Noble Gases Preserve History of Retentive Continental Crust in the Bravo Dome Natural CO₂ Field, New Mexico

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Abstract

Budgets of ⁴He and ⁴⁰Ar provide constraints on the chemical evolution of the solid Earth and atmosphere. Although continental crust accounts for the majority of ⁴He and ⁴⁰Ar degassed from the Earth, degassing mechanisms are subject to scholarly debate. Here we provide a constraint on crustal degassing by comparing the noble gases accumulated in the Bravo Dome natural CO₂ reservoir, New Mexico USA, with the radiogenic production in the underlying crust. A detailed geological model of the reservoir is used to provide absolute abundances and geostatistical uncertainty of ⁴He, ⁴⁰Ar, ²¹Ne, ²⁰Ne, ³⁶Ar, and ⁸⁴Kr. The present-day production rate of crustal radiogenic ⁴He and ⁴⁰Ar, henceforth referred to as ⁴He* and ⁴⁰Ar*, is estimated using the basement composition, surface and mantle heat flow, and seismic estimates of crustal density. After subtracting mantle and atmospheric contributions, the reservoir contains less than 0.02% of the of the radiogenic production in the underlying crust. This shows unequivocally that radiogenic noble gases are effectively retained in cratonic continental crust over millennial timescales.

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This also requires that approximately 1.5 Gt of mantle derived CO₂ migrated through the crust without mobilizing the crustally accumulated gases. This observation suggests transport along a localized fracture network. Therefore, the retention of noble gases in stable crystalline continental crust allows shallow accumulations of radiogenic gases to record tectonic history. At Bravo Dome, the crustal $^4\text{He}^*/^{40}\text{Ar}^*$ ratio is one fifth of the expected crustal production ratio, recording the preferential release of ^4He during the Ancestral Rocky Mountain orogeny, 300 Ma.

1. Introduction

The abundances of radiogenic noble gases in the Earth's atmosphere have long been used to constrain the structure and composition of the Earth's mantle [1, 2, 3]. Roughly 70% of the ^4He and ^{40}Ar degassed from the bulk silicate Earth derives from the continental crust [4, 5]. A clear understanding of the flux of noble gases from the continental crust is hampered by spatial and temporal variability of flux measurements at the Earth's surface. We overcome this limitation by calculating absolute noble gas abundances in the Bravo Dome natural CO₂ reservoir, which represent time-integrated fluxes averaged over thousands of square kilometers and millennial timescales. These abundances are compared with radiogenic production of ^4He and ^{40}Ar in the underlying crust, based on a seismic density profile and heat flux in the region.

1.1. Previous Work on Crustal Degassing

Previous estimates of average crustal degassing fluxes have relied on ^4He and ^{40}Ar accumulation in large regional aquifers [10, 11, 12, 13, 14, 15]. How-

Figure 1: Previously estimated helium fluxes and corresponding radiogenic heat production in the crust [6, 7, 8, 9]. Measurements with close proximity have varying ^4He fluxes, suggesting sporadic and advective ^4He degassing.

17 ever, ^4He residence time estimates rely on knowledge of the ^4He source and
 18 sink terms [10, 16]. Figure 1 shows that estimates of degassing fluxes based on
 19 regional aquifers vary between 3% and 300% of the expected crustal produc-
 20 tion. This variation may reflect heterogeneity of the degassing fluxes or the
 21 inherent difficulty of understanding dynamic aquifer systems [6]. Similarly,
 22 the ^4He flux in lakes has been measured up to three orders of magnitude
 23 greater than expected crustal production [6, 17]. A review of these stud-
 24 ies shows that estimates of the ^4He degassing flux decrease with increasing
 25 spatial and temporal scales [6].

26 Crustal degassing can occur by diffusion along mineral grain boundaries
 27 or by advective transport in a migrating fluid phase. Transient variations
 28 in degassing fluxes have been observed in several field areas [18, 19]. Thus,
 29 the large spatial and temporal ^4He and ^{40}Ar flux averages recorded by the
 30 Bravo Dome gas field represent a significant advantage over extrapolation of
 31 degassing fluxes calculated from discrete points in space and time [19]. For
 32 crustal degassing studies, the Bravo Dome gas field is analogous to a large
 33 subsurface lake, acting as a volume of fluid accumulating flux and partitioning
 34 volatile dissolved gases from below (Figure 2). In fact, the Bravo Dome gas
 35 offers two advantages over lake studies: it scavenges dissolved gases from
 36 the underlying brine through phase equilibrium, and remains isolated from
 37 the atmosphere due to the impervious evaporite cap rock [20].

38 *1.2. Bravo Dome Introduction*

39 Bravo Dome is a large natural gas reservoir in northeastern New Mexico
 40 (Figure 3A). The reservoir covers an area of 3600 km^2 and contained 1.3 Gt of
 41 nearly pure CO_2 before commercial extraction in 1981 [20, 21]. The gas is of

Figure 2: Noble Gas fluxes and CO_2 entry event. **A)** Before the CO_2 entry event, radiogenic gases produced in the crustal basement can only enter the Tubb sandstone via grain boundary diffusion pathways. **B)** During the entry of hot magmatic CO_2 , radiogenic gases were both carried from the mantle and swept from the crustal basement, and then deposited into the reservoir. **C)** After the gas entry, air-derived noble gases have been swept from the residual brine and re-dissolved into the underlying brine aquifer. $^4\text{He}^*$, $^{40}\text{Ar}^*$, and $^{21}\text{Ne}^*$ reaching the Tubb Sandstone through grain boundary diffusion through the underlying basement will partition and become trapped in the gas phase CO_2 . The noble gas compositions then act as a record of crustal degassing.

