083	99	0.9	0.01	–	–	0.4	-4.1	–	–	–	
Boggy Creek-1	BC	Port Campbell, VIC	-38.5261	142.8245	87	10.0	0.1	0.03	0.01	2.3	-5.6	–	–	–	
Buttress-1	BU	Port Campbell, VIC	-38.5167	142.8084	77	19.7	0.8	1.1	–	1.9	-7.6	–	–	–	
<i>CO₂ springs</i>															
Taradale	TA	CVH	-37.1393	144.3500	>99						-9.4	6.1	20.9	2.9	
Locarno	LO	CVH	-37.3113	144.1412	>99						-7.2	6.1	16.7	1.6	
Deep Creek	DC	CVH	-37.3419	144.0733	>99						-8.2	5.6	15.7	0.6	
Glenluce	GL	CVH	-37.1623	144.2225	>99	0.1					-7.8	6.3	16.7	2.2	
Woolnoughs	WO	CVH	-37.2942	144.2065	>99						-6.9	6.2	21.1	1.6	
Clifton Springs	CS	Bellarine Peninsula	-38.1510	144.5659	>99						-6.0	5.5	20.5	3.8	
Sutton	SU	CVH	-37.3480	144.1317	>99						-8.4	6.0	19.7	1.1	
Argyle	AR	CVH	-37.3141	144.1553	>99						-9.2	5.8	15.1	1.0	
Kyneton	KY	CVH	-37.2358	144.4200	>99						-8.0 ^a	6.1	18.3	1.2	
Tipperary	TI	CVH	-37.3391	144.1186	>99						-7.1	6.3	16.5	2.2	

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

211 ^a from Cartwright et al. (2002)

212 Table 2. Noble gas concentrations and isotopic ratios for 3 well gas samples and 10 CO₂ springs.

Sample name	³ He/ ⁴ He (R _C /R _A)	²⁰ Ne/ ²² Ne	²¹ Ne/ ²² Ne	⁴⁰ Ar/ ³⁶ Ar	³⁸ Ar/ ³⁶ Ar	⁴ He x 10 ⁻⁶	²⁰ Ne x 10 ⁻⁹	⁴⁰ Ar x 10 ⁻⁵	⁸⁴ Kr x 10 ⁻⁹	¹³² Xe x 10 ⁻¹⁰
<i>Well gases</i>										
Caroline-1	3.07 (0.12)	–	–	–	–	96.0 (5.0)	2.2 (0.1)	–	–	–
Boggy Creek-1	1.21 (0.01)	–	–	–	–	384.4 (18.6)	124.1 (5.3)	–	–	–
Buttress-1	1.25 (0.01)	–	–	–	–	478.8 (23.2)	15.4 (0.7)	–	–	–
<i>CO₂ springs</i>										
Taradale	1.23 (0.03)	9.73 (0.06)	0.030 (0.001)	314 (1)	0.195 (0.008)	4.0 (0.2)	34.3 (1.5)	5.3 (0.2)	8.2 (0.3)	6.9 (0.4)
Locarno	3.14 (0.09)	9.68 (0.05)	0.030 (0.001)	303 (1)	0.191 (0.003)	5.7 (0.2)	59.1 (2.5)	7.8 (0.3)	10.4 (0.43)	6.5 (0.3)
Deep Creek	2.45 (0.07)	9.92 (0.05)	0.029 (0.001)	301 (5)	0.190 (0.003)	8.9 (0.4)	132.3 (5.6)	22.8 (0.8)	39.5 (1.6)	30.4 (1.6)
Glenluce	1.57 (0.07)	9.71 (0.05)	0.028 (0.000)	308 (1)	0.189 (0.003)	163.0 (6.0)	1372 (58)	94.4 (3.5)	63.1 (2.6)	25.6 (1.3)
Woolnoughs	1.71 (0.07)	9.78 (0.06)	0.030 (0.001)	299 (1)	0.190 (0.003)	0.97 (0.04)	1781 (3.7)	86.0 (3.2)	79.9 (3.3)	36.1 (1.9)
Clifton Springs	1.97 (0.06)	9.73 (0.06)	0.029 (0.001)	323 (1)	0.191 (0.003)	42.0 (2.0)	128.8 (5.5)	22.9 (0.8)	29.8 (1.2)	19.9 (1.0)
Sutton	3.14 (0.03)	–	–	–	–	1.61 (0.05)	42.5 (1.5)	–	–	–
Argyle	3.65 (0.08)	–	–	–	–	87.9 (2.6)	5502 (196)	–	–	–
Kyneton	1.24* (0.04)	–	–	–	–	4.9 (0.1)	13834 (493)	–	–	–
Tipperary	2.70 (0.05)	–	–	–	–	0.48 (0.01)	438.3 (8.9)	–	–	–

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

214 Errors are 1σ standard deviation.

215 * ³He/⁴He reported uncorrected for atmospheric component due to air contamination

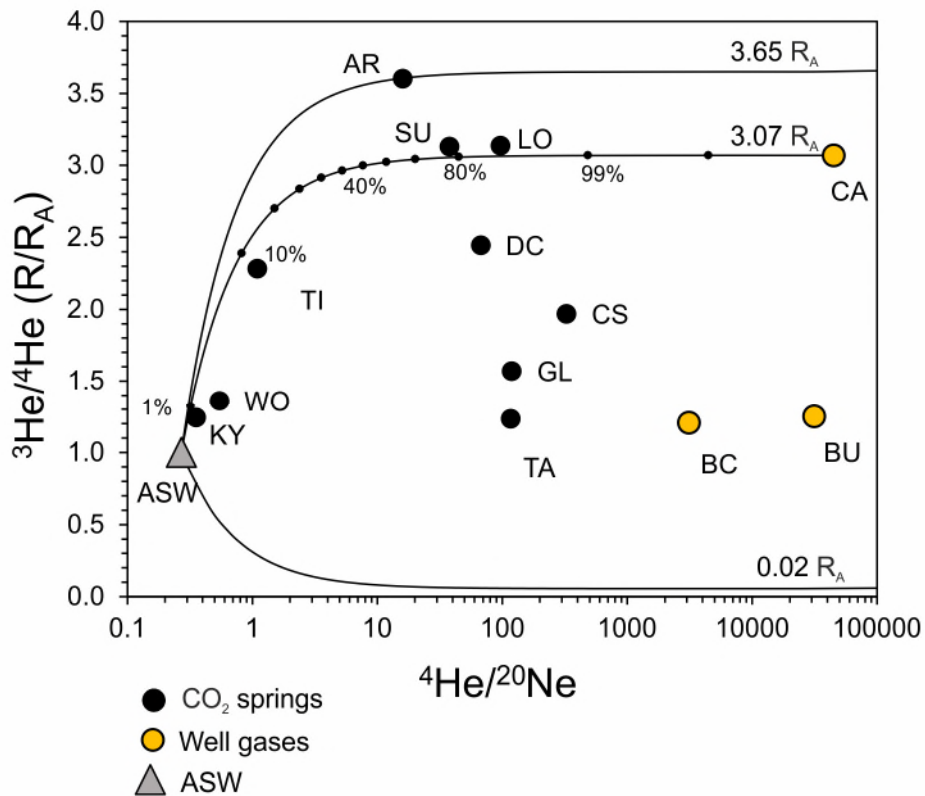
216 3.1. Bulk gas concentrations, $\delta^{13}(\text{CO}_2)$ and water measurements

217 The concentration of CO_2 in the Buttress field is 77 % with the remainder of gas predominately
218 constituting of CH_4 (19.7 %), N_2 (1.9 %) and traces of higher hydrocarbons (0.8 % C_2H_6 , 1.1 % C_3H_{10}).
219 Bulk gas compositions for the other two well gases are taken from the literature. CO_2 concentration
220 in the adjacent Boggy Creek field is slightly higher (87%) (Akbari, 1992). The Caroline field has the
221 highest CO_2 concentrations of 99 % with traces of CH_4 , N_2 and C_2H_6 (Chivas et al., 1987). All mineral
222 spring gas samples were measured to be above 99 % CO_2 with the remainder of gas composed of
223 noble gases. Glenluce is the only spring showing trace amounts of CH_4 (0.1 %). The $\delta^{13}(\text{CO}_2)$ values of
224 the gas samples range from -9.4 to -6 ‰ in springs, and -7.6 to -4.1 ‰ in the well gases. The
225 temperature of the water samples varies from 15.1 – 20.9 °C, pH ranges from 5.6 to 6.3 in CVH
226 springs and 5.5 in Clifton Springs. Total dissolved solids (TDS) values range from 0.63 to 2.85 g/L.

