

Using noble gas isotope and abundance information to place constraints on basinal fluid origin, relative timing, transport mode and mass balance: He-N₂ rich gases in the mid-continent USA

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Noble gases and nitrogen

Noble gases are powerful tracers of subsurface fluid systems. The noble gases from the terrestrial atmosphere are introduced into the subsurface dissolved in groundwater. They can be distinguished isotopically from those produced by the decay of U, Th and K in the crust, which in turn are distinct from those derived from the mantle. Combined with the respective elemental abundance patterns, it is possible to resolve the noble gas contribution from these different sources to any crustal fluid, and constrain the extent of crustal, mantle and atmosphere-derived noble gas involvement in these systems. This has been used to constrain the role of groundwater in the transport of gas and oil, provide an insight into the mechanisms controlling fluid storage, release and transport from the basement, and identify the principle mechanism of mantle volatile input into rift environments.

Helium rich natural gases with few exceptions contain high nitrogen concentrations. Although the inverse is not true, this simply reflects the multiple nature of N₂ sources within natural gases. However, a regionally constant, but different, maximum He/N₂ ratio is frequently found. Examples include natural gases from the mid-continent USA, gases from the Californian Great Valley and Sacramento Basin, USA, the Alberta Basin, Canada, and Osthannover, Germany. On a regional scale this can only occur if the N₂ and He are closely related, with deviations from this ratio due to the addition of excess (He-poor) nitrogen from other sources, or subsequent fractionation. The close relationship between the N₂ and He makes this type of system an obvious candidate with which to apply the unique properties of the noble gases.

The Hugoton/Panhandle giant gas field

In particular, a constant He/N₂ is well documented in the Hugoton/Panhandle giant gas field which extends

350 km across SW Kansas, and the Texas/Oklahoma Panhandles. This reservoir has an in-place gas volume estimated to be 2×10^{12} m³ (STP) gas. The principal pay is from the Permian at depths of 400–900 m. A significant oil reservoir is associated with the NE section of the Texas-Panhandle. The hydrocarbon source is the Anadarko basin, which formed in response to the early Pennsylvanian Amarillo-Wichita uplift. The Kansas-Hugoton section is interpreted as a giant hydrodynamic trap, while the Texas-Panhandle is an anticlinal stratigraphic trap over the Amarillo-Wichita uplift.

Although nitrogen concentrations range locally between 5 and 75%, the average N₂ content of the field is 20%, with CH₄ making up the bulk of the remaining gas. The ⁴He/N₂ in the Hugoton and Panhandle are distinct at ~0.02 and ~0.077 respectively. We have analysed 31 samples in a traverse from North to South down the 350 km length of the field. We have determined the bulk composition and the CH₄, C₂, C₃, N₂, He, Ne, Ar abundance and isotopic composition.

Results and discussion

$\delta C^{13}(CH_4)$, $\delta C^{13}(C_2)$, $\delta C^{13}(C_3)$ are uniform across the entire system, averaging -43‰, -35.5‰ and -30.5‰ respectively, typical of an unassociated thermogenic origin. $\delta N^{15}(N_2)$ decreases systematically from +9‰ in the northernmost Hugoton to +2‰ in the southernmost Panhandle. ³He/⁴He and ²¹Ne/²²Ne ratios are remarkably uniform, averaging 2.8×10^{-7} (0.20 Ra) and 0.040 respectively. These values require that 2% of the ⁴He is mantle-derived and 27% of the ²¹Ne crustal-nucleogenic. The ⁴⁰Ar/³⁶Ar varies between 800 in the north to 1100 in the south and is crudely anticorrelated to $\delta N^{15}(N_2)$. On average these values require that ~70% of the ⁴⁰Ar is radiogenic-crustal in origin.

The single most important observation is that the

atmosphere-derived ^{20}Ne is locally correlated to the N_2 , with Hugoton $^{20}\text{Ne}/\text{N}_2 < \text{Panhandle } ^{20}\text{Ne}/\text{N}_2$. This pattern is identical to the $^4\text{He}/\text{N}_2$. A plot of crustal ^4He vs. atmosphere-derived ^{20}Ne shows a uniform $^4\text{He}/^{20}\text{Ne}$ ratio across the entire 350km section. The ^{20}Ne is derived from air dissolved in the groundwater. The covariance between the ^{20}Ne - ^4He and ^{20}Ne - N_2 is reasonably established by the regional interaction of ^4He and N_2 with the groundwater system.

