COMBINED NOBLE GAS AND STABLE ISOTOPE CONSTRAINTS ON NITROGEN GAS SOURCES WITHIN SEDIMENTARY BASINS.

FINAL Report

for period 15 March 1996 - 14 March 1999
extended to 14 March 2000

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May 2001

Prepared for

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INTRODUCTION.

Nitrogen is one of the major non hydrocarbon gases found in natural gas reservoirs. Many regions in which the gas fields have a high nitrogen content also show a relationship between the concentration of nitrogen and crustal-radiogenic helium. The crustal He will be associated with crustal ^{40}Ar and ^{21}Ne. Noble gases derived from other sources such as the air dissolved in groundwater and magmatic sources can also be quantified from the noble gas isotopic composition. Combined with the distinct elemental abundance patterns it is possible to resolve the extent of crust-, mantle- and atmosphere-derived noble gas involvement in these systems, and thereby constrain the involvement of associated fluids in the source and transport from these different regions. Further information is also available, because the relative elemental abundance pattern of the noble gases from these different sources are, in general, well defined. Because the noble gases are chemically inert, any change in these abundance patterns must reflect physical processes, such as transport, within the subsurface and allow us to assess the role for example of diffusive migration or identify the involvement of non gaseous phases such as oil or groundwater in the fluid system.

OBJECTIVE.

The objective of this project was to combine the information available from both noble gas and stable isotope systematics to understand the origin of nitrogen and related gas sources, transport behaviour and mass balance within natural gas reservoirs and sedimentary basin systems.

SUMMARY OF GOALS ACHIEVIED

1) Noble Gas and Stable Isotopes in Nitrogen Rich Natural Gases

The Hugoton-Panhandle giant gas field, located across SW Kansas and the Texas and Oklahoma panhandles in the USA, is the case type example of high nitrogen concentrations in a natural gas being linked with high helium concentrations (e.g. Pierce A. P., Gott G. B., and Mytton J. W. (1964) Uranium and helium in the Panhandle gas field, Texas, and adjacent areas. In *USGS Prof. Pap.*, Vol. 454-G, pp. 57.). The main focus of the DOE funding was to use a combined study of He, Ne and Ar abundance and isotopic composition together with _^{13}C(C$_1$-C$_3$) and _^{15}N$_{N2}$ to identify the origin of the different gases, and the processes responsible for their emplacement into the gas field. We collected and analysed 31 samples from producing wells in a north-south traverse of the 300km long field. N$_2$ concentrations in the samples vary between 6.6 to 25.8 vol%. The samples reflect the previously observed north-south change in ^{4}He/N$_2$, with values changing from 0.020 to 0.049 respectively. ^{3}He/^{4}He, ^{21}Ne/^{22}Ne and ^{40}Ar/^{36}Ar vary between 0.14-0.25Ra, 0.0373-0.0508, and 818-1156 respectively, and are caused by quantifiable contributions from mantle, crustal and atmosphere-derived sources. The atmosphere-derived ^{20}Ne/^{36}Ar ratios are indistinguishable from groundwater values. The crustal ^{4}He/^{21}Ne* and ^{4}He/^{40}Ar* ratios show a 60% excess of ^{4}He compared to predicted production ratios in the crust. In contrast ^{21}Ne*/^{40}Ar* are almost indistinguishable from predicted production. This is typical of noble gas release from crustal regions less than ~8km depth (Ballentine C. J., Mazurek M., and Gautschi A. (1994) Thermal constraints on rare gas release and migration: Evidence from Alpine fluid inclusions. *Geochim. Cosmochim. Acta* 58, 4333-4348.). The mantle ^{3}He/N$_2$ and groundwater-recharge ^{36}Ar/N$_2$ ratios enables us to rule out significant magmatic or atmosphere contributions to the gas field N$_2$, which is dominantly crustal in origin.