227 3.2. Noble gas results

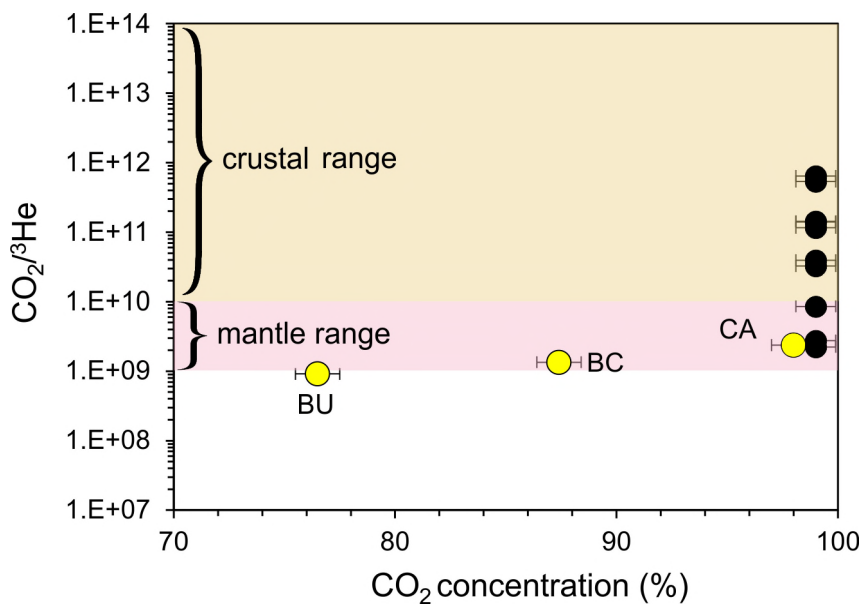
228 $^3\text{He}/^4\text{He}$ ratios are reported normalised to the value of air (where 1 R_A is the atmospheric ratio
229 of 1.4×10^{-6}). $^3\text{He}/^4\text{He}$ R_c/R_A are corrected for ^4He derived from the atmospheric component, using
230 the $^4\text{He}/^{20}\text{Ne}$ value of the sample following the methodology in Craig (1978). It is assumed that all
231 ^{20}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).
232 $^4\text{He}/^{20}\text{Ne}$ ratios of the well gases are 4-5 orders of magnitude above the ASW value (3097-44656)
233 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
234 the measured $^3\text{He}/^4\text{He}$ ratios in spring samples with $^4\text{He}/^{20}\text{Ne}$ ratios <10 (Woolnoughs and
235 Tipperary). Kyneton is the only sample with significant atmospheric contamination ($^4\text{He}/^{20}\text{Ne} = 0.35$)
236 which would make the correction erroneous (Sano et al., 2006) therefore its $^3\text{He}/^4\text{He}$ value is
237 reported uncorrected (1.24 R_A). The $^3\text{He}/^4\text{He}$ ratios of the remaining spring samples range from 1.23
238 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_A . The
239 sample collected from the Caroline CO_2 field in South Australia exhibits a higher value of 3.07 R_A , in
240 agreement with previous measurements (Chivas et al., 1987). All samples are compatible with two-
241 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
242 ASW (Fig. 2).

243 $\text{CO}_2/^3\text{He}$ ratios of the well gases are within or below the Mid-Ocean Ridge Basalt (MORB)
244 range of 1×10^9 to 1×10^{10} (Marty and Jambon, 1987). This is quite distinct from the higher $\text{CO}_2/^3\text{He}$
245 values predicted for near ^3He -free carbonates (O'Nions and Oxburgh, 1988; Sherwood Lollar et al.,
246 1997). CO_2 concentrations in the spring samples are uniform, whilst $\text{CO}_2/^3\text{He}$ ratios vary over two
247 orders of magnitude, 2.26×10^9 and 6.5×10^{11} , across the typical mantle and crustal values (Fig. 3).



248

249 Figure 2. $^3\text{He}/^4\text{He}$ R_A plotted against $^4\text{He}/^{20}\text{Ne}$ ratios of springs and well gases. Solid lines depict binary
 250 mixing between ASW and the highest regional end-member (Argyle, 3.65 R_A), Caroline field and a crustal
 251 end-member (0.02 R_A). Black tick marks show percentage of helium from Caroline end-member in the
 252 mixture. Few springs fall close to the mixing line with the Caroline field, the remaining samples have
 253 variable amounts of crustal component. The errors are smaller than the symbols. Abbreviations of sample
 254 names are given in Table 1.



255

256 **Figure 3. CO₂/³He ratios plotted against CO₂ concentrations for the well gases (yellow circles) and CO₂**
257 **springs (black circles). The shaded area shows the range of CO₂/³He values in the mantle (Marty and**
258 **Jambon, 1987) and crustal (O’Nions and Oxburgh, 1988) sourced volatiles. Well gas samples are within the**
259 **mantle range but with positive correlation between CO₂/³He ratios and CO₂ concentrations. CO₂**
260 **concentrations are uniform in the spring samples, however CO₂/³He ratios are wide-ranging across the**
261 **typical mantle and crustal values. Vertical errors are smaller than symbols. Abbreviations of sample names**
262 **are given in Table 1.**

263 Neon, argon, krypton and xenon concentrations were measured in six CO₂ spring samples
264 (Taradale, Locarno, Deep Creek, Glenluce, Woolnoughs and Clifton Springs) (Table 2). ²⁰Ne/²²Ne
265 ratios of the spring samples range between 9.68 ± 0.05 and 9.92 ± 0.05, close the air value of 9.8
266 (Eberhardt et al., 1965). ⁴⁰Ar/³⁶Ar ratios range from 299 ± 1 to 323 ± 1, slightly above the value of air
267 (298.5) (Lee et al., 2006). In contrast to relatively uniform and air-like isotope ratios, noble gas
268 concentrations are highly variable. ²⁰Ne concentrations vary over three orders of magnitude (3.43 ±
269 0.15 × 10⁻⁸ to 1.4 ± 0.1 × 10⁻⁵); ⁴⁰Ar concentrations vary from 5.3 ± 0.2 × 10⁻⁵ to 9.44 ± 0.43 × 10⁻⁴. ⁸⁴Kr
270 and ¹³²Xe concentrations range from 8.2 ± 0.3 × 10⁻⁹ to 7.9 ± 3 × 10⁻⁸ and 6.5 ± 0.3 × 10⁻¹⁰ to 3.6 ± 0.2
271 × 10⁻⁹, respectively.

272 4. Discussion – link between the CO₂ source in the reservoirs and 273 springs

274 4.1. He-CO₂ abundance system

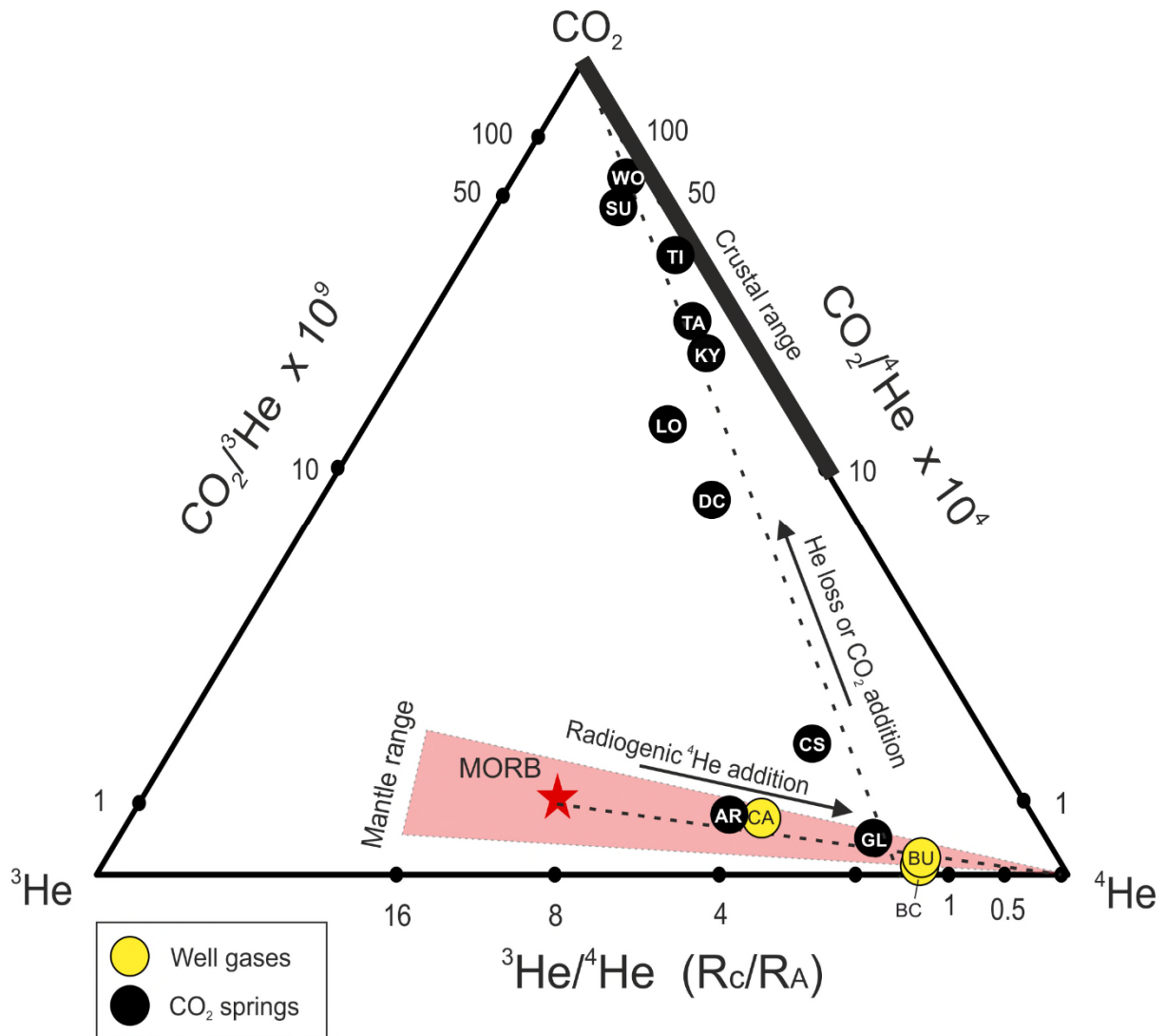
275 The trends in He-CO₂ abundance of well gases and CO₂ springs can be distinguished using a
276 ternary diagram after Giggenbach et al. (1993). This allows depiction of the relative ratios between
277 CO₂-³He-⁴He rather than absolute concentrations (Fig. 4). The MORB end-member (Marty and
278 Jambon, 1987) is displayed for reference with a straight mixing line showing addition of radiogenic
279 ⁴He. Caroline, Buttress, and Boggy Creek well gases as well as Argyle and Glenluce springs fall on a
280 mixing line between MORB and crustal end-members. The rest of the springs lie on the mixing
281 trajectory with low He/high CO₂ end-member (the CO₂ apex of the plot).

