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REVIEW ARTICLE

A RESEARCH UPON EVOLUTION AND PROCESSING OF NOBLE GASES

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A Research upon Evolution and Processing of Noble Gases

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INTRODUCTION

Fluids have a fundamental role as agents for migration and concentration of hydrocarbons and metals within sedimentary basins (e.g., Oliver, 1992; Sverjensky and Garven, 1992; Parnell, 1994; 1998). Tracing the origin and migration pathways of these fluids is thus a prerequisite for correct evaluation of the economic potential of large basins and for refining exploration, appraisal and development of hydrocarbon accumulations.

During the past twenty years, there has been a large effort by the scientific community to introduce new tracing techniques used in inorganic geochemistry for application in petroleum geology (Emery and Robinson, 1993; Cubitt and England, 1995). Noble gases undoubtedly have a relevant place among these new techniques. The main characteristic of these gases (He, Ne, Ar, Kr and Xe) is indeed to be “noble”, i.e. chemically inert. Furthermore, they are scarce, hence their common alias, the “rare gases”. These features make them trace elements par excellence (e.g., Ozima and Podosek, 1983). Their elemental and isotopic compositions can reflect exclusively the origin of fluids in which they are dissolved or the physical processes of transport and mixing of these fluids within the crust (Fig. 1).

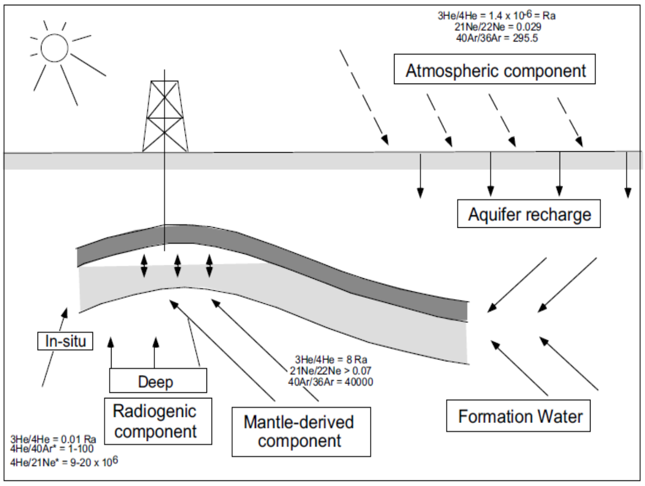

Figure 1. Schematic diagram illustrating the main components of noble gases which may be found in sedimentary fluids. The isotopic signature of noble gases He, Ne and Ar are reported for each component. Modified from Ballentine and O’Nions (1994).

Three different processes can generate noble gases in sedimentary fluids and thus give different information on the origin and movement of these fluids (Fig. 1). Noble gases can be of atmospheric origin (atmosphere contains 0.94% by volume of noble gases, mainly 40Ar) where they are dissolved in the water at the recharge site.

Atmosphere-derived noble gases (ANG hereafter) successively migrate into basin aquifers, transported by the groundwater. Noble gases are more soluble in oil than in water, so oil-water interaction involves preferential partitioning of noble gases into oil, so that their relative concentration in oil reflects the degree of water flow in oil reservoirs. This is an important constraint in tracing secondary oil migration and thus the spatial distribution of hydrocarbon accumulations within a basin (Dahlberg, 1995), as well as on a smaller scale, the possible role of water on hydrocarbon degradation (Lafargue and Barker, 1988).

Nuclear processes involving radioactive elements contained in rocks, such as 235,238U or 40K can generate isotopes of noble gases (4He and 40Ar, respectively). Radiogenic noble gases thus could be used as fluid chronometers. Unfortunately, fluids are not a closed system and mixing between fluids of different provenance makes it difficult to constrain the various sources of radiogenic noble gases, hence the problem in obtaining absolute fluid ages (Solomon et al., 1996; Pintiand Marty, 1998; Bethke et al., 1999). The problem is complicated in the case of hydrocarbon accumulation by water-oil solubility partitioning, which can introduce radiogenic noble gases into hydrocarbons produced in different layers of oil reservoirs and subsequently transported by groundwaters.