Crustal-derived ^{4}He is directly correlated with groundwater-derived ^{20}Ne showing a clear link between the groundwater system and the crustal noble gases. A plot of ^{20}Ne/N$_2$ vs. ^{4}He/N$_2$ shows mixing between two distinct crustal N$_2$ components, one that is associated with the ^{4}He and ^{20}Ne (N$_2$*), and the other with no resolvable noble gas component. δ^{15}N$_{N2}$ values vary from +2.7 ‰ to +9.4 ‰. The N$_2$* and non He-associated nitrogen end-members are inferred to have δ^{15}N$_{N2}$ = -3 ‰ and +13 ‰ and contribute from between 25-60% and 75-40% of the nitrogen respectively. The non He-associated nitrogen is probably related to the hydrocarbon source rocks. The δ^{15}N$_{N2}$* value is not compatible with a crystalline or high grade metamorphic source and, similar to the ^{4}He, is inferred to be from a shallow or low metamorphic-grade source rock. **This is the first time that the isotopic composition of different nitrogen sources in natural gas have been resolved and their origin unambiguously identified.** ^{4}He mass balance requires a regional crustal source. The volume of groundwater required to source the ^{20}Ne in the gas field demonstrates the viability of the groundwater system in providing the collection, transport and focusing mechanism for the ^{4}He and N$_2$*. The N$_2$*/^{20}Ne ratio shows that the N$_2$* transport must be in the aqueous phase, and that the degassing mechanism is reasonably contact between the groundwater and a pre-existing hydrocarbon gas phase. We present in our conclusions a generalised conceptual model for assessing He-associated N$_2$ risk in natural gas

reservoirs (C.J. Ballentine and B. Sherwood Lollar, Regional crustal release and groundwater focussing of He and N_2 into mid continental USA natural gases. *Geochim. Cosmochim. Acta* (2001) submitted). COPY ENCLOSED

II) Noble gases in groundwater.

Noble gas concentrations in groundwater are determined by variables such as recharge temperature, dissolved 'excess' air, recharge salinity, recharge fractionation, and altitude of recharge. Given the age of the groundwater this property is typically used as a paleoclimate record. However, groundwater interacts and equilibrates with fluids derived from other portions of the crust, such as nitrogen or hydrocarbons. This interaction results in the contribution of air-derived noble gases to the crustal fluid and can be used to assess the extent of interaction between the fluid and the groundwater. Constraining the processes which control the noble gas abundance in the groundwater is therefore essential if we are to understand the role that groundwater may play in the transport of basinal fluids in the sedimentary regime. We have developed a rigorous mathematical technique to evaluate the processes which control noble gas abundances in groundwater. Unlike current data handling techniques, our error weighted non-linear inverse method enables us to resolve paleotemperature, excess air and a third variable, such as recharge salinity or altitude, and also provides the confidence or error associated with the data deconvolution. We demonstrate the utility of this technique with a synthetic data set. We then show that current data sets cannot reproduce known recharge altitude or salinity. This must be due to the influence of a ubiquitous physical fractionation process in almost all aquifer systems. We show that all data sets are consistent with a diffusive fractionation process at recharge. This process is not considered in the conceptual model used to resolve literature estimates of paleotemperature. In the case of one key data set used to define the tropical continental paleoclimate record, consideration of recharge fractionation reduces the observed drop in temperature from 5°C to 2°C at the last glacial maximum. This is significantly smaller than expected (C.J. Ballentine and C.M. Hall. An inverse technique for calculating groundwater paleotemperature and other variables using noble gas concentrations in groundwater. *Geochim. Cosmochim. Acta* **63** (1999) 2315-2336).

III) Characterisation of Magmatic and Crustal Noble Gas Input Into Basin Systems.

The ^{3}He/^{22}Ne of the mantle beneath the continental lithosphere, and the average crustal nucleogenic ^{21}Ne/^{22}Ne production are poorly defined. Quantification of these parameters is crucial if noble gases are to be used comprehensively as tracers of crustal fluid systems. Understanding the mechanisms which produce these values provide a fundamental insight into the character and control of the different terrestrial reservoirs supplying the noble gases to the basin systems. I demonstrate that a constant and low mantle ^{3}He/^{22}Ne in all regions of crustal extension is consistent with small melt fraction asthenospheric melts being emplaced into the subcontinental mantle. These melts partially degas, lose a maximum of 15% of their He content by gas/melt phase partitioning and form the dominant source of mantle-derived volatiles in regions of crustal extension. Similarly, nucleogenic ^{21}Ne/^{22}Ne in these systems is constant and almost a factor of ten lower than models of homogenous crustal element distribution would predict. This confirms that mineral scale preferential siting of U and Th with respect to O and F controls the regional nucleogenic ^{21}Ne/^{22}Ne (C.J. Ballentine. Resolving mantle He/Ne and crustal ^{21}Ne/^{22}Ne in well gases. *Earth and Planet. Sci. Lett.* **152** (1997) 233-250).

