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He, Ne and Ar 'snapshot' of the subcontinental lithospheric mantle from CO_2 well gases

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ABSTRACT

The subcontinental lithospheric mantle (SCLM) constitutes a significant portion of the upper mantle sourcing magmatic volatiles to the continents above, yet its geochemical signature and evolution remain poorly constrained. Here we present new interpretation of noble gas datasets from two magmatic CO_2 fields in the SW US, namely Bravo Dome and Sheep Mountain, which provide a unique insight into the volatile character of the SCLM sourcing the Cenozoic volcanism in the region. We identify that reduction of $^3He/^4He_{mantle}$ ratio within the Sheep Mountain CO_2 field can be attributed to radiogenic production within the SCLM. Using a Reduced Chi-Squared minimisation on the variation of derived $^4He/^{21}Ne_{crust}$ ratios within samples from the Sheep Mountain field, combined with a radiogenically raised $^{21}Ne/^{22}Ne_{mantle}$ end member, we resolve $^3He/^4He_{mantle}$ ratios of 2.59 ± 0.15 to 3.00 ± 0.18 R_a. These values correspond with a $^{21}Ne/^{22}Ne_{mantle}$ value of 0.136. Using these $^3He/^4He_{mantle}$ end member values with $^{21}Ne_{mantle}$ resolved from Ne three component analysis, we derive the elemental $^3He/^{22}Ne_{mantle}$ of 2.80 ± 0.16 and radiogenic $^4He/^{21}Ne^*_{mantle}$ range of 1.11 ± 0.11 to 1.30 ± 0.14. A second Reduced Chi-Squared minimisation performed on the variation of $^{21}Ne/^{40}Ar_{crust}$ ratios has allowed us to also determine both the $^4He/^{40}Ar_{mantle}$ range of 0.78 to 1.21 and $^{21}Ne/^{40}Ar_{mantle}$ of 7.66 ± 1.62 to 7.70 ± 1.54 within the field. Combining these ratios with the known mantle production ranges for $^4He/^{21}Ne$ and $^4He/^{40}Ar$ allows resolution of the radiogenic He/Ne and He/Ar ratios corresponding to the radiogenically lowered $^3He/^4He_{mantle}$ ratios. Comparing these values with those resolved from the Bravo Dome field allows identification of a clear and coherent depletion of He to Ne and He to Ar in both datasets. This depletion can only be explained by partial degassing of small melt fractions of asthenospheric melts that have been emplaced into the SCLM. This is the first time that it has been possible to resolve and account for both the mantle He/Ne and He/Ar ratios within a SCLM source. The data additionally rule out the involvement of a plume component in the mantle source of the two gas fields and hence any plume influence on the Colorado Plateau Uplift event.

1. Introduction

The subcontinental lithospheric mantle (SCLM) can be defined as the basal part of the Earth's outer ridged mechanical boundary layer, where heat loss occurs by conduction (Day et al., 2015). The SCLM constitutes a significant portion of the upper mantle, making up ~2.5% by volume of the total mantle (Pearson and Wittig, 2008). The SCLM sources magmatic volatiles to the continents above, yet its geochemical signature and evolution remain poorly constrained. Traditionally, upper mantle characteristics have been deduced from the more conveniently sampled convective mantle, via mid-ocean ridge basalts (MORB). The SCLM has been physically isolated from this convective portion of the upper mantle for over 1×10^9 year (Ga) time scales (McDonough, 1990) as indicated by > 2 Ga Os isotope model ages in SCLM peridotites (Pearson et al., 1995a; Pearson et al., 1995b; Walker et al., 1989). This isolation has resulted in the SCLM developing its own unique isotopic, major and trace element signature (McDonough, 1990). The SCLM potentially contains a significant quantity of noble gases and other trace elements and re-entrainment of this material into the deeper mantle may contribute to the characteristic mantle signature sampled at ocean islands (Gautheron and Moreira, 2002).