Finally, noble gases can be primordial (hereafter “mantle-derived”), i.e. captured during the formation in the earth and preserved in the mantle. Fluids flowing in extensional basins (Ballentine, 1997;

Ballentine et al., 1991; 1996; Ballentine and O'Nions, 1991) or continental rifts (Griesshaber et al., 1992) show a clear noble gas mantle-derived isotopic signature (mainly excesses of primordial 3He and in rarer cases ^{129}Xe and ^{21}Ne). In contrast, hydrocarbon reservoirs located in loading basins (e.g., Po Basin, Italy; Elliot et al., 1993) do not show any resolvable mantle noble gas component, suggesting the thermal structure and tectonic history of the host basin may control the occurrence of mantle-derived noble gases (O'Nions and Oxburgh, 1988). Mantle-derived noble gases are often associated with a major gas component such as methane. This does not mean that natural gas accumulations have a mantle origin, as has been suggested by some authors (Gold and Soter, 1980; Gold and Held, 1987). Abiogenic CH_4 in continental crustal fluids may be less than 1% of the total (Jenden et al., 1993). The occurrence of mantlederived noble gases in subsurface fluids is an illustration of large-scale fluid flow, possibly triggered by tectonic activity, which acts in sedimentary basins and contributes to the transport and accumulations of ores within the crust (Ballentine et al., 1991; Sverjensky and Garven, 1992; Pinti and Marty, 1995, Torgersen, 1993).

In this study we describe the origins of noble gases in hydrocarbon accumulations and the physico-chemical processes responsible for their isotopic and elemental fractionation. These processes are related to the physico-chemical conditions of the hydrocarbon accumulations. Finally, we will present some case studies to illustrate the different responses of noble gases in sedimentary basins affected by different tectonic and thermal histories.

BACKGROUND

In January 2011 it was extensively reported in Canadian and global news media that the Kerr family were forced to move from their property located above the Weyburn oil field as a result of an alleged leakage of CO_2 which had been injected into the oil field below to enhance oil recovery (EOR). A geochemical consultant from Petro-Find, who was hired on behalf of the Kerr's, reported measurements of $\delta^{13}C$ (CO_2) isotope values in soil gases rich in CO_2, which he claimed to be similar to those of the CO_2 injected into the deep oil reservoir (Lafleur, 2010). The Petroleum Technology Research Centre (PTRC), who is responsible for the environmental monitoring of the Weyburn CO2-EOR and storage operation, published a detailed science based response. This correctly stated that Petro Find had not taken into account similar soil gas $\delta^{13}C$ (CO_2) ratios observed in prairie soils comparable to those found on the Kerr property (e.g. Keller and Bacon, 1998; Hendry, 1999).

Petro-Find also failed to mention that $\delta^{13}C$ (CO_2) is not a unique tracer and that several other natural sources could have accounted for the measured isotope values (PTRC, 2011). While this response went some way to addressing the public fears raised by the alleged CO_2 leak, it is clear that more must be done to fully account for the safety and security of the CO_2 stored at Weyburn. It is imperative for both the project and the local community that there is an independent investigation into the alleged leak to establish whether there is any truth in the allegations.

Noble gases are intimately associated with all natural and engineered CO_2 occurrences, and are trace components mixed into the gas mixture in parts per billion quantities. The noble gases are extremely powerful tracers of both CO_2 source, and the subsurface processes that act on CO_2. This is because there are only three distinct sources of noble gases within the subsurface, namely the crust, the mantle and the atmosphere, and these can be discriminated and fingerprinted by their isotopic compositions and abundance ratios.

Crustal noble gases, such as ^{4}He and ^{40}Ar, are produced by the radioactive decay of uranium, thorium and potassium within the crust (Ballentine and Burnard, 2002). Mantle derived noble gases, such as ^{3}He, were trapped within the mantle during the accretion of the Earth and have been degassing ever since (Ballentine, et al., 2002). Atmospheric noble gases, such as ^{20}Ne and ^{36}Ar enter the subsurface dissolved in the groundwater via meteoric recharge (Ballentine, et al., 2002). The distinct elemental and isotopic composition of these three noble gas components allows the contribution from each source to be determined and provides detailed information on the source and transport processes associated with the CO_2.