mantle origin and was emplaced contemporaneously with basaltic volcanism, 1.2 to 1.5 Ma [21]. Bravo Dome is located in continental crust that has been tectonically quiescent since the Ancestral Rocky Mountain orogeny, 300 Ma [22]. Despite being located within 300 km of the Rio Grande rift zone, heat flow and erosion measurements show that this region is geologically similar to the stable midcontinent US [21, 8]. There have also been a number of volcanic events in the region during the Cenozoic. However, as this study shows, even these magmatic events are insufficient to regionally evacuate noble gases from crystalline crust. The Ancestral Rocky Mountains were the sediment source for the Tubb Sandstone reservoir rock. The Tubb Sandstone has not been heated above the zircon (U-Th)/He closure temperature of roughly 180°C since deposition [21, 23].

The gas reservoir formed at a depth of 700 m, directly above 1.4 Ga granitic basement and beneath a regional anhydrite seal [24, 20] (Figure 3B). The stratigraphic location of Bravo Dome, shown in Figures 2 and 3, simplifies the potential sources and sinks of noble gases in the reservoir. Any radiogenic noble gas flux from the underlying crust will become trapped in the gas phase CO₂ underneath the anhydrite seal, isolating it from the atmosphere. Furthermore, only 10% of the original CO₂ has dissolved since emplacement, suggesting that there is very little background groundwater flux [21].

Three phases of fluid emplacement are illustrated in Figure 2. First, the Tubb Sandstone reservoir rock was filled with air-saturated formation brine. In the absence of groundwater recharge, radiogenic gases diffusing upward from the crust would be dissolved in the brine and trapped beneath

67 the Anhydrite seal (Figure 2A). Second, during the CO₂ entry event, heated
 68 mantle CO₂ traveled along a fracture network through the crustal basement,
 69 liberating radiogenic ⁴He* and ⁴⁰Ar* during its ascent. After reaching the
 70 Tubb Sandstone, the CO₂ displaced the initially present formation brine,
 71 and stripped atmospheric noble gases from the residual water (Figure 2B).
 72 Finally, at present day, the radiogenic gases have been stripped from the
 73 crustal migration pathway, and the gas composition reflects a mixture of
 74 direct mantle input, crustal radiogenic gases liberated by the heat of the
 75 CO₂ plume, continuous crustal degassing, and atmospheric derived noble
 76 gases which were previously dissolved in the formation brine (Figure 2C).

77 *1.3. Previous Estimates of Crustal Composition*

78 Uranium and thorium produce ⁴He by α -decay, while ⁴⁰K produces ⁴⁰Ar
 79 by electron capture decay. We will refer to radiogenic, crustally produced ⁴He
 80 and ⁴⁰Ar as ⁴He* and ⁴⁰Ar*. Uranium, thorium and potassium are enriched
 81 in the continental crust by a factor of 50–100 relative to the primitive mantle
 82 [25]. These radioactive isotopes are thought to be enriched in the upper crust
 83 relative to the lower crust [9]. The majority of crustal uranium and thorium
 84 is hosted by accessory minerals such as zircon, monazite and apatite, whereas
 85 potassium is dominantly hosted by feldspar.

86 Radioactive decay provides a significant source of heat in the Earth's
 87 crust. However, there is no consensus regarding the exact distribution of
 88 radioactive elements with depth [26]. Previous studies have encountered
 89 discrepancies between bulk estimates of crustal radioactive content and ob-
 90 served surface heat flux [27]. In this region, the mafic lower crust assumption
 91 is supported by surface heat measurements and mantle heat flux estimates

92 [7, 8].

93

94 2. Bravo Dome Noble Gas Abundances

95 In order to determine the absolute quantities of each noble gas isotope
 96 in the reservoir, we interpolate previously published estimates of reservoir
 97 geometry, pore volume, bottom hole pressure, and noble gas isotope concen-
 98 trations [21, 29, 30]. This volumetric calculation gives an upper bound on
 99 the total amount of radiogenic degassing that has occurred since the em-
 100 placement of the gas.

101 2.1. Subtraction of Mantle Component

102 Elevated gas pressure and $\text{CO}_2/{}^3\text{He}$ and ${}^3\text{He}/{}^4\text{He}$ close to subcontinental
 103 lithospheric ratios confirm that the magmatic CO_2 entered from the western
 104 side of the reservoir [30, 21, 29], and suggest that there may be continued
 105 entry of mantle CO_2 . The maximum $\text{CO}_2/{}^3\text{He}$ ratio in the western side
 106 of the field is $5.35 \cdot 10^9$, and the maximum ${}^3\text{He}/{}^4\text{He}$ ratio is 4.26Ra [29].
 107 Subtracting the concentration observed closest to the gas source, we can
 108 compute the areal density of non-mantle derived noble gas,

$$n(x, y) = \int \frac{\phi_g(c_{\text{NG}} - c_{\text{NG,m}})P_g}{RT} dz \quad \text{mols/m}^2. \quad (1)$$

109 The concentration of each noble gas measured near the gas source, $c_{\text{NG,m}}$,
 110 is assumed to be the mantle input composition, due to MORB ${}^3\text{He}/{}^4\text{He}$
 111 ratios in this area. The noble gas concentration at a particular location
 112 in the reservoir is given by c_{NG} , and is shown in Figures 4A, 4C, 4E, and
 113 4G. These figures show a kriging interpolation of previously published noble

Figure 3: **(A)** Bravo Dome reservoir, surface volcanic outcrops, and faults associated with the Rio Grande rift [28]. The mantle CO_2 in the reservoir is thought to be associated with Cenozoic volcanism. **(B)** Reservoir cross section. The gas directly overlies the Precambrian crystalline basement and is sealed by the Cimarron Anhydrite, allowing the gas phase to effectively partition and trap any crustal degassing.