Noble gases, and the $^3He/^4He$ ratio in particular, provide vital information about the character and processes controlling the mantle volatile source. Previous studies have identified that the isotopic ratio of He within the SCLM is more radiogenic than that of the MORB source mantle-which is typically cited to be 8 ± 1 R_a (Day et al., 2015; Day

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et al., 2005; Dunai and Baur, 1995; Dunai and Porcelli, 2002; Porcelli et al., 1987). This is reflected in the latest $^3He/^4He$ compilation estimate which cites a range of 6.1 ± 0.9 R_a for the SCLM (Gautheron and Moreira, 2002). A recent study of exsolving free gases by Bräuer et al. (2016) measured $^3He/^4He$ ratios from 4.95 to 6.32 R_a in the western-most part of the Pannonian Basin near the Austria/Slovenia border, corroborating earlier measurements of the more radiogenic than MORB signature of the SCLM. The origin of this radiogenic He has proved to be enigmatic and several explanations have been proposed including; alteration of the MORB source mantle by either addition of sediments (Dunai and Baur, 1995); isolation and ageing (Reid and Graham, 1996); or regional low $^3He/^4He$ plume sources (Duncan and Richards, 1991; White and McKenzie, 1995).

The Ne and Ar isotopic composition of the SCLM are even less well constrained, with previous studies documenting small anomalies compared to air values (Barford et al., 1999; Matsumoto et al., 1998) but also a small mantle component similar in character to MORB (Gautheron et al., 2005). These observations have been explained by atmospheric contamination or the recycling of an atmospheric component back into the lithospheric mantle (Gautheron et al., 2005). A number of recent studies (Holland and Ballentine, 2006; Kendrick et al., 2013; Kendrick et al., 2011; Sumino et al., 2010) have proposed that atmospheric derived noble gases can be recycled into the mantle via subduction. Matsumoto et al. (2001) proposed that the SCLM can potentially store these atmospheric noble gases. This issue is critical to rare gas budgets, as the SCLM can be delaminated and recycled back into the convecting mantle (Seber et al., 1996), and thus potentially help explain the numerous OIB which exhibit lower or MORB like $^3He/^4He$ ratios. These include OIB's observed at the Canary Islands (Day and Hilton, 2011), the Comores (Class et al., 2005), the Cook-Austral Archipelago (Hanyu and Kaneoka, 1997; Hanyu et al., 2011), the Azores (Moreira et al., 2012) and St. Helena (Barfod et al., 1999).

Our current knowledge of the characteristics of the SCLM has been deduced from magmas derived from melting of this portion of the mantle and from xenoliths trapped by rapidly rising magmas. However, typically magmas that reach the surface subaerially are strongly degassed and apart from occasional phenocrysts, do not contain a significant quantity of noble gases (Dodson et al., 1998; Dunai and Porcelli, 2002). Hence, the vast majority of data regarding the SCLM has been obtained from analysis of ultramafic xenoliths sourced from continental volcanic provinces (Day et al., 2015). Unfortunately, whilst some volcanic localities allow local mantle $^3He/^4He$ to be determined from these xenoliths, suitable samples are not always available, and air contamination of this sample type often precludes resolution of the heavy mantle-derived noble gases.

Magmatic CO_2 well gases provide a resource that enables the $^3He/^4He$, heavy noble gas isotope and relative abundance determination of the mantle source to be resolved (Ballentine et al., 2005; Holland and Ballentine, 2006). Primordial noble gas isotopes have been studied in well gases since 1961 (Boulos and Manuel, 1971; Butler et al., 1963; Caffee et al., 1999; Hennecke and Manuel, 1975; Phinney et al., 1978; Smith and Reynolds, 1981; Staudacher, 1987; Zartman et al., 1961), but until recently their use in investigating the SCLM in detail has been limited. Here we present noble gas analyses from magmatic CO_2 well gases in the SW US that provide a unique insight into the volatile character of the SCLM sourcing the Cenozoic volcanism in the region. For the first time, we have been able to resolve the mantle He, Ne and Ar ratios of the mantle source beneath these two natural magmatic CO_2 reservoirs. Combining our new data from the Sheep Mountain CO_2 field with previous measurements from the Bravo Dome CO_2 field (Ballentine et al., 2005) suggests that the process responsible for reducing the $^3He/^4He_{mantle}$ ratio within the SCLM is radiogenic production within the mantle. This permits critical analysis of models proposed to account for the SCLM evolution and volatile origin in greater detail than has been previously possible.