Noble gases have been widely used to trace regional flows of groundwater in numerous locations (Castro and Goblet, 2003; Castro et al., 1998). Several studies have successfully demonstrated the potential of noble gases to trace the origins of CO_2 and its fate within reservoirs (Gilfillan et al., 2008; Gilfillan et al., 2009; Lafortune et al., 2009; Nimz and Hudson, 2005). Recent research has shown that noble gases can be used to trace diffuse CO2 migrating from a natural deep CO_2 reservoir through the subsurface to the surface at St. Johns Dome in Arizona (Gilfillan et al., 2011).

Noble gases in trace quantities, therefore, can be used to identify the origins of CO_2 at the land surface. Hence, to determine the origin of the alleged CO_2 anomaly measured in soil gases on the Kerr quarter, the trace noble gases can be measured. We made measurements of a suite of noble gas and carbon stable isotope tracers from four different sources:

1) the water injected into the oil field

2) the CO_2 injected into the oil field

3) the fluids produced from the field

4) the Kerr and Thackery quarter groundwater well waters

We test the hypothesis that migration of dissolved CO_2, which originates either from the free phase CO_2 or water injected into the Weyburn oil field or from the CO_2 contained in the produced fluids, is responsible for the CO_2 anomaly at the surface.

TRAPPING PROCESSES OF NOBLE GASES

Noble gases are extremely rare in meteorites. A remarkable consequence of this scarcity is the impressive variety of different noble gas “components” that can be distinguished in meteorites, i.e., reservoirs with a relatively well-defined elemental and/or isotopic composition of a more or less well-understood origin. Podosek (2003) gives an insightful explanation of this basic feature of noble gas cosmochemistry.

Some components were produced in situ, e.g., the cosmogenic and the radiogenic noble gases discussed elsewhere in this book (Eugster et al., 2006; Krot et al., 2006). Other components were trapped by the meteoritic materials or their precursors.

Among all elements, N is most similar to the noble gases in cosmochemical behavior. Although in a few minerals N belongs to the crystal structure, more often than not it is present as an ultratrace element only. Often N has also been trapped (or produced in situ) by similar processes as noble gases, and its variability in isotopic composition in meteorites is among the largest of all elements. Furthermore, N and noble gases are often analyzed in parallel on the same sample.

The multitude of trapped gas components allows one to study a wide variety of processes throughout most of the epochs discussed in this book, and some longstanding problems in noble gas cosmochemistry have their roots in the fact that it is not always clear in what particular epoch a certain component received its identity.

Component Separation : Early workers separated various noble gas components by stepwise heating or physical separation of bulk meteorite samples (Reynolds and Turner, 1964; Black and Pepin, 1969; Eberhardt, 1974). Such work provided clear-cut evidence that presolar solids had survived in meteorites. Investigating these, Lewis et al. (1975) found that most of the primordial noble gases of the Allende carbonaceous chondrite reside in the residue that remains after dissolving the bulk meteorite in HF and HCl. Since this landmark paper, work on primordial noble gases largely concentrated on acid-resistant residues and much of the subsequent discussion will be focused on such data. Notwithstanding the huge success of this approach, it also has its potential pitfalls; however, since primordial gas components residing in acidsoluble phases might go largely undetected, just as the “burning the haystack to find the needle” approach to isolate presolar grains will fail to recognize less-resistant types of such grains. Indeed, we will discuss also recent in vacuo etch studies of bulk meteorite samples that have allowed characterization of primordial noble gas components in a way never before possible.