114 gas concentrations [29]. Sample locations are shown as white squares. The
 115 measured gas pressure before commercial production in 1981 is P_g , and ϕ_g is
 116 the volume fraction of gas at a location in the reservoir. The areal density
 117 $n(x, y)$ indicates the number of mols per square meter of each isotope at a
 118 given location, integrated vertically over the entire gas column (Figures 4B,
 119 4D, 4F, and 4H).

120 Integrating the areal density over the area of the reservoir gives the total
 121 number of non-mantle mols of each noble gas,

$$N = \iint n(x, y) dx dy \quad \text{mols.} \quad (2)$$

122 Combining the interpolation uncertainties of the gas volume fraction ϕ_g , gas
 123 density ρ , gas thickness H_g , and isotope concentration c_{NG} , we compute the
 124 uncertainty in the areal density of each isotope,

$$\sigma_n^2 = \left[\left(\frac{\sigma_{H_g}}{H_g} \right)^2 + \left(\frac{\sigma_\phi}{\phi} \right)^2 + \left(\frac{\sigma_\rho}{\rho} \right)^2 + \left(\frac{\sigma_f}{f} \right)^2 \right] n^2. \quad (3)$$

125 The total abundance and associated uncertainty of each noble gas are given
 126 in Table 1. The uncertainties in the noble gas abundances are substantial,
 127 approximately $\pm 50\%$. Most of the uncertainty is induced by the reservoir
 128 geometry and affects all isotopic abundances equally. Therefore, the uncer-
 129 tainty of ratios of total abundances is very small.

130 2.2. Atmospheric Component

131 Using the non-radiogenic isotopes ^{20}Ne , ^{36}Ar , and ^{84}Kr , we can estimate
 132 the input of noble gases from the pre-emplacement air-saturated water in
 133 the formation. We estimate the equivalent volumes of air-saturated water

Bravo Dome Non-Radiogenic (Atmospheric) Noble Gas Isotopes

Isotope	Total Mols	Non-Mantle Mols	V _{ASW}	V _{rw} Volumes
²⁰ Ne	6 ± 3000	3100	0.4 km ³	0.05
³⁶ Ar	(1.1 ± 0.5) · 10 ⁵	7.7 · 10 ⁴	1.7 km ³	0.2
⁸⁴ Kr	410 ± 190	250	0.16km ³	0.02

Bravo Dome Radiogenic (Crustal) Noble Gas Isotopes

Isotope	Total Mols	Non-Mantle Mols	V _{ASW}	V _{rw} Volumes
⁴ He	(3.4 ± 1.5) · 10 ⁸	2.3 · 10 ⁸	1.2 · 10 ⁵ km ³	1.3 · 10 ⁴
²¹ Ne	38 ± 17	21	0.9 km ³	0.1
⁴⁰ Ar	(11 ± 5) · 10 ⁸	2.6 · 10 ⁸	20 km ³	2.2

Table 1: Quantities of total and non-mantle derived noble gases in the Bravo Dome natural CO₂ field. V_{ASW} refers to the volume of air-saturated water containing the observed number of non-mantle mols. The gas reservoir contains 9 km³ of residual water (V_{rw}), while the atmospheric gas quantities correspond to less than 2 km³ of degassed air-saturated water (V_{ASW}). This finding is in agreement with the two-stage fractionation model of [30].

134 required to provide the observed amount of noble gases in the gas phase,
 135 given by

$$V_{\text{ASW}} = \frac{N}{P_{\text{atm,NG}} K_{\text{NG}}}, \quad (4)$$

136 where $P_{\text{atm,NG}}$ is the partial pressure of each noble gas in the atmosphere and
 137 K_{NG} is the Henry's law coefficient.

138 The reservoir model of Bravo Dome indicates that the gas cap shown in
 139 Figure 3B has a pore volume of 23 km³ [21]. The silt within this gas cap
 140 still contains 9 km³ of brine that will be referred to as residual water, V_{rw} ,
 141 below. Assuming equilibrium partitioning of components between gas and
 142 water, Table 1 shows that the observed abundances of non-radiogenic at-
 143 mospheric isotopes represent degassed volumes of air-saturated water, V_{ASW} ,
 144 much less than V_{rw} . The low abundance of atmospheric isotopes shows that
 145 the emplacement stripped the residual water of dissolved gases, as previously
 146 suggested in the two stage dissolution model of [30].

