

Final Project Report, November 1, 2015**“New Tracers of Gas Migration in the Continental Crust”****DOE Basic Energy Sciences****Mark D. Kurz****Woods Hole Oceanographic Institution****mkurz@whoi.edu**

The central goal of this project was to enhance understanding of gas distribution and migration in the continental crust using new measurements of noble gases in whole rocks and minerals from continental bedrock samples. Existing noble gas data sets are dominated by measurements of gas and fluid phases from gas wells, ground waters and hot springs. There are very few noble gas measurements from the solid continental crust itself, which means that this important reservoir is poorly characterized and gas migration rates are poorly constrained. We proposed to carry out whole-rock and mineral-separate of helium, neon, and argon measurements on existing bedrock samples near the Texas Panhandle gas field, which constitutes the southern limb of the giant Hugoton-Panhandle oil and gas field. The original proposal included a more extensive sample suite and more expansive objectives, but the budget was cut significantly, and this project was limited to a proof-of-concept.

Instrumentation

One goal of this research was to develop instrumentation to allow noble gas measurements in continental crustal rocks, some of which contain hydrocarbons. Hydrocarbons can cause interferences in noble gas extraction lines and mass spectrometry. In order to allow processing of such samples without contaminating our extraction lines, we constructed a separate dedicated extraction line for this sample type. The extraction line is shown in Figure 1, and is now fully operational.

Figure 1. The extraction line dedicated to hydrocarbon rich rock samples, gas wells, and hydrothermal gases. The pneumatic valves are controlled by the laptop at right, allowing automated operation. An ultra-high-vacuum double-vacuum resistance furnace is at left. There are two turbo-molecular pumps: the one at lower left provides secondary vacuum for the furnace and the one at right provides vacuum for the extraction line. In order to construct this extraction line within budget, we used two recycled components: the furnace turbomolecular pump and the quadrupole mass spectrometer (top center).

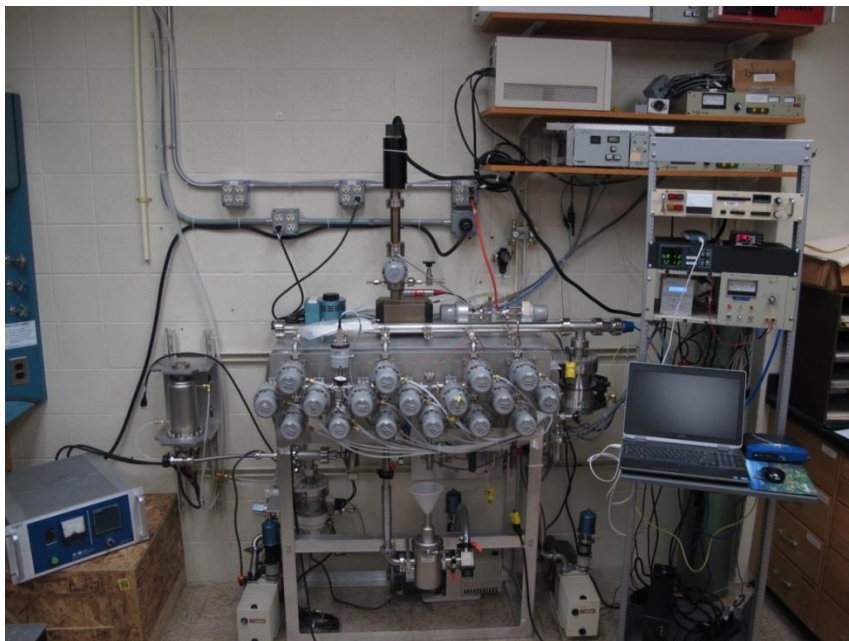




Figure 2. MAP 215-50 Mass spectrometer used to measure helium, neon, and argon at Woods Hole Oceanographic Institution (WHOI). The extraction line shown in figure 1 was designed to pre-purify samples for transfer to this system, thus avoiding hydrocarbon contamination. Samples are transferred to this system using stainless steel containers.