The ^{20}Ne concentration in groundwater is fixed on recharge. It is therefore, simple to calculate the $\text{N}_2/^{20}\text{Ne}$ for a nitrogen saturated meteoric water as a function of temperature and pressure (depth). Significant degassing of the groundwater will preserve a $\text{N}_2/^{20}\text{Ne}$ ratio characteristic of the depth at which saturation occurred. The average $\text{N}_2/^{20}\text{Ne} = 2 \pm 0.5 \times 10^6$. This requires degassing at a depth of ~ 300 – 600 m, assuming hydrostatic pressure, and is entirely consistent with the bottom hole pressure of 435 psi measured across the field and the pressure recorded by isolated fields in the same producing horizon such as (730 psi) and Quinduno (890 psi). The systematic difference between Panhandle and Hugoton $\text{N}_2/^{20}\text{Ne}$ but not $^4\text{He}/^{20}\text{Ne}$ may be ascribed to solubility related fractionation effects (He and Ne have a very similar solubility coefficient in both oil and water, and therefore will not be fractionated by this type of process) such as differences in degassing conditions (salinity or gas/water volume ratio variations) or subsequent interaction of the Panhandle gases with the oil phase present in this part of the reservoir.

The constancy of the $\text{N}_2/^4\text{He}/^{20}\text{Ne}$ across the field despite the widely varying methane composition requires that the methane: 1) post dates the nitrogen; 2) contributes negligible portions of atmosphere-derived ^{20}Ne , and therefore has had little interaction with the groundwater system; and 3) contributes negligible quantities of radiogenic noble gases.

The abundance ratio of the different noble gas components can be compared. On a plot of crustal-radiogenic $^4\text{He}/^{40}\text{Ar}$ or $^{21}\text{Ne}/^{40}\text{Ar}$ vs. atmosphere-derived $^{20}\text{Ne}/^{36}\text{Ar}$, the magnitude of fractionation from end-member compositions is linear and coherent, with correlation coefficients >0.9 . The radiogenic $^4\text{He}/^{21}\text{Ne}$ is uniform across the entire field and indistinguishable from average crustal production (1.6×10^7). The covariance of atmosphere and crustal-radiogenic component He/Ar and Ne/Ar fractionation can only occur if these

differently sourced components were mixed before fractionation occurred. The constant crustal $^4\text{He}/^{21}\text{Ne}$ is consistent with the fractionation process being solubility/phase related, as discussed above. These results require that the radiogenic noble gases are stored, released and transported to near surface regions without fractionation from their elemental production ratios. This can only occur if they originate from regions with $T > 250^\circ\text{C}$ and are transported by an advective, single phase carrier fluid.

If it is assumed that the groundwater has completely degassed, the volume of groundwater required to source the atmosphere-derived noble gases now in the gas field is $1.4 \times 10^{12} \text{ m}^3$, which at 15% porosity would occupy 20 times the current reservoir volume. This is conservative because it is unlikely that complete degassing occurred. If it is assumed that the magnitude of fractionation observed in the radiogenic $^4\text{He}/^{40}\text{Ar}$ component is due to gas/water phase equilibrium, in-reservoir gas/water volume ratios are estimated to be ~ 0.001 . This increases the volume estimates for the associated groundwater water by a factor of 10. This volume of water is equivalent to half the entire volume of groundwater currently estimated to be in the Anadarko basin below a depth of 2 km.

The volume of rock required to produce the radiogenic noble gas is now considered. The minimum estimate is based on the volume of in-place ^4He ($\sim 1.4 \times 10^{10} \text{ m}^3$ (STP)). From the time of the Amarillo Uplift in the mid Pennsylvanian (310Ma), and assuming average crustal U (2.8 ppm) and Th (10.7 ppm) concentrations, this requires $\sim 2 \times 10^5 \text{ km}^3$ rock, similar to the entire present day volume of the Anadarko basin below 2 km. Because of the requirement for $T > 250^\circ\text{C}$, this limits the Anadarko basin source to regions below 8km depth. It becomes clear that this basin cannot source the ^4He in the Hugoton/Panhandle gas field. If the volume of ^4He dissolved in the associated groundwater is considered, this volume estimate requires a 100 times greater volume of rock in 310 Ma. Although longer storage periods will require proportionally less volume, it would appear that the source of the ^4He must be due to the regional release of stored radiogenic noble gases from the deep crystalline crust. With crystalline rock NH_4 concentrations of ~ 20 ppm, $\sim 20\%$ would have to be released from the rock sourcing the ^4He to account for the N_2 in the gas field.