147 2.3. *In-Situ Production of ⁴He**

148 In order to estimate the maximum contribution of in-situ production of
 149 ⁴He* within the Tubb Sandstone, we assume concentrations of uranium and
 150 thorium equal to literature values for the upper crust. This gives uranium
 151 and thorium concentrations of 2.8 ppm and 11.2 ppm [9]. By multiplying
 152 the uranium and thorium concentrations by porosity and gas thickness, we
 153 compute the maximum quantity of a given radioactive isotope, i , in the
 154 Bravo Dome reservoir. The molar mass of the isotope is given by M_i , the
 155 mass fraction in the sediment is c_i , and the total number of mols in the
 156 sediment is

Figure 4: Concentration and areal density plots of ^{40}Ar , ^4He , ^{36}Ar , and ^{20}Ne in the Bravo Dome reservoir, computed using Kriging interpolations on either side of a fault. The mantle component is removed by uniformly subtracting a concentration equal to the lowest concentration in the west. White squares indicate wells sampled for a given noble gas [29]. The top shows the interpolated gas phase concentration of noble gases. The bottom shows the areal density of the noble gases in the gas phase. (A, B) ^{40}Ar , (C, D) ^4He , (E, F) ^{36}Ar , (G, H) ^{20}Ne .

$$N_{i,\text{sed}} = \left(\frac{c_i \rho}{M_i}\right) \iiint (1 - \phi) dx dy dz. \quad (5)$$

157 These calculations show that the sediment contains a maximum of $4.4 \cdot 10^9$
 158 mols of ^{238}U , $1.8 \cdot 10^{10}$ mols of ^{232}Th , and $4.2 \cdot 10^8$ mols of ^{235}U .

159 Because the zircon (U-Th)/He ages in the Tubb Sandstone preserve de-
 160 trital ages, we assume that the only $^4\text{He}^*$ from the sediment that has entered
 161 the gas is the $^4\text{He}^*$ that is directly ejected from minerals [21]. The frac-
 162 tion retained, known as the F_T correction, was computed for several Tubb
 163 sandstone zircons [21, 31]. For the calculation of in-situ ^4He production, we
 164 assume an F_T correction of 0.80, meaning that 80% of the produced ^4He has
 165 been retained in the mineral grains. This value for the F_T correction falls in
 166 the range computed for four Tubb Sandstone zircons [21]. Over the roughly
 167 250Ma since the end of the Permian, we calculate that the total $^4\text{He}^*$ released
 168 into the Bravo Dome pore fluid from ^{238}U , ^{235}U , and ^{232}Th is $5.6 \cdot 10^8$ mols.

169 This quantity of $^4\text{He}^*$ is greater than the total measured amount of ^4He
 170 in the reservoir, $3.5 \cdot 10^8$ mols. However, this calculation assumes that the
 171 groundwater in the shallow Tubb Sandstone, currently at 700 m depth, has
 172 been stagnant and retentive of ^4He for 250 Ma. Additionally, atmospheric
 173 derived isotopes suggest that a small fraction of the pre-emplacement dis-
 174 solved noble gas isotopes in the formation brine are currently present in the
 175 Bravo Dome gas, because they were swept by the gas plume and redissolved
 176 into the underlying brine [30].

177 The volumes of atmospheric derived noble gases in Bravo Dome corre-
 178 spond to between 0.02 and 0.2 residual water volumes (Table 1). Therefore,
 179 ^{20}Ne V_{ASW} values show that only about 2% of the pre-emplacement dissolved

180 volatile gas in the formation brine is present in the Bravo Dome gas today.
 181 Assuming a comparable amount of $^4\text{He}^*$ is retained, this would lead to a
 182 maximum in-situ remaining $^4\text{He}^*$ quantity of $0.02 \cdot ^4\text{He}_{\text{FT}} = 1.1 \cdot 10^7$ mols. If
 183 100% of the in-situ production of $^4\text{He}^*$ remained trapped in the groundwater
 184 system without being advected away or vented to the atmosphere in the last
 185 250 Ma, pre-emplacement dissolved $^4\text{He}^*$ can only account for a maximum
 186 of 3% of the observed $3.5 \cdot 10^8$ mols of non-mantle ^4He in the gas phase.

187 *2.4. In-Situ Production of $^{40}\text{Ar}^*$*

188 The closure temperatures for $^{40}\text{Ar}^*$ in feldspar, biotite, and muscovite are
 189 all above 200°C [32]. Because the Tubb Sandstone zircons have never been
 190 reset since deposition [21], we assume that the $^{40}\text{Ar}^*$ production within the
 191 sediment remains trapped within mineral grains. As an upper bound, we
 192 use the bulk upper crust estimate of K_2O content of 3.4%, leading to a total
 193 potassium estimate of $2.7 \cdot 10^{14}$ mols, and the ^{40}K total of $3.2 \cdot 10^{10}$ mols [9].
 194 After 250 Ma, this amount of ^{40}K will produce $7.6 \cdot 10^8$ mols of $^{40}\text{Ar}^*$ within
 195 the Tubb Sandstone reservoir rock.

196 Since the end of the Permian, the total amount of $^{40}\text{Ar}^*$ produced in the
 197 Tubb Sandstone sediment, $11 \cdot 10^8$ mols, is similar to the total ^{40}Ar found in
 198 the Bravo Dome gas field. To estimate the maximum amount of the in-situ
 199 produced $^{40}\text{Ar}^*$ that could be in the gas phase, we assume that all produced
 200 $^{40}\text{Ar}^*$ was dissolved in the brine before CO_2 emplacement. The fraction of
 201 this $^{40}\text{Ar}^*$ that has partitioned from the brine into the gas phase is similar to
 202 the fraction of ^{36}Ar , approximately 20%. The maximum amount of in-situ
 203 produced $^{40}\text{Ar}^*$ in the gas phase is $1.5 \cdot 10^8$ mols, which constitutes less than
 204 15% of the total reservoir ^{40}Ar .