NOBLE GAS ISOTOPE

The noble gases are those elements on the extreme right of the periodic table. The name is derived from their unreactive character, a consequence of having outer electron orbitals filled. Isotopes of all 6 noble gases are produced to some degree by nuclear processes. 4He is, of course, produced by alpha decay while 40Ar is produced by electron capture decay of K. Isotopes of Kr and Xe are produced by U fission, while Rn consists of only short-lived isotopes of the U and Th decay series. In addition, 129Xe is the decay product of the extinct radionuclide 129I (half life: 15.8 Ma) and the heavy Xe isotopes were produced by fission of the extinct nuclide ^{244}Pu (half life 82 Ma). While neon isotopes are not produced directly by radioactive decay, significant variations occur in Ne isotopes as a consequence of reaction between ‘fissogenic’ neutrons and magnesium as well as between alpha particles and 18O. Finally, cosmicray interactions can also produce isotopic variations in the noble gases, as we have already seen. Cosmicray interactions produce a great many nuclides, but because noble gases are so rare the effects are more significant than for other elements. In addition to nuclear processes noble gas isotope ratios also vary as a consequence of mass-dependent fractionations. The processes that produced these fractionations mainly occurred in the young solar system and Earth and provide important insights into that very early episode of history, as was recognized more than half a century ago (Damon and Kulp, 1958).

RARE GAS COMPONENTS IN BASINS

Noble gas isotopes in natural systems originate from a variety of sources and processes. For the purpose of tracing sources of hydrocarbons and associated volatile elements and the processes having fractionated them, it is convenient to consider only three major end-members: the atmosphere, the sediments and/or the underlying crust, and the mantle (Fig. 1). Atmospheric noble gases are primarily introduced in basin fluids by circulating groundwaters. At recharge areas of basin aquifers, atmospheric noble gases dissolve in surface waters in proportions depending on their respective solubilities. They are then isolated from the surface when groundwaters leave the saturated zone, and are transported along the water flow paths. They are eventually transferred in hydrocarbon reservoirs during water-oil-gas exchange.

Natural radioactivity produces a variety of noble gas isotopes in proportions depending on residence time and on parent element contents in reservoir rocks and in the basement. These radiogenic isotopes therefore have the potential to address the chronological dimension of basin evolution. Basins often develop during extension and stretching of the continental crust, which often allows the generation of magmas at depth and the release of mantle-derived volatiles including noble gases in those basins. Each of these components produce noble gases with specific isotopic compositions that can help in addressing important problems such as hydrocarbon-water interaction, fluid residence time underground, or contributions of mantlederived heat or CO_2 to the oil fields. For an extensive description of sources and processes contributing noble gases to the natural environment, the reader should consult the book by Ozima and Podosek (1983) and other reviews by Lupton (1983), Farley and Neroda (1998), Mazor and Bosch (1987), O'Nions and Ballentine (1993) and Ballentine and O'Nions (1994).

THE ATMOSPHERIC COMPONENT

The atmosphere is well mixed with respect to noble gases and, with the exception of helium, noble gases are conservative in this reservoir. They are contributed by degassing of the mantle via magmatism, primarily through volcanism along mid-ocean ridges, by the release of volatile elements by the crust during weathering reactions and, recently, by use of fossil fuels. Generally, the abundance of atmospheric noble gases in natural system is high relative to that in crustal or mantlederived rocks, which requires specific precautions when sampling and analyzing rocks or fluids in order to minimize contamination by air-derived volatiles. A notable exception is helium, which escapes from the Earth's gravitational field. The two isotopes,3He and 4He, have residence times in air of ~ 0.2 Ma and ~ 3 Ma, respectively (e.g., Torgersen, 1989). Consequently, the abundance of He in air is low, and He in underground fluids is dominated by nonatmospheric component(s) such as radiogenic He or mantle-derived He (see below). For the other noble gases, it can be considered as a first approximation that the atmospheric composition remained constant during the geological duration of typical basin formation and evolution (Tables 1 and 2).

Gas	Molecular/atomic weight (^{12}C = 12 g/mol)	Molecular/atomic fraction
Dry air	28.9644	1
He	4.0026	$5.24 \pm 0.05 \times 10^{-6}$
Ne	20.179	$1.818 \pm 0.004 \times 10^{-5}$
Ar	39.948	$9.34 \pm 0.01 \times 10^{-3}$
Kr	83.80	$1.14 \pm 0.01 \times 10^{-6}$
Xe	131.30	$8.70 \pm 0.10 \times 10^{-8}$

Table 1. Noble gas concentrations in dry air (modified from Ozima and Podosek, 1983).