Noble gas measurements in continental crust

The initial plan for this project was to use bedrock from drill cores housed at the University of Texas (Bureau of Economic Geology). Preliminary conversations with the staff and scientists at this facility indicated that suitable samples existed in the collection. Once we attempted to identify specific material it became clear that there were very few Precambrian basement samples, if any, in the collection. Most of the rock core samples in the UT BEG collection were obtained by oil and gas prospecting, and did not penetrate basement. Since this was one of the main priorities of the project, we pursued other sources of samples, with the assistance of UT staff. We initiated a collaboration with Dr. Melanie Barnes, at Texas Tech, who has devoted considerable effort to studying Precambrian basement rocks. She generously provided a suite of Precambrian basement from the Texas panhandle, with known ages and geochemistry, all from drill cores and including a range of lithologies (granites, rhyolites, gabbros). We successfully made helium, neon, and argon measurements as proposed. The results demonstrate the utility of the approach. In all cases, noble gases were measured first by crushing in vacuum to release gases held in fluid inclusions, followed by a separate extraction of the gases in the solid matrix (powder, by melting in vacuum). This simple procedure yields important insights into the noble gas sites in the crust. Crushing released only 0.07 to 0.27 of the total helium, so only a small

fraction of the helium is contained in melt inclusions. More importantly, systematically higher $^3\text{He}/^4\text{He}$ values are obtained by crushing, demonstrating strong isotopic disequilibrium in all the samples. The data obtained by melting vary between 0.016 and 0.091 Ra (where 1 Ra = the atmospheric $^3\text{He}/^4\text{He}$ ratio of 1.384×10^{-6}), while the data obtained by crushing the same samples show higher $^3\text{He}/^4\text{He}$, with a much narrower range (0.11 to 0.18 Ra). If we exclude the highest value (from one of the gabbros), the average $^3\text{He}/^4\text{He}$ is 0.125 ± 0.01 , a remarkably narrow range of values given the range in lithologies, ages, and trace element abundances (particularly Th and U). This isotopic disequilibrium, with radiogenic and nucleogenic isotopic compositions in the solid phase (melting extraction), is also observed in the neon and argon isotopes.

The preliminary interpretation of the helium isotopic disequilibrium, coupled with relatively uniform $^3\text{He}/^4\text{He}$ in all lithologies (by crushing only), is that the crushed values reflect a relatively recent gas migration event within the crust. It is also worth noting that the helium in the Texas panhandle gas field has $^3\text{He}/^4\text{He}$ distinct (0.21 ± 0.03) from those observed in the Precambrian bedrock. The difference is not huge, but it will be worth exploring further.