282 Based on the observed trends, two main processes can be identified. Addition of radiogenic
283 ⁴He to the MORB-type component lowers the ³He/⁴He, decreases CO₂/⁴He and does not affect
284 CO₂/³He ratio (the trend towards the ⁴He apex of the graph). All CO₂ well gas and spring samples
285 exhibit variation in ³He/⁴He ratios due to radiogenic ⁴He addition. Subsequently, either helium loss or
286 CO₂ addition increases both CO₂/³He and CO₂/⁴He but does not affect the ³He/⁴He ratios. The second

287 process affects the majority of the springs (excluding Glenluce and Argyle) but none of the well gas
288 samples (trajectory towards the CO₂ apex of the plot).

289 To evaluate this two-step process in the following discussion, we select two samples to use as
290 initial end-members. Argyle spring is representative of the regional high-mantle end member, least
291 affected by radiogenic ⁴He addition (exhibiting the highest measured ³He/⁴He ratio 3.65 of R_c/R_A,
292 [⁴He] = 8.8 ± 0.3 × 10⁻⁵ cm³(STP)/cm³). The highest He concentrations were measured in Glenluce
293 sample (³He/⁴He 1.57 R_c/R_A, [⁴He]=1.6 ± 0.1 × 10⁻⁴ cm³(STP)/cm³), which is the least affected by
294 secondary He loss or CO₂ addition.

295 The ³He/⁴He ratio can be modified by dilution with non-CO₂ gas (usually methane) with a
296 different He isotopic signature (Sherwood Lollar et al., 1994), radiogenic ⁴He accumulation in situ
297 (Newell et al., 2015; Liu et al., 2016) or He stripping from formation water during gas migration
298 through lithological units enriched in ⁴He (Sano et al., 1990; Sakamoto et al., 1992). The resulting
299 ³He/⁴He ratio can then be overprinted by addition of CO₂ from a different source (O'Nions and
300 Oxburgh, 1988) or phase fractionation during degassing (Matthews et al., 1987). If the well gases
301 and CO₂ springs share a common source, then these processes can be accounted for and gas
302 composition can be traced back to a single initial end-member.



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Figure 4. Ternary diagram (after Giggenbach et al., 1993) showing the relationship between the concentrations of CO₂, ³He, ⁴He expressed as their ratios. MORB value used for reference is 8 ± 1 R_A (Marty and Jambon, 1987). The dashed lines show mixing between different components. The two clear trends are: 1) Radiogenic ⁴He addition, which shifts gas composition to the right apex of the ternary plot, 2) CO₂ 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/CO₂ addition trendline. Abbreviations of sample names are given in Table 1.

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4.2 Radiogenic ⁴He addition

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⁴He 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, ³He is produced by thermal neutron capture by ⁶Li, 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

317 ³He released from mantle fluids and can be considered to be negligible in the context of in-situ
318 crustal helium accumulation.

319 After production, radiogenic helium is either trapped in the pore spaces in-situ or mobilised by
320 any migrating water or gas phase present in the subsurface and then transported elsewhere. If a
321 natural gas trap exists in-situ, helium will preferentially accumulate in the gas phase due to its low
322 solubility in water.

323 4.2.1. Radiogenic ⁴He accumulation in-situ

324 The initial ³He/⁴He ratio of mantle-sourced gas can be reduced by direct accumulation of ⁴He
325 produced in the crust, or by mixing with ⁴He-rich methane. The former would be applicable to CO₂
326 springs, the latter to well gases containing CO₂ and CH₄ mixtures. In both cases, the final ⁴He
327 concentrations are controlled by the rate of ⁴He production in the crust. The contents of radiogenic
328 ⁴He accumulated in-situ in a natural gas trap can therefore be considered as a function of time since
329 the initial emplacement of the gas in the trap, given a known crustal helium production rate (Liu et
330 al., 2016). Under this assumption, we can estimate the residence time required for the observed
331 ³He/⁴He ratios in both the well gases and the springs.

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

$$334 \quad {}^4P = 0.2355 \times 10^{-12} \times [U] \times (1 + 0.123 \times [Th]/[U] - 4) \quad (1)$$

$$335 \quad J_{He} = {}^4P \times \rho \times (1 - \phi)/\phi \quad (2)$$

336 Where:

337 [U], [Th] – concentrations in ppm

338 ⁴P – crustal ⁴He production rate in cm³ STP/g yr

339 J_{He} – ⁴He production rate cm³ STP/yr

340 ρ – density of the crust in g/cm³

341 ϕ – porosity of the rocks as a fraction

342 Assuming ⁴He has been accumulating in mantle-sourced CO₂ with a known initial composition,
343 the final ³He/⁴He ratio is expressed as a function of time modified from Newell et al. (2015):

344 ${}^3\text{He}/{}^4\text{He}(t) = F \times {}^3\text{He}_m / (J_{\text{He}} \times t + \times {}^4\text{He}_m)$ (3)

345 Where:

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

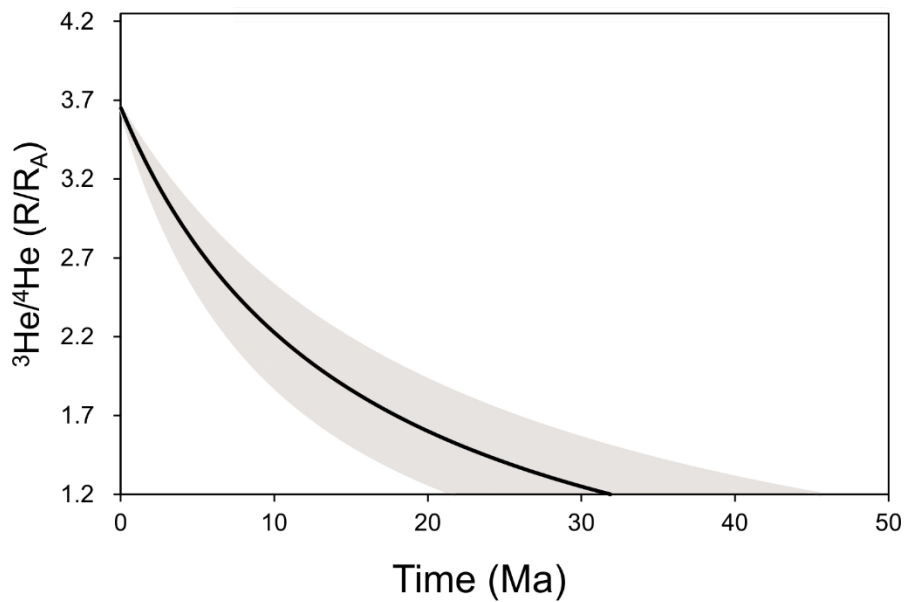
347 He_m – helium concentration of the mantle-source end-member

348 t – time in years

349 The final result is independent of the timing of CO₂ emplacement as it records the total ⁴He
350 accumulated since the start of the gas trap filling, so in the case of CO₂/methane mixture, the
351 recorded age will be that of the methane emplacement. Argyle spring concentrations are taken as
352 representative of the initial mantle-sourced end-member, based on the highest measured ³He/⁴He
353 ratio (3.65 R_c/R_A). This ratio is significantly lower than SCLM or MORB values, but we assume this to
354 be representative of the end-member at the time of emplacement. Similar value is measured in the
355 Caroline field which has likely been emplaced at a similar time to Mount Gambier eruptions dated at
356 5 ka (Roberston et al., 1996), so we assume this to be a regional feature and that some radiogenic
357 ⁴He accumulation occurred within the melt before the gas emplacement.

358 Assuming an average reservoir porosity of 25 % (Watson et al., 2003), average crustal ²³⁸U and
359 ²³²Th concentrations of 2.8 and 10.7 mg/kg and average crustal density of 2.5 g/cm³ (Rudnick and
360 Fountain, 1995) the estimated age of filling of the of Boggy Creek field is 32 Ma (Fig 5). Assuming ± 5
361 % and ± 10 % uncertainty in porosity and ²³⁸U and ²³²Th concentrations respectively, the
362 accumulation age could vary between 22 and 45 Ma (showed in shaded area in Fig 5). The model
363 only considers ⁴He accumulated in-situ and does not account for other ⁴He sources in the total
364 budget which could include: the initial ⁴He contents in the gas phase acquired from the source rock,
365 helium stripped from water during the two stages of methane and CO₂ migration in the reservoir
366 and any external ⁴He flux, caused by heat release associated with regional tectonic events or
367 volcanism. The model also assumes all radiogenic ⁴He produced in the crust is released into the pore
368 water. Contribution from any of the outlined processes would act to decrease the modelled range,
369 so the calculated accumulation age range can therefore be taken as a maximum estimate.

370 Methane in Port Campbell traps is associated with the last hydrocarbon generation stage that
371 commenced during the mid-Paleogene (Duddy, 1997; Boreham et al., 2004), which closely matches
372 the range of accumulation ages calculated. The ³He/⁴He ratios observed within the Boggy Creek and
373 Buttress fields can plausibly be explained by an Argyle-type end-member mixing with methane
374 containing radiogenic ⁴He, confirming the binary mixing with methane trend depicted in Figure 4.



375

376 **Figure 5. $^3\text{He}/^4\text{He}$ ratio vs time since gas emplacement calculated for the composition of the Boggy Creek-1**
 377 **sample. To achieve the current $^3\text{He}/^4\text{He}$ ratio measured in Boggy Creek (1.21 R_A), Argyle-type CO_2 (3.65 R_A)**
 378 **would have to mix with methane that has been emplaced at 32 Ma. Shaded area shows uncertainty.**

379 The same calculation can be applied to the CO_2 springs. The ^{238}U - ^{232}Th contents are assumed
 380 to be the same; the porosity of a fracture-dominated metasedimentary aquifer is estimated to be
 381 lower ($10 \pm 5\%$). To reduce the initial $^3\text{He}/^4\text{He}$ ratios of 3.65 to the lowest measured value of 1.23 R_A ,
 382 it would take 9 Ma years on average and between 4-15 Ma within the uncertainty of the parameters.
 383 To account for the range of observed $^3\text{He}/^4\text{He}$ ratios, this scenario requires emplacement of separate
 384 gas pockets for each individual spring at different times between 9 Ma and present and retention
 385 within the crust before the onset of the recent migration to the surface.