Isotope	Isotopic ratio	Normalization	Abundance (% atom.)
Helium			
3	1.386±0.01	1	0.000140
4	10^6	714800	~100
Neon			
20	100	9.80	90.50
21	0.296	0.0290	0.268
22	10.20	1	9.23
Argon			
36	0.3384±6	1	0.3364
38	0.0553	0.1869	.0632
40	100	295.5	99.60
Krypton			
78	0.6087±20	1.994	0.3469
80	3.9599±20	12.973	2.2571
82	20.217±4	66.23	11.523
83	20.136±21	65.97	11.477
84	100	327.6	57.00
86	30.524±25	100	17.398
Xenon			
124	0.3537±11	2.337	0.0951
126	0.3300±17	2.180	0.0887
128	7.136±9	47.15	1.919
129	98.32±12	649.6	26.44
130	15.136±12	100	4.070
131	78.90±11	521.3	21.22
132	100	660.7	26.89
134	38.79±6	256.3	10.430
136	32.94±4	217.6	8.857

Table 2. Isotopic composition of noble gases in air (modified from compilation of Ozima & Podosek, 1983). Uncertainties refer to the last digits.

The radiogenic component : Natural radioactivity of $^{235,\ 238}U$, ^{232}Th and ^{40}K produces a number of noble gas isotopes either directly, or through induced nuclear reactions. Notably, U and Th decay produces ^{4}He and, via neutron activation of ^{6}Li, tritium (3H) which decays with a half-life of 12.3 years to ^{3}He. Because the yield of the last reaction is low, the $^{3}He/^{4}He$ ratio of the radiogenic component is low, generally of the order of 10-9-10-8 depending on the relative abundances of U, Th versus Li and on other neutron absorbing elements. Such isotopic compositions characterize fluids evolving in crustal environments away from zones of recent magmatism. Other isotopes of interest produced by natural radioactivity include ^{21}Ne, ^{40}Ar and $^{131-136}Xe$. Because air contains significant amounts of these isotopes, it is often difficult to extract the radiogenic signal from the atmospheric one. One way to do so is to consider ^{21}Ne, ^{40}Ar and $^{131-136}Xe$ isotopes in excess of those present in the atmosphere (labeled with an asterisk to distinguish them from those derived from air).

THE ATMOSPHERIC NOBLE GAS ISOTOPES

It has been shown that one of the main reservoirs of noble gas isotopes interacting with a petroleum system is ASW. All the atmospheric noble gases are dissolved in the aquifer waters, implying that their original concentrations are known, as their atmospheric concentration and solubility coefficients are well constrained. Some noble gas isotopes there are sourced uniquely from ASW, being unradiogenic and with sufficiently low mantle concentrations (compared to ASW) to be neglected; notably ^{20}Ne, ^{36}Ar, ^{84}Kr and ^{132}Xe can be considered to be ASW-derived. Therefore, from their concentrations in aquifers, their measured concentrations in a hydrocarbon phase are consequently related to the amount of aquifer water exchanged with the hydrocarbon phase: no interaction at all would imply zero concentrations in the hydrocarbon phase (which is never seen), whereas high oil/water ratios would feed the hydrocarbon phase with high concentrations of these isotopes. Several papers have already demonstrated the geological interest in these fossil interactions recorded by the noble gas isotopes. With well known initial concentrations and physical properties, exchanges between oil, gas and water phases can readily be traced: Ballentine et al. (1991) investigated noble gas partitioning in the Pannonian Basin, Ballentine et al. (1996) in The Magnus Opus field, with direct measurements of noble gas concentrations in the oil phase, Battani et al. (2000) for the giant gas fields of the Indus Basin, and Prinzhofer et al. (2000) for the gas accumulations of the Mascupana Basin, Mexico.