Figure 5: Thin-section photomicrographs of detrital components and diagenetic features in Tubb sandstone reservoir rock. All photos taken in cross-polarised light. **A)** Close-up of K-feldspar grain in arkosic sandstone matrix. Note pervasive hematite cement along grain boundaries and tight packing of quartz matrix. K-feldspar grain boundaries are largely undisturbed and show few concave portions indicative of pressure dissolution. **B)** Typical arkosic sandstone. K-feldspar grain maintains elongate grain boundaries. **C)** and **D)** K-feldspar in well-sorted arkosic sandstones. Note, in **D)**, the dense packing structure of the quartz matrix and evidence for pressure dissolution along K-feldspar grain boundary.

205 However, in situ production as the source of the $^{40}\text{Ar}^*$ in the gas would
206 require widespread breakdown of the feldspars and mica in the sediment.
207 While photomicrographs show some evidence of pressure dissolution during
208 compaction and cementation of the sandstone matrix, subsequent dissolution
209 appears to be minor (Figure 5).

210 *2.5. Comparison with interpretations based on noble gas isotope ratios*

211 Previous studies have made extensive use of noble gas isotope ratios
212 of subsurface gas samples to determine gas sourcing and interaction with
213 groundwater [33, 30]. In contrast, we examine estimates of absolute noble gas
214 abundances obtained from geostatistical interpolation of point estimates and
215 a detailed reservoir model. Previous interpretation of the discrete measure-
216 ments of the $^{20}\text{Ne}/^{36}\text{Ar}$ and $^{20}\text{Ne}/^{84}\text{Kr}$ ratios in Bravo Dome suggested that
217 the CO_2 plume stripped atmospheric noble gases from the pre-emplacement
218 formation brine, which then re-dissolved after the CO_2 entry continued. Our
219 calculations of the total noble gas abundance in the gas plume supports this
220 interpretation. Table 1 shows that the total abundances of the atmospheric
221 gases ^{20}Ne , ^{36}Ar , and ^{84}Kr are between 2% and 20% of the quantities pre-
222 dicted by degassing of the residual water in the gas cap.

223 *2.6. Noble Gas Totals*

224 The volumes of air saturated water required to account for all of the
225 non-mantle ^4He and ^{40}Ar shows that roughly 10% of the non-mantle ^{40}Ar
226 and 4 ppm of the non-mantle ^4He is sourced from the atmosphere, with
227 the remainder sourced from crustal production (Table 1). Due to the low
228 total abundance, we cannot deconvolve ^{21}Ne contributions from the mantle,

crust, and atmosphere. The Bravo Dome crustal ratio, ${}^4\text{He}^*/{}^{40}\text{Ar}^* \approx 1$, is much lower than the bulk crustal production ratio of ${}^4\text{He}^*/{}^{40}\text{Ar}^*$, which varies between 4 and 8 [33]. This discrepancy can be explained by several hypotheses: *a*) differing accumulation ages, *b*) differing source volumes, *c*) enrichment of ${}^{40}\text{K}$ in the noble gas source rocks, or *d*) fractionation during or after emplacement.

3. Geotherm and Radioactive Content

In order to estimate the radiogenic production of ${}^4\text{He}^*$ and ${}^{40}\text{Ar}^*$ in the underlying crustal basement beneath Bravo Dome, we use surface heat flux measurements and a seismic density profile to constrain the temperature, heat flux, and total radioactive content [34, 8]. The resulting profiles are shown in Figure 6. The geotherm calculated below assumes a high temperature at the base of the crust. The diffusive fluxes calculated below are thereby maximum estimates.

3.1. Heat Flux and Composition

Crustal radioactivity produces heat along with ${}^4\text{He}^*$ and ${}^{40}\text{Ar}^*$. The total crustal heat generation in this region is equal to the difference between the mantle heat flux of 28 mW/m² and the surface heat flux of 58 mW/m², as shown in Figure 6A [7, 8]. We use the density profile of the crust (Figure 6B) to estimate the amount of U, Th, and K with depth [34]. Felsic upper crust has a density of 2700 [kg/m³] and mafic lower crust has a density of 3000 [kg/m³] [35]. Therefore, we compute the fraction of felsic crust with depth,

$$f(z) = \frac{\rho(z) - 3000}{2700 - 3000}, \quad (6)$$

Figure 6: **(A)** Calculated crustal heat flux, constrained by surface and mantle fluxes [8, 7]. **(B)** Crustal density profile derived from seismology [34]. **(C)** Calculated heat production beneath Bravo Dome, split into contributions from ^{40}K , uranium, and thorium and constrained by surface heat flux. **(D)** Calculated thermal conductivity, which varies inversely with temperature for both mafic and felsic end members. **(E)** Calculated geothermal profile beneath Bravo Dome.