386 Multiple gas injection events could be associated with discrete episodes of seismic or volcanic
 387 activity, although the latter is unlikely because the volcanic cones are far fewer than the individual
 388 mineral springs (>100) (Shugg, 2009), and given the predominately monogenetic eruptive character
 389 of the NVP extrusives (Boyce, 2013) volcanic activity is unlikely to produce so many different gas
 390 pulses. Irrespective of the gas emplacement mechanism, the heavily folded and fractured Ordovician
 391 metasedimentary sequence is unlikely to act as an effective gas trap for millions of years. In-situ ^4He
 392 accumulation in CO_2 springs is therefore an unlikely process to account for the observed variation in
 393 $^3\text{He}/^4\text{He}$ ratios.

394 4.2.2. Radiogenic ^4He stripping from enriched pore-water

395 An alternative model to in-situ generation is modification of magmatic $^3\text{He}/^4\text{He}$ ratios by
 396 dilution of mantle He by interaction with radiogenic helium-rich basement fluids during lateral

397 movement of the CO₂. Stagnant fluids in basement rocks with high U/Th concentrations are enriched
398 in radiogenic ⁴He well above ASW levels with ³He/⁴He ratios in the crustal range (0.02 R_A) (Bottomley
399 et al., 1984; Weinlich et al., 1999; Holland et al., 2013; Warr et al., 2018). Isolated stagnant pockets
400 of these fluids within the Cambrian – Ordovician basement sequence are a likely source of ⁴He for
401 the migrating mantle CO₂. In this case, the process is still governed by the helium production rate in
402 the crust (similar to the in-situ ⁴He accumulation discussed above), but the controlling factor is
403 distance migrated through the basement rather than time.

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

413 The mechanism of interaction with these fluids depends on whether CO₂ migrates in the gas phase
414 or dissolved in water. In case of the former, the governing factor is differences in solubility as helium
415 is strongly partitioned from the fluid to the migrating gas phase. If CO₂ migrates dissolved in water,
416 the mixing with the crustal fluids can be described by a mechanical dispersion model (Sano et al.,
417 1990). Assuming that mantle fluids are supplied through a single conduit at a constant rate under
418 steady-state homogeneous and isotropic conditions under an equal hydrostatic pressure, ³He/⁴He is
419 calculated as a function of the radial distance to the conduit (*r*) following the approach detailed in
420 Sano et al. (1990) of deriving the location-specific helium dispersion constant (α) by fitting a least
421 squares function to the measured ³He/⁴He and radial distance data points.

$$422 \quad {}^3\text{He}/{}^4\text{He}(r) = ({}^3Pr^2 + \alpha {}^3\text{He}_m) / ({}^4Pr^2 + \alpha {}^4\text{He}_m) \quad (4)$$

423 Where:

424 *r* – radial distance from the main gas conduit

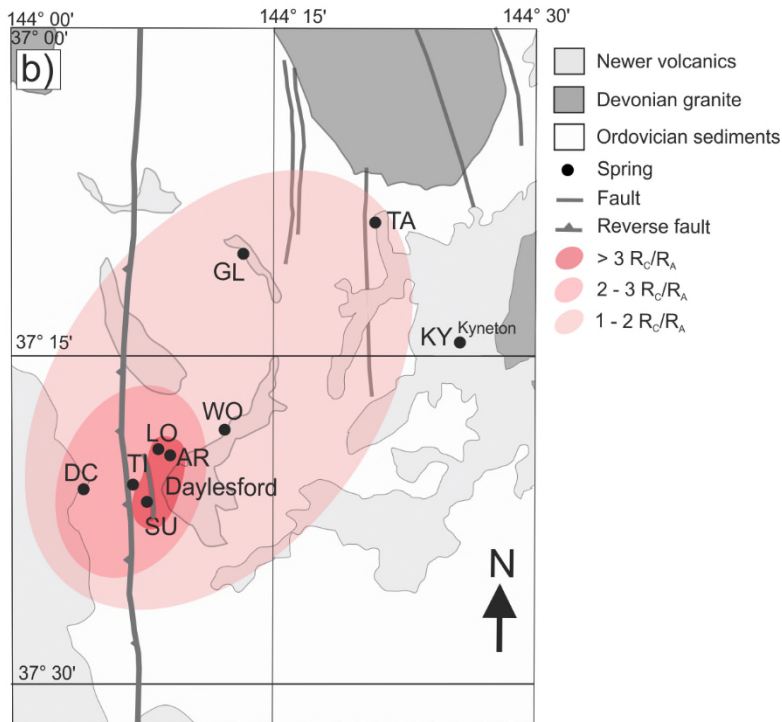
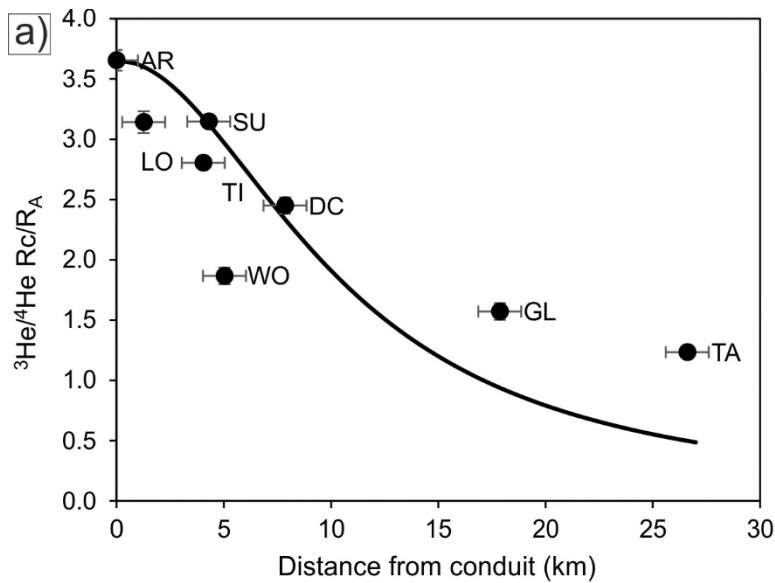
425 α – helium dispersion constant, dependent on the pore network geometry

426 *P* – crustal helium production rate in atoms/cm³s, calculated under the same crustal density and U,
427 Th content assumptions as in the ⁴He accumulation model.

428 Similar decreases in $^3\text{He}/^4\text{He}$ ratios with increasing distance from a central volcanic cone has been
429 observed in various active volcanoes (Marty and Jambon, 1987; Williams et al., 1987; Sano et al.,
430 1990; Sakamoto et al., 1992). The calculated hydrodynamic dispersion coefficient (methods in Sano
431 et al., 1990) is $0.035\text{ cm}^2/\text{s}$, which compares well with the estimates in the original model (0.09 and
432 $0.055\text{ cm}^2/\text{s}$).

433 The overall average rate of $^3\text{He}/^4\text{He}$ decrease in 4 volcanic locations reviewed by Sakamoto et al.
434 (1992) varied between 0.3 to $0.5\text{ RA}/\text{km}$. The average rate of $^3\text{He}/^4\text{He}$ decrease in CVH is $0.1\text{ RA}/\text{km}$,
435 potentially reflecting fluid migration via more efficient fracture networks and conduits in a faulted
436 sequence relative to the previously investigated volcanic and volcanoclastic sequences. Fractured
437 aquifers have lower tortuosity relative to porous ones, which results in shorter effective travel
438 distance for the same total flow path distance (Clennell, 1997) and therefore lower rate of
439 interaction with radiogenic basement fluids per distance travelled.

440 Springs with the highest $^3\text{He}/^4\text{He}$ ratios are clustered near the N-S trending Muckleford Fault
441 and a smaller parallel fault striking along Lake Daylesford (Fig 6b). Previous studies have shown that
442 clusters of NVP volcanic vents are commonly aligned parallel to nearby basement faults throughout
443 the province (van Otterloo et al., 2013; Cas et al., 2017). Mantle xenoliths were found in the vicinity
444 of the faults, suggesting fast mantle upwelling rates through the lithosphere were prevalent during
445 periods of magmatic activity (van Otterloo et al., 2014). While further work is required to provide
446 geomechanical and structural geological evidence for current fluid migration along the fault zones in
447 the CVH, the spatial distribution of $^3\text{He}/^4\text{He}$ ratios suggests that these basement lineaments
448 potentially play an important role in the currently active mantle- CO_2 ascent to the surface.



449

450 **Figure 6 a).** Plot of $^3\text{He}/^4\text{He } R_c/R_A$ values relative to the distance from the Argyle spring (highest $^3\text{He}/^4\text{He}$
 451 ratio), inferred to be closest to the conduit. $^3\text{He}/^4\text{He}$ ratios decrease with increasing radial distance. The
 452 solid line is $^3\text{He}/^4\text{He}$ dispersion with distance model calculated based on Sano et al. (1990). **b)** Geographical
 453 distribution of CO₂ springs. Springs with the highest $^3\text{He}/^4\text{He}$ ratios are clustered close to N-S trending
 454 basement-scale Muckelford thrust fault and parallel smaller fault near Lake Daylesford. Shaded areas show
 455 $^3\text{He}/^4\text{He}$ ratio ranges which decrease with increasing distance from the Argyle spring. Kyneton spring is
 456 excluded due to atmospheric contamination. Abbreviations of sample names are given in Table 1.