NOBLE GAS CONSTRAINTS ON HYDROCARBON ACCUMULATION

In recent years noble gases have been extensively used as natural tracers to study sources, water-rock interactions, migration, and mixing of basin fluids. The noble gas species in basin fluids can originate from the atmosphere-equilibrated groundwater, and any flux into basin traps. Therefore, they are greatly suitable for a complementary tool to study the role of groundwater on transporting hydrocarbon. However, so far these properties of noble gas have been little exploited in the central area of Western Sichuan Basin, and the fluid-related phenomena of gas accumulation are still poorly understood. The purpose of the present paper is to present helium and argon isotope abundance in hydrocarbon-rich reservoirs of the area, and discusses the degree of interaction between hydrocarbon and groundwater. Such studies would impose further constraints in the understanding of the phenomena of hydrocarbon accumulation in the area.

The Western Sichuan Basin is located along the western margin of the Sichuan Basin, and is a NE-SW elongate foreland basin superimposed up on the Paleozoic basement during the Meso-Cenozoic tectonic episodes. The central area of the foreland basin is bounded on the west by the Longmenshan Thrust-Nape Belt and on the east by the Longquanshan Fracture Zone, covering approximately 9000 km^2. The area began to subside during the late episode of Indosinian Orogeny, and accompanied to accumulate 3000 — 4000 m thick of Upper Triassic marine-continental organic- rich, classic and pelitic sediments with coal beds, as well as continued to be filled with interbeded fluvio-lacustrine red sandstone and mudstone up to 2500 m thick in the Lower Jurassic through Lower Cretaceous time. These strata and the basement were subjected to intense disturbance during the Yanshan and Himalayashan Movements, resulting in regional erosion surfaces and well-developed fissures swarms, and were overly by the younger Quaternary sediments.

Seven samples were collected from the Xiaoquan, Xinchang and Hexincliang gas fields, taking at depths from 650111 to 4566 m. A detailed study of the total gas composition and carbon isotopic ratios of all samples have been given elsewliere. Briefly, the samples are dominated by hydrocarbons with content of >99% by volume and wetness >0.5%, their methane t > $\delta^{13}C(CH_4)$ and ethane t) $\delta^{13}C(C_2H_6)$ values are > -37%o and > -27%o, respectively, the data indicate that the hydrocarbons in these gas fields are thermogenic; in addition, their isotopic and compositional variations with depths clearly show that the Xiaoquan and Hexincliang hydrocarbons are in situ accumulation in the Upper Triassic strata, while the Xinchang Jurassic hydrocarbons are derived frothe deeply buried and mature source rocks of Upper Triassic age and have experienced a long distance migration.

CONCLUSIONS

In the above section, we have selected a few studies that cover contrasting tectonic regimes. Ballentine et al. (1996) were able to quantify interactions between oil and seawater in the Magnus oilfield, East Shetland Basin, northern North Sea. He concluded that the amounts of 20Ne and 36Ar that are found in the oil phase require a seawater/oil phase ratio of 110, which is approximately the ratio thought to be present at depth. They accordingly concluded that the Magnus oil has achieved complete static equilibrium with the groundwater in the reservoir drainage volume and placed these results in the framework of the cementation history of the reservoir. These findings are at odd with those obtained for the Pannonian, Vienna, and Paris basins for which noble gas data strongly suggest water/oil ratios much higher than presently observed, and therefore, active hydrodynamics in these basins.

The use of noble gases to trace sources of hydrocarbons and processes having lead to their accumulation is still in its infancy, despite the unique information they are able to deliver. One of the limits to their applicability is the inherent difficulty in analyzing very small amounts of gases (down to 10-20 moles for 3He) extracted from chemically complex hydrocarbons. This requires working with ultra-high vacuum lines, but purification of hydrocarbons in such lines is extremely difficult. As a result, only a handful of laboratories are able to carry out such analyses. Studies in this field were primarily carried out in the spirit of the basic understanding of natural processes (although often funded by energy companies or agencies). However, the technological and scientific transfer to oil and gas companies is not obvious and limited by the somewhat “high-tech” aspect of such research that is not yet fully known by executives in charge of reservoir exploration and exploitation.

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