2. Tectonic setting of Colorado Plateau and Rocky Mountain natural CO_2 reservoirs

The Colorado Plateau is a massive, high-standing tectonic block located in the south-western US, centred on the Four Corners of the states of Colorado, New Mexico, Utah, and Arizona. It is abruptly flanked to the east by the Rio Grande rift and the majestic Rocky Mountains, the result of at least 2 km of uplift during the Laramide Orogeny and later Cenozoic uplifts (Parsons and McCarthy, 1995). To the south it is bounded by the Mogollon Rim and on the west by the Basin and Range Province, the result of pervasive tectonic extension that began around 17 Ma in the Early Miocene time.

2.1. Cenozoic volcanism and the Colorado Plateau Uplift event

In the late Cenozoic the cessation of subduction along the Pacific margin triggered extensive basic magmatic activity and accompanying lithosphere extension, block faulting and local uplift across the western US (Becker et al., 2014; Fitton et al., 1991). These events had a dramatic effect on the Colorado Plateau which was uplifted some 2 km (Erdman et al., 2016), with the most recent uplift event raising the south-western margin of the Plateau by approximately 1 km, between 6 and 1 Ma (Parsons and McCarthy, 1995). However, it is the lack of significant deformation of the region that is even more significant, especially given the rapid nature of the uplift event. Both the Rio Grande rift and the Basin and Range province have experienced similar degrees of uplift and have suffered extensive compression and internal faulting, whilst the Colorado Plateau has remained a rigid block, resistant to significant deformation (Becker et al., 2014; Erdman et al., 2016; Parsons and McCarthy, 1995).

The scale of the uplift event and the dominance of basaltic magmatism throughout imply some degree of mantle influence in the process, though the exact mechanism remains highly contentious. Several mechanisms have been proposed including; crustal thickening caused by horizontal compression (Dilek and Moores, 1999); dynamic topography (Moucha et al., 2008), thermal expansion due to a mantle plume (Fitton et al., 1991; Wilson, 1973); a reduction in the density of the mantle caused by physical thinning or thermal expansion of the lithosphere lid (Roy et al., 2009) or by the presence of a plume component (Parsons and McCarthy, 1995); and complete or partial lithosphere delamination of the Farallon Plate following flat slab subduction (Beghoul and Barazangi, 1989; Bird, 1979; Humphreys, 1995; Levander et al., 2011; Thompson and Zoback, 1979; Zandt et al., 1995).

2.2. Regional geology of Colorado Plateau and Rocky Mountain reservoirs

Within the Colorado Plateau and surrounding Rocky Mountain region there are at least nine producing or abandoned gas fields that contain up to 2800 billion m^3 of natural CO_2 (Allis et al., 2001; Miocic et al., 2013; Miocic et al., 2016; NETL, 2014). In this paper we detail the results from two separate gas fields, namely Sheep Mountain (Huerfano County, CO), and Bravo Dome (Harding County, NM), both of which contain extremely high concentrations of magmatic CO_2 (> 95% CO_2). The background geology and location of these sites is outlined in detail in Gilfillan et al. (2008).

2.2.1. Sheep Mountain

The Sheep Mountain gas field is located at the northern end of the Raton Basin, some 45 km northwest of the town of Walsenburg, south central Colorado. This region was extensively tilted and folded as a result of uplift to the west during by the Laramide Orogeny in the late Cretaceous-early Tertiary time (Woodward, 1983). As a result of this event, large volumes of lava were extruded from vents along the Sierra Grande arch, within the Raton Basin and on the eastern margin of the basin. Intrusive activity accompanied these volcanics, producing extensive sills and laccoliths including the distinctive peaks of Little Sheep