457 4.3. Evaluating models to account for CO₂/³He and δ¹³C(CO₂) variation

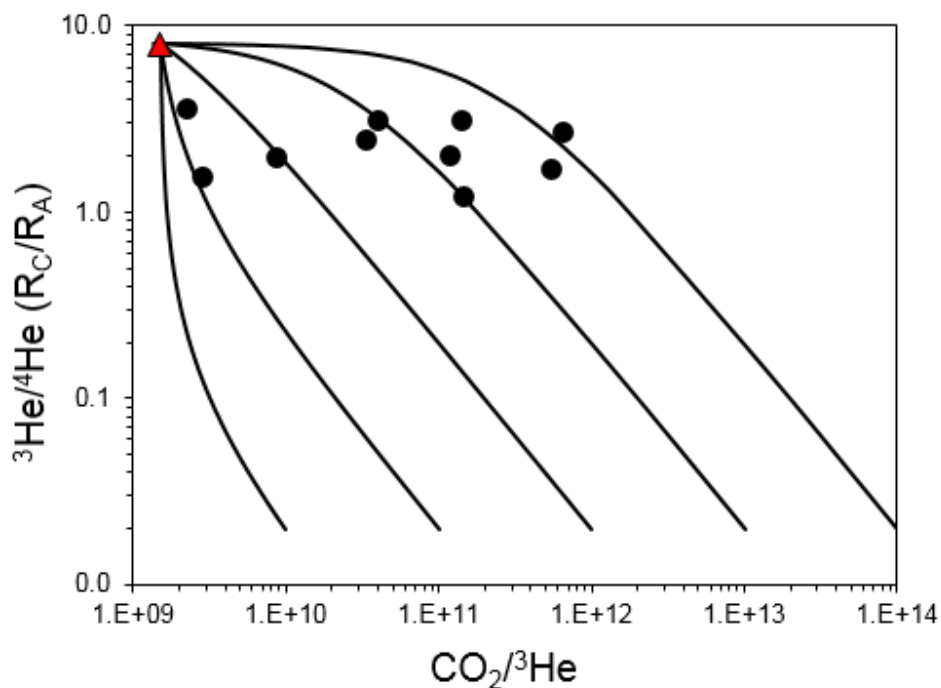
458 The combination of CO₂, helium and δ¹³C(CO₂) values is commonly used to identify the
459 presence of mantle volatiles. This is because CO₂/³He ratios have been well constrained for mantle-
460 derived melts, fluids and volatiles, with an average MORB value accepted as 1.5 ± 0.5 × 10⁹ (Sano and
461 Marty, 1995; Marty and Tolstikhin, 1998). ³He is not produced in significant amounts in the crust, so
462 low ³He/⁴He ratios and associated CO₂/³He ratios between 10¹⁰ – 10¹⁵ are typically associated with a
463 crustal CO₂ source (O’Nions and Oxburgh, 1988). The CO₂/³He ratios observed in ten CO₂ samples
464 from the Victorian mineral springs vary over two orders of magnitude (2.8 × 10⁹ to 6.5 × 10¹¹),
465 encompassing the range typical of mantle and crust end-members. A trend in increasing CO₂/³He
466 ratios is therefore commonly associated with admixture of crustal CO₂ and/or degassing in open
467 system (e.g. Crossey et al., 2009; Newell et al., 2015; Ruzié et al., 2013), defined by Rayleigh
468 fractionation. Here, we test both of these possibilities.

469 Crustal end-members can have a wide range of CO₂/³He ratios but a narrow range of ³He/⁴He
470 ratios (0.01 – 0.07 R_A) (Ozima and Podosek, 2002). Figure 7 shows CO₂/³He values plotted against
471 ³He/⁴He R_c/R_A ratios with binary mixing curves representing mantle (8 R_A) source and various crustal
472 components. Significantly, samples with high CO₂/³He ratios do not necessarily show lower ³He/⁴He
473 ratios, as would be expected in the case of mixing with ³He-poor crustal CO₂ source and trend
474 perpendicular to the calculated mixing lines. To explain the range of measured CO₂/³He ratios,
475 variable amounts of mixing with a wide range of different crustal reservoirs (CO₂/³He – 10¹⁰ - 10¹⁴)
476 would need to be invoked, which is unlikely in the setting where bedrock lithology is uniform across
477 the area.

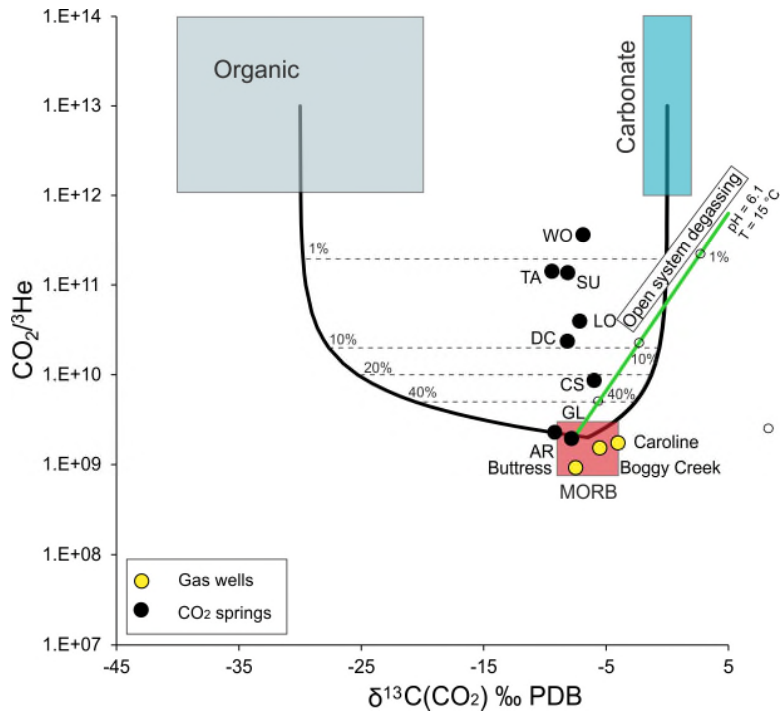
478 Crustal CO₂ addition can be further assessed by combining He data with δ¹³C(CO₂) values
479 (Sano and Marty, 1995). The range of δ¹³C(CO₂) values measured in the springs (-9.4 to -6‰) partly
480 overlap the typical mantle range (-7 to -4‰) (Wycherley et al., 1999). However, increasing CO₂/³He
481 ratios do not consistently correlate with δ¹³C(CO₂) change towards carbonate or organic end-
482 members (Fig. 8). Instead, a vertical trend exists, which would require mixing with an end-member
483 with constant proportions of both organic and carbonate-sourced CO₂. To explain the highest
484 observed CO₂/³He ratios, 99 % of non-mantle (crustal/organic mixture) CO₂ addition is required. Such
485 significant amounts of crustal CO₂ sourced by dissolution of bedrock minerals would liberate cations
486 contained in the dissolving minerals and increase the TDS values of the water. Figure 9 shows that
487 there is no clear positive correlation between the CO₂/³He ratios in the volatiles and TDS values in
488 their associated waters. Alternatively, CO₂ and helium loss during open system degassing can be
489 evaluated using Rayleigh fractionation modelling. Figure 8 also shows a calculated open system

490 Rayleigh fractionation line, assuming average pH of 6.1 and 15 °C temperature. The calculated
 491 fractionation factor between He/CO₂ is 0.012; the enrichment factor $\ln 10^3 \alpha \delta^{13}\text{C}(\text{CO}_2)_{\text{aq}}/(\text{CO}_2)_{\text{g}}$ is
 492 2.2‰. Open system degassing under measured conditions would result in a similar fractionation in
 493 CO₂/³He ratio but a significantly more extensive than observed fractionation of $\delta^{13}\text{C}(\text{CO}_2)$ values. We
 494 therefore conclude that degassing under open system conditions is not supported by the data.

495 Previous geochemical modelling work showed that CO₂ does not cause significant amounts of
 496 bedrock mineral dissolution in the Ordovician aquifer (Karolytè et al., 2017) and there is no
 497 geological evidence for addition of large amounts of crustal CO₂ from other sources (e.g. carbonate
 498 metamorphism). The possibility of significant amounts of organic CO₂ addition is also ruled out,
 499 because the observed trend on Figure 8 cannot be explained by addition of organic CO₂ in the
 500 absence of the crustal component. Based on the combined evidence from $\delta^{13}\text{C}(\text{CO}_2)$ -He, CO₂
 501 abundance and TDS contents of the mineral waters, we conclude that there is no significant crustal
 502 CO₂ addition to the mantle volatiles sampled at the CVH and Clifton Springs. CO₂ loss during
 503 degassing under open system conditions is also not supported by the data.

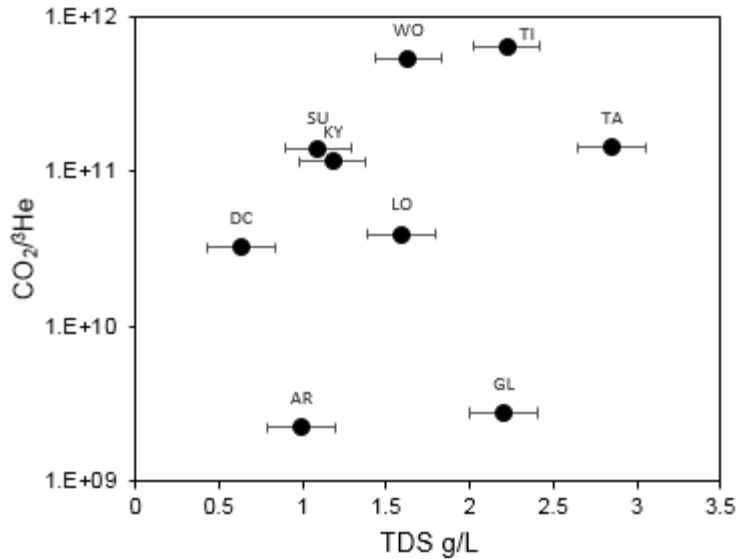


504
 505 **Figure 7. Binary mixing plot between MORB (red triangle) (³He/⁴He 8 R_A, CO₂/³He 1.5 x 10⁹) and various**
 506 **crustal end-members (CO₂/³He 10¹⁰-10¹⁴). The springs form a near-horizontal trendline and do not follow**
 507 **any of the mixing lines, suggesting that mixing does not control the variation in CO₂/³He values. All error**
 508 **bars are smaller than the printed symbols.**