This first work showing that partial degassing of a deep magma fractionates the noble gases predicts that the magmatic CO_2/^{3}He ratio should also be fractionated by the same process. We used this property to investigate the origin of CO_2 in the West Texas Val Verde basin natural gas fields. Except for regions of recent crustal extension the dominant origin of CO_2 in basinal fluids has previously been assumed to be from crustal organic matter or mineral reactions. We show that a Rayleigh fractionation model for a partially degassed magmatic source is consistent with observed CO_2/^{3}He and δ^{13}C(CO_2) in these CO_2-rich natural gases in the Val Verde basin and with the previously established mantle ^{3}He/^{22}Ne systematics. Regional changes in CO_2/^{3}He and CO_2/CH_4 are explained if the CO_2 input predates the basin CH_4 generation, which occurred at ~280Ma. Uplift to the north of this study occurred between 310-280Ma and provides the only tectonic event with appropriate timing and location to be the source of the magmatic CO_2. Identification of magmatic CO_2 in a foreland basin suggests that CO_2 origin in mid-continent basinal systems needs to be re-evaluated. The inferred closed system preservation of natural gas in a trapping structure of ~300Ma is far higher than the residence time predicted by diffusion models in other systems (C.J. Ballentine, M.Schoell, D.Coleman and B.A. Cain, 300-Myr-old magmatic CO_2 in natural gases of the west Texas Permian basin. *Nature* **409** (2001) 327-331).

Publications funded or part funded by DOE grant DE-FG02-96ER14615

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Invited or Keynote presentations funded or part funded by DOE grant DE-FG02-96ER14615

2000   'Noble gas concentrations in groundwater or other subsurface fluid phases and data Inversion: How far can we go?' **Fall AGU, San Francisco**

2000   'Quantifying the role of groundwater in basin scale natural gas transport.' **University of Nancy, France**

2000   'Noble gas geochemistry: From the esoteric to the practical' **University of Manchester, UK**

2000   'Quantifying the role of groundwater in basin scale natural gas transport.' **Institute Francais du Petrole, Paris, France**

2000   'Quantifying the role of groundwater in basin scale natural gas transport.' **University of Bern, Switzerland**

1999 'Magmatic noble gases in the shallow crust: a window into mantle geochemistry and a tool in hydrocarbon exploration' **MIT, Cambridge, USA**

1999 'Process oriented noble gas geochemistry.' Dept. Earth Science, **University of Bristol, UK**

1998 'Using noble gas isotopic and abundance information to place constraints on basinal fluid origin, relative timing, transport mode and mass balance' **ETH Zurich, Switzerland**

1998 'Using noble gas isotopic and abundance information to place constraints on basinal fluid origin, relative timing, transport mode and mass balance: H-N_2 rich gases in the Mid-continental USA.' **8th V.M. Goldschmidt Conference, Toulouse, France**

1998 'Using noble gas isotopic and abundance information to place constraints on basinal fluid origin, relative timing, transport mode and mass balance' **Rice University, Houston, Texas, USA**

1998 'Using noble gas isotopic and abundance information to place constraints on basinal fluid origin, relative timing, transport mode and mass balance' **Exxon, Houston, Texas, USA**

1996 'Resolving the mantle $^{4}He/^{22}Ne$ and crustal $^{21}Ne/^{22}Ne$ production in well gases: Understanding mantle and crustal degassing in continental rifts' **University of Leeds, UK**

1996 'The role of noble gases in understanding fluid transport in sedimentary basins' Turner Lecturer, **University of Michigan, USA**