



# Noble gases preserve history of retentive continental crust in the Bravo Dome natural CO<sub>2</sub> field, New Mexico



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## ABSTRACT

Budgets of <sup>4</sup>He and <sup>40</sup>Ar provide constraints on the chemical evolution of the solid Earth and atmosphere. Although continental crust accounts for the majority of <sup>4</sup>He and <sup>40</sup>Ar 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 CO<sub>2</sub> 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 <sup>4</sup>He, <sup>40</sup>Ar, <sup>21</sup>Ne, <sup>20</sup>Ne, <sup>36</sup>Ar, and <sup>84</sup>Kr. The present-day production rate of crustal radiogenic <sup>4</sup>He and <sup>40</sup>Ar, henceforth referred to as <sup>4</sup>He\* and <sup>40</sup>Ar\*, 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 radiogenic production in the underlying crust. This shows unequivocally that radiogenic noble gases are effectively retained in cratonic continental crust over millennial timescales. This also requires that approximately 1.5 Gt of mantle derived CO<sub>2</sub> 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 <sup>4</sup>He\*/<sup>40</sup>Ar\* ratio is one fifth of the expected crustal production ratio, recording the preferential release of <sup>4</sup>He during the Ancestral Rocky Mountain orogeny, 300 Ma.

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## 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 (Turekian, 1959; Allègre et al., 1996; Coltice et al., 2000). Roughly 70% of the <sup>4</sup>He and <sup>40</sup>Ar degassed from the bulk silicate Earth derives from the continental crust (Torgersen, 1989; Bender et al., 2008). 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 CO<sub>2</sub> reservoir, which represent time-integrated fluxes averaged over thousands of square kilometers and millennial timescales. These abundances are compared with radiogenic production of <sup>4</sup>He and <sup>40</sup>Ar in the underly-

ing crust, based on a seismic density profile and heat flux in the region.

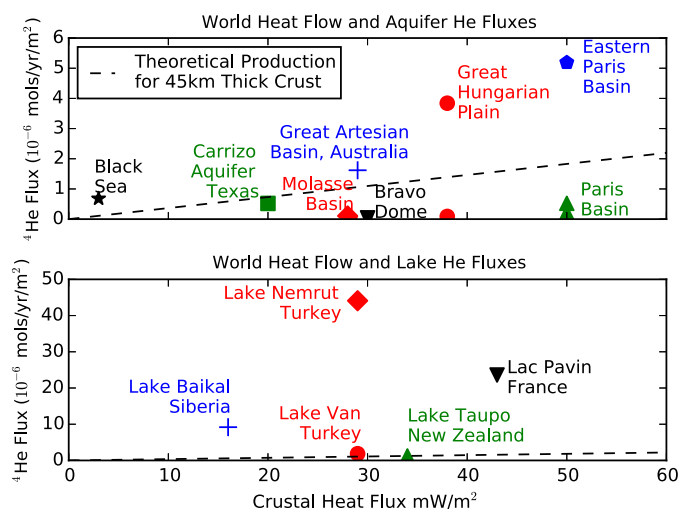
### 1.1. Previous work on crustal degassing

Previous estimates of average crustal degassing fluxes have relied on <sup>4</sup>He and <sup>40</sup>Ar accumulation in large regional aquifers (Torgersen and Stute, 2013; Torgersen and Clarke, 1985; Stute et al., 1992; Marty et al., 1993; Castro et al., 2000; Top and Clarke, 1981). However, <sup>4</sup>He residence time estimates rely on knowledge of the <sup>4</sup>He source and sink terms (Torgersen and Stute, 2013; Zhou and Ballentine, 2006). Fig. 1 shows that estimates of degassing fluxes based on regional aquifers vary between 3% and 300% of the expected crustal production. This variation may reflect heterogeneity of the degassing fluxes or the inherent difficulty of understanding dynamic aquifer systems (Torgersen, 2010). Similarly, the <sup>4</sup>He flux in lakes has been measured up to three orders of magnitude greater than expected crustal production (Torgersen, 2010; Kipfer et al., 2002). A review of these studies shows that estimates of the <sup>4</sup>He degassing flux decrease with increasing spatial and temporal scales (Torgersen, 2010).

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**Fig. 1.** Previously estimated helium fluxes and corresponding radiogenic heat production in the crust (Torgersen, 2010; Artemieva and Mooney, 2001; Blackwell et al., 2011; Rudnick and Fountain, 1995). Measurements with close proximity have varying  $^4\text{He}$  fluxes, suggesting sporadic and advective  $^4\text{He}$  degassing.

Crustal degassing can occur by diffusion along mineral grain boundaries or by advective transport in a migrating fluid phase. Transient variations in degassing fluxes have been observed in several field areas (Kampman et al., 2012; Lowenstern et al., 2014). Thus, the large spatial and temporal  $^4\text{He}$  and  $^{40}\text{Ar}$  flux averages recorded by the Bravo Dome gas field represent a significant advantage over extrapolation of degassing fluxes calculated from discrete points in space and time (Lowenstern et al., 2014). For crustal degassing studies, the Bravo Dome gas field is analogous to a large subsurface lake, acting as a volume of fluid accumulating flux and partitioning volatile dissolved gases from below (Fig. 2). In fact, the Bravo Dome gas offers two advantages over lake studies: it scavenges dissolved gases from the underlying brine through phase equilibrium, and remains isolated from the atmosphere due to the impervious evaporite cap rock (Broadhead, 1990).