509

510 **Figure 8. $\text{CO}_2/{}^3\text{He}$ ratios vs $\delta^{13}\text{C}(\text{CO}_2)$ values for gas samples in relation to mixing between the mantle,**
 511 **carbonate and organic CO_2 end-members based on Sano and Marty (1995). Caroline, Boggy Creek and**
 512 **Buttruss well gases fall within the mantle range. Spring samples do not show a coherent trend towards**
 513 **either an organic or carbonate CO_2 end member. The observed trend would require > 99% contribution of a**
 514 **component with constant proportions of both organic and carbonate-sourced CO_2 . Green line shows**
 515 **Rayleigh fractionation during degassing under average measured pH and temperature, open circles indicate**
 516 **percentage of gas left. The data do not fall on either the mixing or open system degassing curves (discussed**
 517 **in text). Abbreviations of sample names are given in Table 1.**



518

519 **Figure 9. CO₂/³He vs TDS measured in water, sampled via hand pumps from tube bores. CO₂/³He values are**
 520 **not correlated with TDS. A positive correlation would be expected if crustal CO₂ were added as a result of**
 521 **bedrock mineral dissolution.**

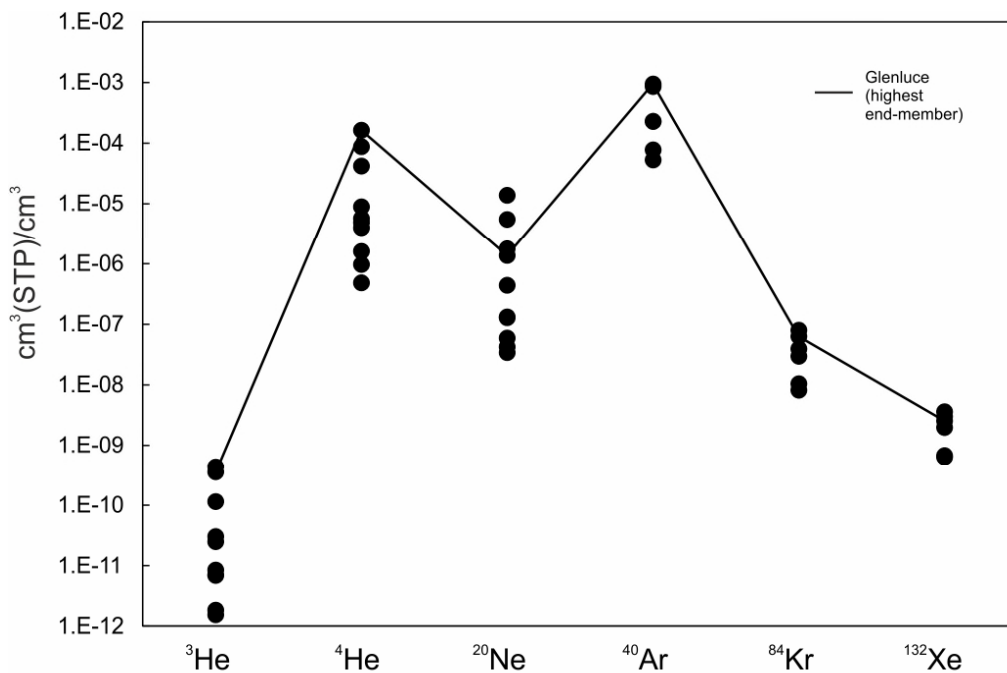
522 Alternatively to mixing with different CO₂ sources, the variability of δ¹³C(CO₂) values (-9.4 to -
 523 6‰) can be explained by degassing in separate individual systems under a range of different pH and
 524 temperature conditions. Equilibrium fractionation between δ¹³C(CO₂) in aqueous and gaseous
 525 phases is controlled by the temperature and the relative amounts of HCO₃⁻ and H₂CO₃, which are pH-
 526 dependent. If H₂CO₃ is the dominant dissolved inorganic carbon (DIC) species, degassing CO₂ is
 527 slightly enriched in ¹³C. Conversely, when HCO₃⁻ dominates the system, degassing CO₂ is relatively
 528 depleted in ¹³C (Deines et al., 1974). The pH values measured in mineral water bores range from 5.5
 529 to 6.1 and temperatures are 15 – 21 °C. In this particular range of conditions, the ratio of HCO₃⁻ to
 530 H₂CO₃ in DIC varies significantly. The resulting calculated equilibrium enrichment factors between
 531 DIC and gaseous CO₂ range from -3.4 to -0.43‰. Degassing under different DIC speciation conditions
 532 therefore can fully account for the observed 3.4‰ variability in δ¹³C(CO₂) values of the spring gases.

533 The trends observed in our data are not unique to this study. CO₂/³He ratios ranging between
 534 10⁹ to 10¹⁴ combined with δ¹³C(CO₂) values without an obvious trend towards organic or carbonate
 535 end-member is a common observation, commonly interpreted as a result of simple mantle and
 536 crustal end-member mixing (Aka et al., 2001; Crossey et al., 2009; Mao et al., 2009). Other workers
 537 recognised that simple mixing is not a conclusive interpretation (Italiano et al., 2014) and suggested
 538 contribution of a solubility fractionation process (Matthews et al., 1987; Hilton, 2009; Newell et al.,
 539 2015). Where open system Rayleigh fractionation is proposed, it is commonly not conclusively
 540 supported by evidence from δ¹³C(CO₂) values (Ruzié et al., 2013; Bräuer et al., 2016). In the following

541 section, we explore how this trend can alternatively be explained by fractionation during a two-step
 542 process of dissolution and degassing.

543 4.4 Noble gas abundance modification by solubility in water

544 The variation observed in ^3He concentrations in the mineral spring samples is also replicated in ^4He
 545 and other noble gases. Figure 10 shows the distribution of noble gas concentrations in all studied
 546 springs. Importantly, the variance in observed gas concentrations decreases with element mass (Fig.
 547 10), indicating a solubility-controlled process. If mantle CO_2 is transported to the surface in solution,
 548 this process can be modelled as dissolution and subsequent degassing.



549 **Figure 10. Noble gas concentrations of CO_2 spring samples in cm^3 (STP)/ cm^3 . The variation in concentrations**
 550 **decreases with increasing molecular mass. Solid black line shows the concentrations measured in Glenluce**
 551 **spring, which has the highest helium concentrations and least fractionated $\text{CO}_2/^3\text{He}$ ratios.**
 552

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

$$556 \quad C_{iw} = \frac{C_{ig}}{K_i} \quad (5)$$

557 Where C is concentration, subscripts g and w denote gas and water phases and K_i is dimensionless
 558 Henry's constant for noble gas i. K_i is temperature, pressure and salinity dependent (Kipfer et al.,
 559 2002). The final concentrations in both phases depend on the volumetric gas/water ratio. The
 560 equilibrium concentrations in the water (C_{iw}^{eq}) are expressed as (Zartman et al., 1961):

561 $C_{iw}^{eq} = C_{it} \times F_w$ (6)

562 $F_w = \frac{C_{iw}V_w}{C_{iw}V_w + C_{ig}V_g}$ (7)

563 Where V is volume, C_{it} is the total noble gas budget, and F_w is the fraction of noble gases in the
 564 water. Combining equations 5-7, C_{iw}^{eq} is:

565 $C_{iw}^{eq} = C_t \times (1 + \frac{V_g}{V_w} K_i)^{-1}$ (8)

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

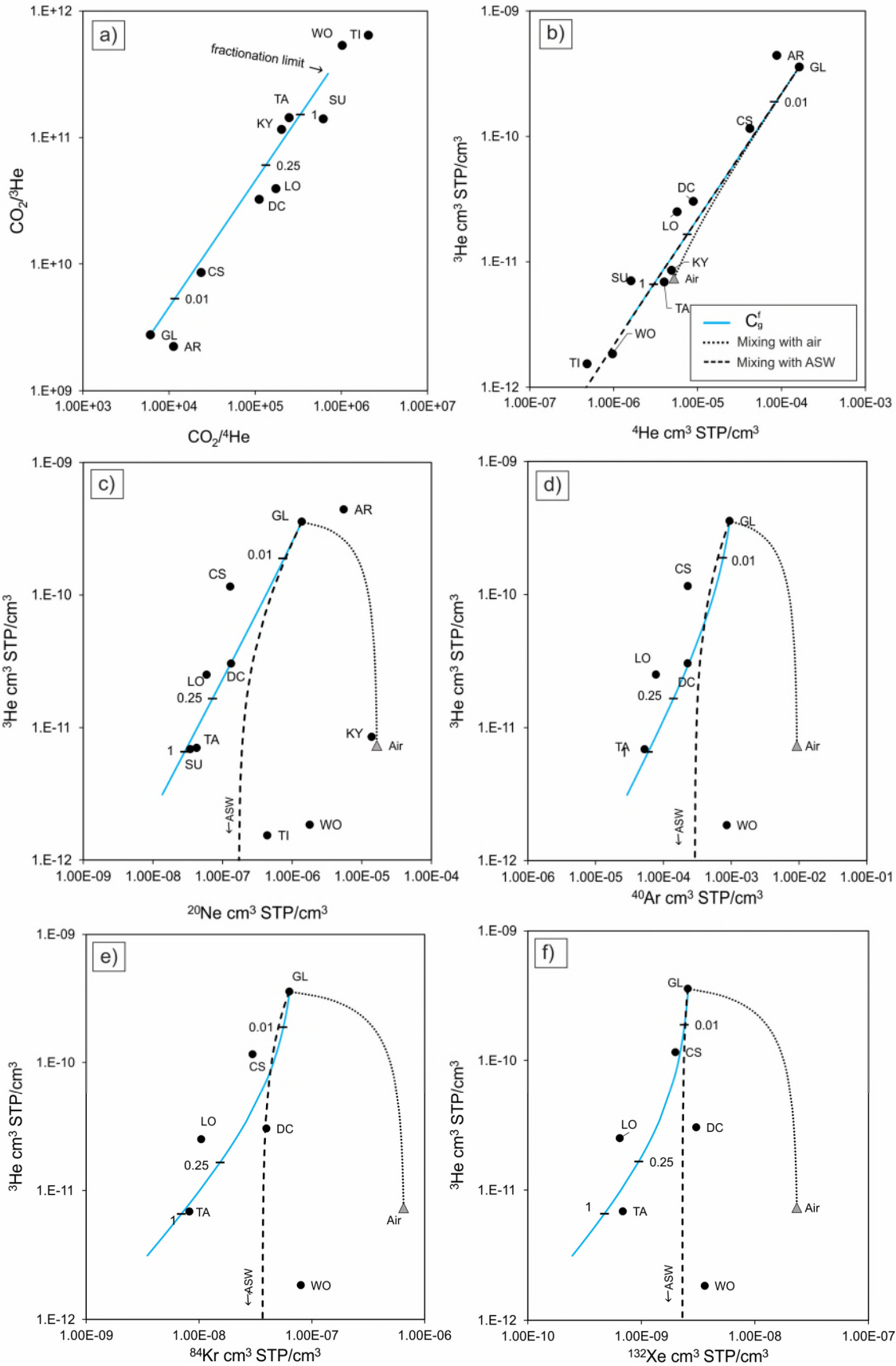
570 $C_{ig}^f = C_{iw}^{eq} \times (1 + (\frac{V_g}{V_w})^{-1} \frac{1}{K_i})^{-1}$ (9)