251 where $\rho(z)$ is the density profile estimated from seismic data [34]. While
 252 this mapping from density to composition is overly simplified, it does pro-
 253 vide first-order information about the distribution of mineralogy with depth.
 254 Figure 6B shows a gradual increase of the mafic component with depth
 255 and no clear transition from felsic upper to mafic lower crust. We use lit-
 256 erature values for uranium, thorium, and K_2O mass fractions in the lower
 257 crust [9]. We then compute the felsic upper crustal heat production required
 258 to match the observed surface heat flow [8]. Upper crustal uranium and
 259 thorium concentrations are estimated from the heat production by varying
 260 the K_2O between the published middle and upper crustal concentrations [9].
 261 The decays of ^{238}U , ^{235}U , ^{232}Th , and ^{40}K emit different amounts of energy.
 262 The ^{40}K β -decay energy is approximately 50 times smaller than the multiple
 263 α decays of uranium and thorium [36]. This effect makes the heat produc-
 264 tion from uranium and thorium larger than the production from potassium
 265 (Figure 6C).

266 Heat flux constraints show that the total crustal radioactive content in
 267 northeastern New Mexico is less than literature values for bulk crust [9, 7, 8].
 268 Figure 7 shows upper crustal uranium and thorium mass fractions computed
 269 from the heat flux beneath Bravo Dome, along with several measurements of
 270 uranium and thorium content from drill cores in the nearby Texas Panhan-
 271 dle basement. The computed upper crustal uranium and thorium fractions
 272 are similar to measured values of quartz monzonite and granite, although
 273 much lower than measurements from rhyolite and trachyte [24, 9]. For the
 274 radiogenic gas and heat production assumptions used in this study, we use
 275 upper crustal radioactive element concentrations corresponding to the up-

Figure 7: Bravo Dome upper crustal radioactive composition estimates from heat flow together with nearby basement samples [24]. The gray area shows the possible values for U and Th, given an upper crustal K_2O range between 1.8% and 3.4%. Uranium and thorium upper crustal values fall near measured values of quartz monzonite in this region, but are well below global averages denoted as R&F Upper Crust [9].

per corner of the black area shown in Figure 7. This point corresponds to lower than bulk upper crustal estimates for uranium, thorium, and potassium concentrations.

3.2. Thermal Conductivity

Thermal conductivity varies inversely with temperature and is given by

$$k_j(T) = A_j + \frac{B_j}{350 + T(^{\circ}C)} \left[\frac{W}{m^{\circ}K} \right] \quad (7)$$

where the coefficients A_j and B_j refer to the coefficients for the felsic or mafic end members [37]. To match the observed surface heat flux and to remain

below the crustal solidus, we use A_f of 1.64 W/(m°K), A_m of 2.18 W/(m°K),
 B_f of 807 W/m, and B_m of 474 W/m. Mixing the two conductivity val-
ues using (6) we can obtain conductivity as a function of temperature and
composition

$$k(f, T) = f k_f(T) + (1 - f) k_m(T) \left[\frac{\text{W}}{\text{m}^\circ\text{K}} \right]. \quad (8)$$

In the shallow sedimentary portions of the crust, we compute the porosity
from density, and assume the pore space to be filled with water. We then
compute the conductivity as a mixture of sediment and water. The thermal
conductivity profile is plotted in Figure 6D.

3.3. Solution for Temperature

Heat production is equal to the derivative of heat flux,

$$\frac{dq}{dz} = -H(z). \quad (9)$$

The heat production of a given radioactive isotope i with a decay constant
 λ_i is given by

$$H_i(z) = E_i \lambda_i r_i \rho(z) \quad [\text{W/m}^3], \quad (10)$$

where E_i is the energy released by one decay of isotope i , r_i is the concen-
tration of i in the rock, and $\rho(z)$ is the density at depth z .

Because conductivity and temperature are co-dependent, we iteratively
solve the thermal diffusion equation for temperature as a function of depth
(Figure 6E). First, we use the known surface conductivity, k_s , and heat flux,
 q_s , to determine the surface temperature gradient,

$$\left. \frac{dT}{dz} \right|_{z=0} = \frac{-q_s}{k_s}. \quad (11)$$

301 We then numerically solve for the temperature towards the bottom of the
302 crust.

303 4. Grain Boundary Diffusion Model

304 Two end-member transport scenarios may account for the release of the
305 crustal radiogenic noble gas inventory beneath Bravo Dome: *i.* advection
306 of noble gases by a migrating fluid phase, and *ii.* diffusion of the noble
307 gases along grain boundaries. To test whether diffusion is a viable transport
308 mechanism for crustal degassing, we calculate the maximum diffusive flux of
309 $^4\text{He}^*$ and $^{40}\text{Ar}^*$.

310 In order to estimate a maximum possible diffusive flux of $^4\text{He}^*$ and $^{40}\text{Ar}^*$
311 from the crust, we solve the diffusion equation with radioactive production
312 of $^4\text{He}^*$ and $^{40}\text{Ar}^*$ over a 1D crustal column. The production term in this
313 equation is calibrated using the heat flow constraints established in the pre-
314 vious section. The heat flux constraint leads to upper crustal U, Th, and
315 K_2O values of 1.13 ppm, 4.4 ppm, and 1.6%. Lower crustal values are taken
316 from literature, and are set to 0.2 ppm, 1.2 ppm, and 0.6% [9].