## 1.2. Bravo Dome introduction

Bravo Dome is a large natural gas reservoir in northeastern New Mexico (Fig. 3A). The reservoir covers an area of 3600 km<sup>2</sup> and contained 1.3 Gt of nearly pure CO<sub>2</sub> before commercial extraction in 1981 (Broadhead, 1990; Sathaye et al., 2014). The gas is of mantle origin and was emplaced contemporaneously with basaltic volcanism, 1.2 to 1.5 Ma (Sathaye et al., 2014). Bravo Dome is located in continental crust that has been tectonically quiescent since the Ancestral Rocky Mountain orogeny, 300 Ma (Kluth and Coney, 1981). 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 (Sathaye et al., 2014; Blackwell et al., 2011). 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 (Sathaye et al., 2014; Wolf et al., 1996).

The gas reservoir formed at a depth of 700 m, directly above 1.4 Ga granitic basement and beneath a regional anhydrite seal (Barnes et al., 2002; Broadhead, 1990) (Fig. 3B). The stratigraphic location of Bravo Dome, shown in Figs. 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 CO<sub>2</sub> underneath the anhydrite seal, isolating it from the atmosphere. Furthermore, only 10% of the original CO<sub>2</sub> has dissolved since emplacement, suggesting that there is very little background groundwater flux (Sathaye et al., 2014).

Three phases of fluid emplacement are illustrated in Fig. 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 the Anhydrite seal (Fig. 2A). Second, during the CO<sub>2</sub> entry event, heated mantle CO<sub>2</sub> traveled along a fracture network through the crustal basement, liberating radiogenic  $^4\text{He}^*$  and  $^{40}\text{Ar}^*$  during its ascent. After reaching the Tubb Sandstone, the CO<sub>2</sub> displaced the initially present formation brine, and stripped atmospheric noble gases from the residual water (Fig. 2B). Finally, at present day, the radiogenic gases have been stripped from the crustal migration pathway, and the gas composition reflects a mixture of direct mantle input, crustal radiogenic degassing, and atmospheric derived noble gases which were previously dissolved in the formation brine (Fig. 2C).

## 1.3. Previous estimates of crustal composition

Uranium and thorium produce  $^4\text{He}$  by  $\alpha$ -decay, while  $^{40}\text{K}$  produces  $^{40}\text{Ar}$  by electron capture decay. We will refer to radiogenic, crustally produced  $^4\text{He}$  and  $^{40}\text{Ar}$  as  $^4\text{He}^*$  and  $^{40}\text{Ar}^*$ . Uranium, thorium and potassium are enriched in the continental crust by a factor of 50–100 relative to the primitive mantle (Hofmann, 1988). These radioactive isotopes are thought to be enriched in the upper crust relative to the lower crust (Rudnick and Fountain, 1995). The majority of crustal uranium and thorium is hosted by accessory minerals such as zircon, monazite and apatite, whereas potassium is dominantly hosted by feldspar.

Radioactive decay provides a significant source of heat in the Earth's crust. However, there is no consensus regarding the exact distribution of radioactive elements with depth (Hacker et al., 2015). Previous studies have encountered discrepancies between bulk estimates of crustal radioactive content and observed surface heat flux (Mareschal and Jaupart, 2013). In this region, the mafic lower crust assumption is supported by surface heat measurements and mantle heat flux estimates (Artemieva and Mooney, 2001; Blackwell et al., 2011).

## 2. Bravo Dome noble gas abundances

In order to determine the absolute quantities of each noble gas isotope in the reservoir, we interpolate previously published estimates of reservoir geometry, pore volume, bottom hole pressure, and noble gas isotope concentrations (Sathaye et al., 2014; Cassidy, 2005; Gilfillan et al., 2008). This volumetric calculation gives an upper bound on the total amount of radiogenic degassing that has occurred since the emplacement of the gas.

### 2.1. Subtraction of mantle component

Elevated gas pressure and CO<sub>2</sub>/<sup>3</sup>He and <sup>3</sup>He/<sup>4</sup>He close to sub-continental lithospheric ratios confirm that the magmatic CO<sub>2</sub> entered from the western side of the reservoir (Gilfillan et al., 2008; Sathaye et al., 2014; Cassidy, 2005), and suggest that there may be continued entry of mantle CO<sub>2</sub>. The maximum CO<sub>2</sub>/<sup>3</sup>He ratio in the western side of the field is  $5.35 \cdot 10^9$ , and the maximum <sup>3</sup>He/<sup>4</sup>He ratio is 4.26 Ra (Cassidy, 2005). Subtracting the concentration observed closest to the gas source, we can compute the areal density of non-mantle derived noble gas,

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