571 For the purpose of investigating a shallow degassing process, equilibration with fresh water at
 572 atmospheric pressure and 20 °C temperature is assumed. Henry's constants and activity coefficients
 573 for water conditions were calculated from empirical equations from Crovetto et al. (1982) for Ne, Ar,
 574 Kr and Xe and Smith (1985) for He, following the methodology in Ballentine and Burnard (2002).
 575 Henry's constant for CO₂ is calculated using empirical equations from Crovetto (1991). Assuming the
 576 density of fresh water (0.996 cm³/g) (Weast et al., 1988), concentrations in ASW are converted from
 577 cm³STP/g_{H₂O} to cm³STP/cm³ for Figure 11.

578 The highest helium concentrations and lowest CO₂/³He ratio were measured in the Glenluce spring.
 579 We therefore assume that Glenluce is the least solubility fractionated end-member. For the purpose
 580 of the model, we make a simplifying assumption that the Glenluce sample represents the total
 581 amount of CO₂ and noble gases from both the mantle and ASW sources (C_t). This end-member
 582 equilibrates with a volume of water which, in theory, is noble gas free. When $\frac{V_g}{V_w} \rightarrow 0$, $F_w \rightarrow 1$, all
 583 gases are dissolved in water. All gas contents are transferred into the water phase C_{iw}^{eq} and the ratios
 584 are equal to the initial ones. When $\frac{V_g}{V_w} \rightarrow \infty$ and $F_w \rightarrow 0$, only a small fraction of noble gas contents
 585 are dissolved in water. In this case, the ratios are the most fractionated and the concentrations in
 586 water are low. After the equilibration, the water separates from the gas source, migrates to the
 587 surface and degasses. We make a simplifying assumption that the water degasses entirely, $\frac{V_g}{V_w} \rightarrow \infty$,
 588 all dissolved gases are transferred into the gas phase and therefore the final measured $C_{ig}^f \rightarrow C_{iw}^{eq}$.

589 Figure 11 shows CO₂/He ratios, ³He concentrations relative to ⁴He, ²⁰Ne, ⁴⁰Ar, ⁸⁴Kr and ¹³²Xe and the
590 calculated solubility curves C_{ig}^f . The data points fall on the modelled line and is clearly
591 distinguishable from mixing with ASW, which is more enriched in all atmospheric noble gases. Air
592 and ASW components are potentially introduced by inclusion of small amounts of air and water into
593 the copper tube during sampling and are the most significant in Kyneton, Tipperary and Woolnoughs
594 samples. Tipperary and Woolnoughs springs include a combination of ASW and air components,
595 which is obvious in different element pair plots (Fig. 11 c,d,e,f) and less apparent in ³He vs ⁴He (Fig.
596 11b) because air and ASW have similar ³He/⁴He ratios. Figure 11b also clearly shows that the original
597 concentrations in Kyneton spring have been overprinted by admixture of air, most likely during
598 sample collection and clearly identified in the ⁴He/²⁰Ne ratios. The ASW component is more evident
599 in the heavier atmospheric noble gases in the Deep Creek sample (Fig. 11 ,d,e,f).

600 With the exceptions discussed above, all other samples plot close to the modelled solubility
601 fractionation line. The maximum extent of fractionation between CO₂ and He is limited by the ratio
602 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
603 concentrations with decreasing F are consistent across all noble gas elemental pairs. When $\frac{V_g}{V_w}$ is
604 unity, 47% of the total CO₂ is dissolved but only 1% of helium. The resulting CO₂/³He ratio is 1.4 x
605 10¹¹, which is the highest in the sample group, excluding the previously discussed samples which are
606 contaminated with air. This means that dissolution in water under equal gas/water ratios explains
607 the maximum observed fractionation of CO₂/³He values. According to the model, the minimum $\frac{V_g}{V_w}$
608 ratio required to dissolve the entire sample without fractionating the CO₂/³He is 0.0005, or 2000
609 times more water than gas.



610

611

612

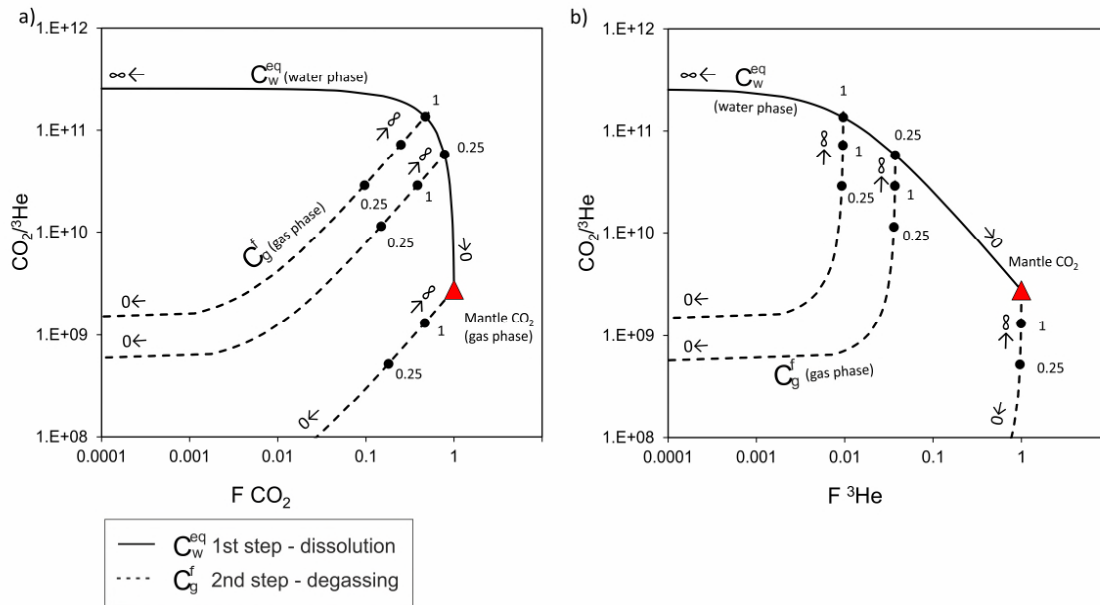
Figure 11. CO_2/He ratios (a) and ${}^3\text{He}$ concentrations relative to ${}^4\text{He}$ (b), ${}^{20}\text{Ne}$ (c), ${}^{40}\text{Ar}$ (d), ${}^{84}\text{Kr}$ (e) and ${}^{132}\text{Xe}$ (f) in $\text{cm}^3(\text{STP})/\text{cm}^3$. The solid blue line shows the concentrations in the gas phase after a two-step dissolution

613 and degassing. First, water equilibrates with gas under different gas/water ratios. Second, the water of that
614 composition degasses entirely. Tick marks show gas/water ratios during the dissolution stage. Dashed lines
615 show mixing with ASW at 20 °C; dotted line shows mixing with air. Some deviations from the modelled line
616 occur due to mixing with ASW and/or air. a) The extent of CO₂/He fractionation during dissolution is limited
617 by K_{CO_2}/K_{He} . All samples fall within this range except for TI and WO. c) shows that this is because TI and WO
618 have a contribution between ASW and air components, plotting between these end-members. This is
619 consistently replicated for Woolnoughs spring in c) d) and e). Ar, Kr and Xe concentrations of CS, DC, LO and
620 TA springs are within the limits of mixing with ASW and calculated model line. Abbreviations of sample
621 names are given in Table 1.

622

623 The model results are not a strict interpretation of the geological system, but rather an indication of
624 how the water controls the noble gas budget. The samples with high noble gas concentrations and
625 mantle CO₂/³He ratios might alternatively be interpreted to represent the residual gas cap migrating
626 the gas phase after the equilibration with water or having had minimal interaction with the water.
627 However, in cases where gas migrates dissolved in water and degasses at the surface, equilibration
628 in equal volumes of gas and water is needed to fractionate the CO₂/³He ratios by two orders of
629 magnitude. This is a significant consideration for the use of CO₂/³He ratios in interpretation of gas
630 provenance in gases equilibrating with water.