317 In order to estimate the maximum possible flux, we assume that grain
318 boundaries are represented by 1% water-saturated porosity, ϕ . We then use
319 established data for the diffusivity of helium and argon in water, and com-
320 pute the concentration profile of $^4\text{He}^*$ and $^{40}\text{Ar}^*$ in crustal grain boundaries
321 after 1.5 Ga. The diffusion coefficient is dependent on temperature and esti-
322 mated using an Arrhenius relationship from experimental data [38, 39]. The

diffusion-production equation is solved numerically, with C_i representing the ${}^4\text{He}^*$ or ${}^{40}\text{Ar}^*$ concentration on the grain boundaries

$$\frac{\partial C_i}{\partial t} = -\frac{\phi}{\tau} \frac{\partial}{\partial z} \left(D(z) \frac{\partial C_i}{\partial z} \right) + G_i(z, t), \quad (12)$$

$$\left. \frac{dC_i}{dz} \right|_{z=45\text{km}} = 0 \quad \text{and} \quad C|_{z=0} = 0. \quad (13)$$

$G_i(z, t)$ represents the radioactive production of the noble gas i . $G_i(z, t)$ is related to the heat production terms defined in the previous section. Each decay of ${}^{238}\text{U}$, ${}^{235}\text{U}$, and ${}^{232}\text{Th}$ produces 8, 7, and 6 ${}^4\text{He}^*$ atoms respectively. The decay of ${}^{40}\text{K}$ is branched, such that only 11% of ${}^{40}\text{K}$ decays produce an atom of ${}^{40}\text{Ar}^*$ [40]. The grain boundary tortuosity τ is prescribed to be $\sqrt{2}$. For the ${}^4\text{He}^*$ system, we assume that 20% of the ${}^4\text{He}^*$ produced below the zircon closure temperature reaches the grain boundaries through direct α ejection, leading to a sharp reduction in ${}^4\text{He}^*$ production reaching the grain boundaries in the shallow area below 180°C [23, 31]. Other uranium and thorium bearing minerals such as apatite and monazite will release ${}^4\text{He}^*$ at lower temperatures, and these effects are accounted for in the partial ${}^4\text{He}^*$ release in the shallow regions [40]. In the case of ${}^{40}\text{Ar}^*$, we assume that all ${}^{40}\text{Ar}^*$ is retained within mineral grains below 250°C [32]. Model calculations (Figure 8A, 8B), show that diffusive migration accounts for the loss of less than 1% of the total ${}^4\text{He}^*$ and ${}^{40}\text{Ar}^*$ produced over 1.5 Ga within a crustal column.

The diffusion model shows that diffusive mass transport alone cannot explain the abundances of radiogenic noble gases observed in Bravo Dome. This suggests that tectonically quiescent crust retains noble gases. The noble

Figure 8: Diffusion models for **(A)** ${}^4\text{He}$ and **(B)** ${}^{40}\text{Ar}$. In the shallow crust, ${}^4\text{He}^*$ and ${}^{40}\text{Ar}^*$ are trapped within U, Th, and K bearing minerals. Above 180°C and 260°C respectively, ${}^4\text{He}^*$ and ${}^{40}\text{Ar}^*$ diffuse out of minerals and into grain boundaries, where they are free to diffuse to the atmosphere. We show two extreme cases, one with 0% connected porosity and subsequently no diffusive transport (blue), and a case with a uniform crustal porosity of 1% (red). Even with 1% porosity, the diffusive flux of radiogenic gases to the atmosphere is negligible, less than 1% of the total produced over 1.5 Ga.

gases were likely mobilized by the hot magmatic CO_2 entry event which formed Bravo Dome, ~ 1.5 Ma. At present, the gas sampled at the CO_2 entry point has an elevated pressure and has reverted to a mantle isotope signature [21, 30]. This composition is likely due to the purging of radiogenic noble gases from the migration pathway. Noble gas advective transport at Bravo Dome corroborates previous findings that advective fluid events are required to mobilize ${}^4\text{He}$ in the crust [41, 19].

351 5. Crustal Volume Swept by CO₂ Event

352 Using the concentrations of U, Th, and K derived from the heat flux and
 353 seismic profiles, we can make an estimate of the radiogenic production of
 354 ⁴He* and ⁴⁰Ar*. This leads to a bulk crustal production ratio ⁴He*/⁴⁰Ar* ≈ 5.
 355 Figure 8A and 8B show the grain boundary concentration of ⁴He* and ⁴⁰Ar*
 356 after 1.5 Ga as a function of depth, assuming no loss to the atmosphere.
 357 In order to estimate the volume and ages of crust required to produce the
 358 observed quantities of crustal ⁴He* and ⁴⁰Ar*, we use the crustal concentra-
 359 tions of U, Th, and K computed from the surface heat flux, average over the
 360 entire crustal column, and integrate over the accumulation time, t_{acc} ,

$$V(t_{acc}) = \left(\frac{N \text{ mols}}{\int_0^{45\text{km}} \int_0^{t_{acc}} G(z, t) dt dz} \right) \cdot 45\text{km}. \quad (14)$$

361 For visualization purposes, we consider the radii of cylinders stretching from
 362 the surface to the bottom of the crust which is equivalent to the volumes
 363 $V(t_{acc})$,

$$r(t_{acc}) = \left(\frac{V(t_{acc})}{\pi \cdot 45\text{km}} \right)^{1/2}. \quad (15)$$

364 These equivalent crustal radii, $r(t_{acc})$, are plotted in Figure 9.

365 To estimate the crustal volumes required to produce the radiogenic no-
 366 ble gas abundances preserved in Bravo Dome, we require estimates of the
 367 accumulation ages of ⁴He* and ⁴⁰Ar*. U-Pb geochronology and ⁴⁰Ar/³⁹Ar
 368 thermochronology show that the crust in this region has been retentive of
 369 ⁴⁰Ar* for between 1.34 Ga and 1.4 Ga [42, 43]. Detrital zircon (U-Th)/He
 370 ages from the Tubb sandstone reflect sourcing from the Ancestral Rocky

Mountain orogeny, implying that the crust proximal to Bravo Dome has been retentive of $^4\text{He}^*$ since 280-310 Ma [44, 45, 21, 22].