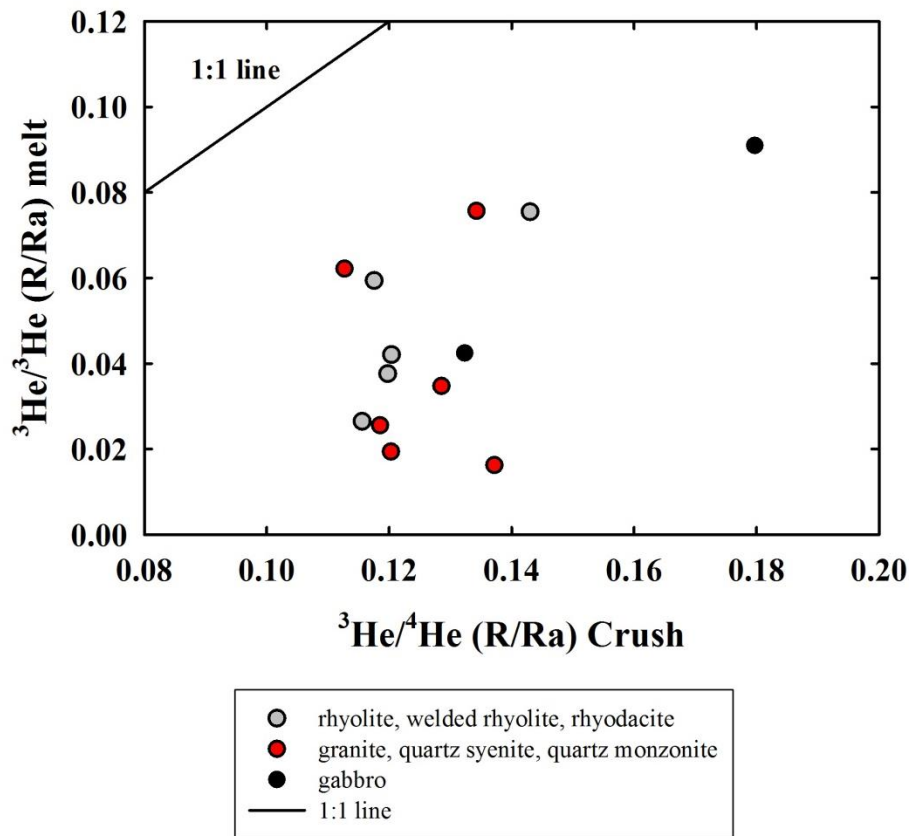


Figure 3. A comparison of $^3\text{He}/^4\text{He}$ by crushing and melting in the Precambrian basement samples. The 1:1 line in the upper left indicates agreement between crushing and melting. The data shows that the $^3\text{He}/^4\text{He}$ by crushing is much higher, and less variable, than by melting. This could indicate the importance of Th and U decay within the solid matrix, which would lower the $^3\text{He}/^4\text{He}$.

Another indication of gas migration is illustrated by the $^4\text{He}/^{40}\text{Ar}^*$ data. The $^4\text{He}/^{40}\text{Ar}$ crustal production ratio is approximately $5 (\pm 1)$, which serves as an important reference value for the new Texas panhandle Precambrian basement data. As shown in figure 4, all of the new data obtained for this project are well below the production ratio, suggesting helium loss. In addition, the granites show a correlation between the ^4He total concentration (crush plus melt) and $^4\text{He}/^{40}\text{Ar}^*$ which is also suggestive of helium loss. This is not a proof of mechanism for the gas distribution within the Panhandle Precambrian bedrock samples analyzed here, but demonstrates that the approach yields some clear constraints. Further measurements in younger reservoir rocks, such as sandstones and shales, would provide useful comparisons with the new bedrock data. We hope to prepare at least one manuscript on these new data, in collaboration with Dr. Barnes, and anticipate putting the new extraction line to use with additional samples from the Texas panhandle.