631 Figure 12 shows a theoretical fractionation model of mantle-derived CO₂ under the same ambient
632 atmospheric conditions as the previous model. A sample with the starting concentrations of [CO₂] =
633 0.99 and [³He] = 1.2 x 10⁻¹² cm³STP/cm³ is dissolved in water under different gas/water ratios. The
634 figure shows how the decreasing fraction of moles relative to the starting value, transferred to the
635 water and gas phases during the two-stage process, translates to CO₂/³He ratios. When the
636 gas/water ratio is low during the dissolution step, all gasses are dissolved into the water phase and
637 the ratio is unchanged. As the gas/water ratio decreases, overall less gas is transferred into the
638 water phase, but the water becomes more enriched in CO₂ relative to helium. The second step
639 considers degassing after the equilibration, when the remaining non-dissolved gas is removed from
640 the system and the water degasses under three scenarios ($\frac{V_g}{V_w} \rightarrow 0, 0.25$ and 1). This effectively shows
641 that in a multi-step dissolution and degassing process, the CO₂/³He ratio is entirely dependent on the
642 gas/water ratios and the extent of fractionation is limited by the ratio of Henry's constants K_{CO_2}/K_{He} .
643 In practice, the process is relevant to the point where the gas concentrations are above those in
644 ASW and the signal is not entirely diluted. Where CO₂ is the main carrier gas, this effect may not be
645 intuitively obvious, because the measured CO₂ concentrations are always > 99 % and the observed
646 variation is the ³He concentrations.



647

648 **Figure 12. Theoretical model of two step dissolution and degassing of mantle CO_2 and the effect on the**
 649 **$\text{CO}_2/{}^3\text{He}$ ratio. F is the fraction of moles in the modelled phase relative to the starting value. Symbols with**
 650 **arrows indicate $\frac{V_g}{V_w}$ ratios approaching infinity and zero, black dots mark specific calculated ratios. The solid**
 651 **black line shows the water phase during dissolution stage (step 1). The dashed lines show the resulting gas**
 652 **phase after degassing of the water phase under three different scenarios ($\frac{V_g}{V_w} \rightarrow 0, 0.25, 1$) (step 2). The**
 653 **maximum fractionation of $\text{CO}_2/{}^3\text{He}$ is limited by the relative ratio of $K_{\text{CO}_2}/K_{\text{He}}$.**

654

655 4.4.1. Summary

656 The geological interpretation of the proposed solubility fractionation model requires two stages of
 657 phase separation - dissolution followed by degassing. Mantle CO_2 equilibrates with individual
 658 aquifers under different gas/water ratios. Following this, CO_2 -saturated water and the remaining gas
 659 separate and ascend independently, driven by the differences in buoyancy force. Continuous
 660 seepage of dry CO_2 (up to 6000 ppm) has been identified in the localised fractures of the Ordovician
 661 sandstone outcropping near the Tipperary spring (Roberts et al., 2019), confirming the decoupled
 662 CO_2 and water migration. Water migrates to the surface through individual conduits, forming
 663 individual mineral water bodies and eventually springs. This model is consistent with the $\delta^{13}\text{C}(\text{CO}_2)$
 664 data, explained by degassing under measured temperature and pH conditions with each spring
 665 acting as a separate system. This appears to be a plausible interpretation of the CVH mineral springs,
 666 which show high variability in dissolved carbon and cation contents, indicating restricted individual
 667 aquifers for separate springs (Cartwright et al., 2002; Weaver et al., 2006). Mineral water degasses
 668 at the surface and all noble gases and CO_2 are assumed to be stripped from the water phase. The

669 final measured noble gas budgets are strongly controlled by the initial stage of equilibrating with
670 water.

671 4.5 Model summary and application to CO₂ tracing

672 This case study of south-east Australian CO₂ gas reservoirs and natural springs provides a framework
673 for investigating genetic link between CO₂ stored in reservoirs and migrating into shallow aquifers.

674 Our findings suggest that the combined helium, CO₂ abundance and $\delta^{13}\text{C}(\text{CO}_2)$ system allows to
675 distinguish between key processes that modify the initial geochemical composition: admixture of
676 crustal or organic sourced CO₂, mixing with non-CO₂ crustal gases and fractionation between water
677 and gas phases in either open or closed system. Helium isotopic signature is a particular strength for
678 source identification in CO₂ spring samples because it can be corrected for atmospheric component.
679 In contrast, neon and argon isotope ratios are likely to be close to the values of air.

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

693 Radiogenic ⁴He can also be added by mixing with a crustal CO₂ source. In this case, decreasing
694 ³He/⁴He ratios should correlate with an increase in CO₂/³He and either a negative or positive shift in
695 $\delta^{13}\text{C}(\text{CO}_2)$ values, following a trajectory of mixing lines. Alternatively, it is possible that ⁴He addition is
696 decoupled from a secondary phase separation process controlling $\delta^{13}\text{C}(\text{CO}_2)$ values and CO₂/³He
697 ratios. In this case, no clear correlation between and CO₂/³He and ³He/⁴He is expected. If the system
698 is characterised by progressive gas loss in an open system, generally a significant progressive
699 enrichment of $\delta^{13}\text{C}(\text{CO}_2)$ values is expected in non-geothermal temperatures.

700 Alternatively, the sample suite may effectively represent a series of individual systems, where water
701 and gas equilibrate under different gas/water ratios. In this case, no particular trend is anticipated.
702 The variation of $\delta^{13}\text{C}(\text{CO}_2)$ values can instead be controlled by the phase separation at different pH
703 and temperature conditions. Temperature and pH readings of waters should always be taken to
704 account for this effect. All noble and major gas concentrations and their relative ratios, including
705 $\text{CO}_2/{}^3\text{He}$ are modified by dissolution in water and/or degassing, while elemental ratios are not
706 expected to change. This can be tested by modelling fractionation under different gas/water ratios,
707 which should be consistent across all element pairs. Importantly, we show how solubility models can
708 be tested by incorporating Ne, Ar, Kr and Xe concentration data, which are often not interpreted in
709 natural spring studies because of the air-like isotopic ratios. While $\text{CO}_2/{}^3\text{He}$ is expected to be easily
710 modified, ${}^3\text{He}/{}^4\text{He}$ ratio is not altered by phase partitioning and is a reliable indicator of gas
711 provenance.

712

713 5. Conclusions

714 ${}^3\text{He}/{}^4\text{He}$ and $\text{CO}_2/{}^3\text{He}$ ratios in well gas and CO_2 spring samples in the Otway Basin and the
715 Central Victorian Highlands show unambiguous evidence for a predominantly mantle origin for the
716 CO_2 stored in the gas fields and actively migrating to the surface at the springs. The main processes
717 modifying noble gas geochemical signatures are crustal ${}^4\text{He}$ addition and noble gas elemental
718 fractionation between the water and gas phases.

719 ${}^3\text{He}/{}^4\text{He}$ ratios in well gases vary due to mixing with methane, which has crustal helium
720 contents directly dependent on gas residence time in the reservoir. The ${}^3\text{He}/{}^4\text{He}$ ratio variation in
721 CO_2 springs is controlled by interaction with ${}^4\text{He}$ -enriched basement pore fluids and is directly
722 dependent on the radial distance to the gas supply conduit. The observed decline in ${}^3\text{He}/{}^4\text{He}$ ratios
723 with distance suggests that CO_2 is supplied from a single conduit in the area around Argyle spring.
724 ${}^3\text{He}/{}^4\text{He}$ ratios are the highest in samples clustered near the Muckleford Fault and smaller parallel
725 faults in its vicinity, suggesting that one of these basement lineaments could be acting as a pathway
726 for mantle CO_2 to reach the shallow subsurface.

727 The variability of noble gas abundance patterns observed in the CO_2 springs can be explained by
728 solubility fractionation during equilibration with groundwater. If gas is dissolved in water,
729 transported and exsolved at the surface, a two-step dissolution and degassing process can be
730 considered. If gases ascend to the surface dissolved in water, original $\text{CO}_2/{}^3\text{He}$ ratios are unlikely to
731 be preserved. In CVH springs, $\text{CO}_2/{}^3\text{He}$ ratios in the range of $10^{11} - 10^{12}$ correlate with decreasing

732 concentrations of all noble gases and can be explained by variation of gas/water ratios during
733 dissolution in water. Gas/water ratios up to 1 during the dissolution stage can explain the maximum
734 observed fractionation in CO₂/³He ratios. The δ¹³C(CO₂) values are controlled by dissolution and
735 degassing at pH range of 5.8 - 6.3. This internally consistent model explains the abundance and
736 isotopic signature in He, Ne, Ar, Kr, Xe and δ¹³C(CO₂).

737 Taking these processes into account, noble gas compositions observed in well gases in Port
738 Campbell, Mount Gambier, as well as CO₂ springs in CVH and Clifton Springs are traced back to a
739 single end member of ³He/⁴He of 3.07 - 3.65 R_A, proving a common source. This implies a uniform
740 regional gas composition in the Otway basin and CVH.

741 Importantly, we present evidence that ³He loss resulting in high CO₂/³He ratios, commonly
742 associated with crustal CO₂ addition, can be explained without the need to invoke mixing with
743 crustal CO₂, which is especially important in the absence of a clear mixing trend in δ¹³C(CO₂) values.
744 Hence, CO₂/³He values should be compared to the concentrations of other noble gases and used
745 with caution when assessing the origin of CO₂ degassing at surface springs.

746 The techniques outlined in this paper can be used to identify the origin of CO₂ seeps at the
747 surface and their connectivity to reservoir gases. Hence, they can be applied to CO₂ sequestration or
748 other industrial fugitive gas monitoring settings, such as surrounding shale gas operations. Helium-
749 CO₂ abundance relationship can be used to determine the gas connectivity as long as the industrial
750 gas has a different initial He isotope ratio to the ASW end-member. The genetic link between
751 separate CO₂ seeps can be tested by applying solubility fractionation modelling to account for
752 changes in noble gas concentrations caused by interaction with water. Noble gases are particularly
753 sensitive tracers to small-scale gas migration and should be considered for surface monitoring of any
754 industrial site where emission of fugitive gas is possible.

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765

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