Using $^4\text{He}^*$ and $^{40}\text{Ar}^*$ bulk crustal ages and the calculated radiogenic parent concentrations, we calculate the crustal volumes needed to provide the observed amount of radiogenic gas in Bravo Dome. Assuming a closed system of radiogenic gases throughout the 45 km thick crust, a cylinder with a radius between 450 m and 510 m is required to produce the observed amount of $^4\text{He}^*$. Similarly, the $^{40}\text{Ar}^*$ catchment radius is between 300 m and 400 m (Figure 9). The small scale of these radii relative to the overall gas reservoir suggest that the gases migrated through a narrow fracture network in the crystalline basement. Furthermore, the different catchment volumes for $^4\text{He}^*$ and $^{40}\text{Ar}^*$ imply that $^4\text{He}^*$ and $^{40}\text{Ar}^*$ were fractionated from each other during the Ancestral Rocky Mountain tectonic event. Preferential removal of $^4\text{He}^*$ from the basement relative to $^{40}\text{Ar}^*$ is consistent with the higher diffusivity of $^4\text{He}^*$ in crustal minerals [40]. Furthermore, a larger fraction of $^4\text{He}^*$ resides in grain boundaries of the crust where it is susceptible to transport by fluid advection [33].

5.1. Diffusion of Dissolved Gas through Evaporite Seal

A competing hypothesis to explain the low $^4\text{He}/^{40}\text{Ar}$ ratio observed at Bravo Dome is diffusive loss of ^4He through the anhydrite reservoir seal. In order to estimate the maximum flux of ^4He through the 10 m thick evaporite seal overlying the Tubb Sandstone reservoir rock, we assume that the anhydrite contains 1% connected, water filled porosity. The gas in Bravo Dome, and across the US mid-continent region tends to be severely under-pressured due to tight evaporite seals [21, 46], suggesting that the true effec-

Figure 9: Crustal ^4He and ^{40}Ar production volumes. Estimates for accumulation ages correspond to regional $^{40}\text{Ar}/^{39}\text{Ar}$ (1.3 Ga-1.4 Ga, dark red) and Zircon (U-Th)/He ages (280 Ma-310 Ma, dark blue). Using these ages, we estimate that the Bravo Dome gas entry event mobilized radiogenic ^4He from a volume of 43 km^3 , equivalent to a cylinder of 45 km thick crust with a 550 m radius. The range of possible values shown here corresponds to the black area in Figure 7.

396 tive connected porosity approaches zero in these deposits. The diffusive flux
 397 of dissolved ^4He is

$$J = -\frac{D\phi}{\tau} \frac{dC}{dz}. \quad (16)$$

398 Assuming 1% porosity throughout the seal, 100 ppm ^4He concentration,
 399 and a diffusivity, D , of $3.1 \cdot 10^{-9} \text{ m}^2/\text{s}$, the ^4He flux is $2 \cdot 10^{-7} \text{ mol}/(\text{m}^2 \text{ yr})$.
 400 Integrated over the reservoir age of 1.2 Ma and area of $3.6 \cdot 10^9 \text{ m}^2$, the total
 401 mols of ^4He lost is $8.64 \cdot 10^8$ mols, greater than the total amount of ^4He in
 402 the reservoir. Argon is more soluble and less diffusive than helium, with
 403 a diffusivity of $1.65 \cdot 10^{-9} \text{ m}^2/\text{s}$ at the reservoir temperature, 30°C [39, 20].
 404 These effects cause the flux of helium through a porous caprock to be only
 405 1.3 times higher than the flux of argon.

406 Similarly, the diffusivity of CO_2 at 40°C is half that of ^4He , but CO_2 is
 407 roughly 1000 times more soluble in water. The large solubility of CO_2 leads
 408 to a 500 times greater diffusive flux for CO_2 through trapping formations
 409 [47, 48, 38]. Because of this solubility effect, natural CO_2 reservoirs require
 410 nearly impervious seals to prevent loss of CO_2 through aqueous diffusion.
 411 Similar impervious evaporites have served as effective traps over geologic
 412 time for large commercial helium and CO_2 reservoirs [49, 50, 20, 30].

413 6. Conclusion

414 The noble gas volumes observed in the Bravo Dome natural CO_2 reservoir
 415 and crustal scale diffusion models demonstrate that crystalline continental
 416 crust retains noble gases. The flux of $^4\text{He}^*$ and $^{40}\text{Ar}^*$ from the continental
 417 interiors to the atmosphere is sporadic and localized. At Bravo Dome, the
 418 abnormally low $^4\text{He}^*/^{40}\text{Ar}^*$ ratio is best explained by preferential fraction-

419 ation by regional tectonic history. The radiogenic gas volumes show that
420 a large scale fluid migration event such as the Bravo Dome CO₂ entry was
421 only able to mobilize 0.02% of underlying crustal noble gases. Accordingly,
422 ⁴He and ⁴⁰Ar mass-balance constraints on mantle structure and atmospheric
423 formation should consider the potential correlation between degassing and
424 the global supercontinent cycle.

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