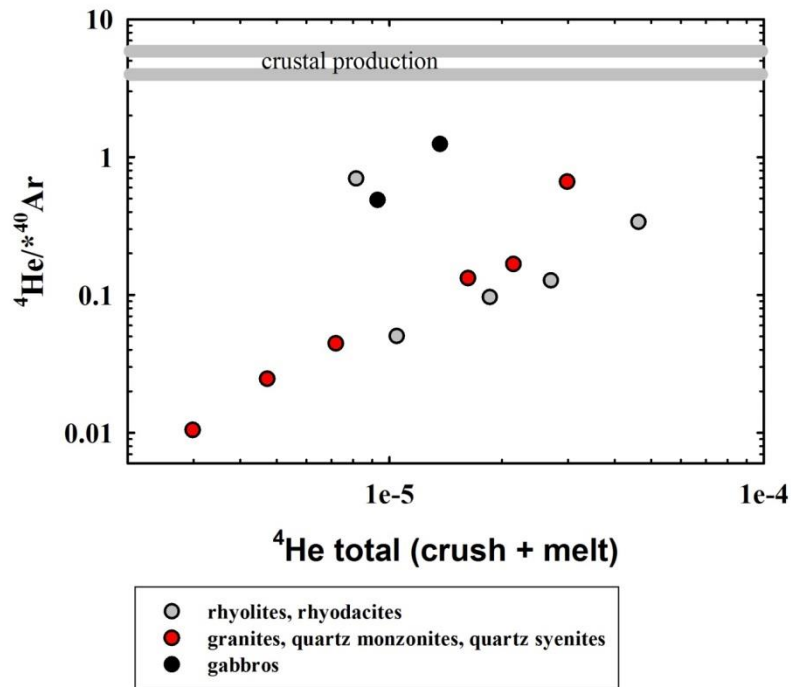


Figure 4. Total ^4He plotted against $^4\text{He}/^{40}\text{Ar}^*$ for the Texas Panhandle Precambrian basement samples. $^{40}\text{Ar}^*$ is the amount of radiogenic argon in the sample, defined as $^{40}\text{Ar}^* = [^{40}\text{Ar}/^{36}\text{Ar} (\text{measured}) - ^{40}\text{Ar}/^{36}\text{Ar} (\text{air})] * ^{36}\text{Ar}$, so the $^4\text{He}/^{40}\text{Ar}^*$ ratio gives an indication of fractionation from the radiogenic crustal production ratio, which is $5 (\pm 1)$ and is related to the abundances of Th and U relative to potassium. The preliminary explanation for the low $^4\text{He}/^{40}\text{Ar}^*$ ratios, relative to the production ratio, and the correlation with ^4He total, is that the samples have undergone loss of helium relative to argon.

Noble gas measurements in mafic veins

In a related effort to constrain noble gas behavior relating to melt migration in the crust and mantle, we measured helium concentrations and isotopic compositions in transects through two centimeter-scale veins, with millimeter resolution, in two different tectonic settings (some funding for this effort came from NSF). One is a clinopyroxenite vein in the Josephine Ophiolite (Oregon, USA), hosted by harzburgite. The vein has ^4He concentrations up to 10 times higher than the host harzburgite. Because pyroxenite veins are thought to form through mantle melt percolation, the enrichment confirms that helium behaves as an extremely incompatible element. There is a sharp helium concentration contrast at the vein/host interface, suggesting that the concentration variations were produced during vein emplacement, and that clinopyroxene has higher helium solubility and storage capacity. Total $^3\text{He}/^4\text{He}$ in the host harzburgite ranges from 6.5 to 7.1 Ra, in agreement with previous measurements (Recanati et al., 2012). The bulk $^3\text{He}/^4\text{He}$ in the vein varies between 4.5 and 5.3Ra, significantly lower than the harzburgite, reflecting radiogenic production since vein emplacement or slab related fluxes. A second transect was measured across an amphibole diorite vein hosted by granoblastic basalt in 15 Ma ocean crust, formed at the superfast spreading East Pacific Rise (recovered near 1500 meters depth in ODP Hole 1256D). The amphibole and plagioclase at the vein center have 5-10 times higher abundances of He, Ne, and Ar, and slightly higher $^3\text{He}/^4\text{He}$ and $^{40}\text{Ar}/^{36}\text{Ar}$, compared to the host basalt. These two studies show that isotopic and concentration variations have been preserved since emplacement at ~ 15 Ma and ~ 157 Ma, and that mantle helium isotopic compositions are retained over these time scales. The isotopic variations suggest that it may be possible to determine Th-U-He vein emplacement ages, if the Th and U heterogeneities can be understood; preliminary ICP-MS studies suggest that there are huge Th and U variations within the vein material. These preliminary data are not necessarily representative of the crust or mantle, as they are the first studies of this kind, and represent such different tectonic settings, but they highlight the importance of melting and melt migration. The ocean crustal vein data demonstrates the potential importance of amphibole in determining crustal noble gas inventories, with implications for subduction zone fluxes and crust-melt interactions at mid-ocean ridges. These data may also provide important constraints on mantle models, suggesting that preferential melting of these vein types would yield lower $^3\text{He}/^4\text{He}$ than host mantle, and that vein melting cannot explain unradiogenic noble gas isotopic signatures, found at some hotspots.