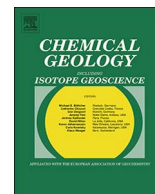




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## The noble gas isotope record of hydrocarbon field formation time scales

Igor N. Tolstikhin<sup>a,e,\*</sup>, Chris J. Ballentine<sup>b</sup>, Boris G. Polyak<sup>c</sup>, Edward M. Prasadov<sup>d,f</sup>,  
Olga E. Kikvadze<sup>c</sup>

<sup>a</sup> Geological Institute, Kola Scientific Center, Apatity 184209, Russia

<sup>b</sup> Department of Earth Sciences, University of Oxford, South Parks Road, Oxford OX1 3AN, UK

<sup>c</sup> Geological Institute, Russian Academy of Sciences, Moscow 119017, Russia

<sup>d</sup> St. Petersburg State University, 199034 St. Petersburg, Russia

<sup>e</sup> Space Research Institute, Moscow 117997, Russian Academy of Sciences, Russia

<sup>f</sup> A.P. Karpinsky Russian Geological Institute (VSEGEI), 199106 St. Petersburg, Russia

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### ABSTRACT

Noble gases may be considered as the most prominent tracers of natural fluids, including hydrocarbons. The atmosphere is the only source of  $^{20}\text{Ne}$ ,  $^{36}\text{Ar}$ ,  $^{84}\text{Kr}$ ,  $^{130}\text{Xe}$  in subsurface environments, and their concentrations in pore waters after recharge are known from the solubility data. This allows modelling of noble gas partitioning between coexisting gas, oil and water phases in the course of hydrocarbon formation, migration, and storage. Radiogenic isotopes,  $^4\text{He}^*$ ,  $^{21}\text{Ne}^*$ ,  $^{40}\text{Ar}^*$ ,  $^{136}\text{Xe}^*$ , after being released from source rocks, are mixed with air-derived noble gases already present in the pore space. Concentrations of radiogenic species in the pore space of “typical” hydrocarbon fields are generally so high, that they can hardly be accumulated in situ and thus indicate noble gas transfer from ground waters. The time bearing ratios  $^4\text{He}^*/^{20}\text{Ne}$ ,  $^{21}\text{Ne}^*/^{20}\text{Ne}$ ,  $^4\text{He}^*/^{40}\text{Ar}_{\text{AIR}}$ ,  $^{40}\text{Ar}^*/^{40}\text{Ar}_{\text{AIR}}$  in hydrocarbon fields are thus proportional to the time interval between the ground water recharge and noble gases partitioning into the hydrocarbon phase(s), the ‘recharge – partition interval’. The largest available data set allows the recharge-partition intervals to be constrained for a large number of hydrocarbon fields, situated in different tectonic settings (ancient plates, young plates, mobile belts). These intervals increase systematically with the ages of hydrocarbon source and trap lithologies and are comparable with these ages. This important feature, valid *in general* for different hydrocarbon fields, implies: (i) local sources of radiogenic noble gas isotopes in ground waters; (ii) relatively recent formation of hydrocarbon fields and (iii) their short formation time scales.

In some cases the duration of formation of a hydrocarbon field can be constrained. For example, nearly constant  $^{21}\text{Ne}^*/^{20}\text{Ne}$ ,  $^{40}\text{Ar}^*/^{40}\text{Ar}_{\text{AIR}}$  ratios, measured in samples from the Magnus oil field (North Sea), give an accumulation time scale  $\approx 10$  Ma. It should be emphasized that the above noble gas isotope ratios give the time estimates, which are independent of geological reconstructions.

Sometimes the noble gas inventory in a hydrocarbon field and ground waters allows characterization of the source rock volume, involved in formation of the field; generally this volume exceeds that of the hydrocarbon field rocks by orders of magnitude.

### 1. Introduction: noble gas isotopes in ground waters

With our present state of knowledge, the classification of terrestrial noble gases might include many different sources and domains that host them. However, for the sake of simplicity and with a hope that this simplification will not affect substantially discussion of our major subject, time scales derived from noble gas abundances in hydrocarbon accumulations, we consider here the two dominant sources, the continental crustal rocks and the atmosphere.

Generally atmospheric noble gases are transferred into the subsurface by air saturated water (ASW), either by aquifer recharge or during burial of surface rocks bearing air saturated pore waters (e.g., Bosch and Mazor, 1988; Ballentine et al., 1991, 1996; Hiyagon and Kennedy, 1992; Aeschbach-Hertig et al., 2008; Prinzhofer, 2013; Barry et al., 2016). Even though some fractionation and degassing/ingassing processes take place at recharge, the “initial” concentrations of air saturated noble gases ( $^{20}\text{Ne}$ ,  $^{36}\text{Ar}$ ,  $^{84}\text{Kr}$ ,  $^{132}\text{Xe}$ ) in ground (or pore) waters can be reasonably well constrained from the solubility data and some

\* Corresponding author.

E-mail address: [igor.tolstikhin@gmail.com](mailto:igor.tolstikhin@gmail.com) (I.N. Tolstikhin).

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(generally not large) contribution from air in excess of the solubility limits. This contribution can be estimated by using concentrations of all air-derived noble gases in ground water samples (e.g. Ballentine and Hall, 1999; Peeters et al., 2002; Aeschbach-Hertig et al., 2008).

After being produced in a mineral, radiogenic noble gas isotopes (we include in this term nucleogenic and fission isotopes, e.g.,  $^{21}\text{Ne}^*$ ,  $^{136}\text{Xe}^*$ ) are partially retained within the mineral and partially released into a pore water. Comparison of apparent whole-rock  $^{238}\text{U} - ^{235}\text{U} - ^{232}\text{Th} - ^4\text{He}^*$  and  $^{40}\text{K} - ^{40}\text{Ar}^*$  ages with those known from e.g.  $^{87}\text{Rb} - ^{87}\text{Sr}$  or U-Th-Pb isochron dating (for about 60 samples, Tolstikhin, 1985) allows the loss parameter  $L$  ( $L$  = fraction of radiogenic atoms released from a host rock into pore space divided by the total amount produced) to be constrained. For  $^4\text{He}^*$  the loss parameter,  $L_4$ , is generally quite high,  $> 0.9$ , whereas for  $^{40}\text{Ar}^*$   $L_{40}$  was found to be  $\approx 0.4$  (see Footnotes to Table 1). These values are likely to vary depending on the dominant mineral type and thermal history of the system investigated (Ballentine and O'Nions, 1994; Baxter, 2003).

Measurable concentrations of U and Th in a rock along with He concentrations in the rock – pore-water (gas, oil) system in principle allow the He residence time in this system to be quantified. To apply such simplest modelling, expressed by Eqs. (1a)–(4) below, the following assumption should be taken into account: i) there has been no gain/loss of radioactive parent isotopes into or from the rock, and ii) the radiogenic species generated in the water-bearing rocks is the only source of radiogenic noble gas species present in the rock-water system.

These assumptions are in many cases valid for the U-Th- $^4\text{He}^*$  system, especially if a helium flux from external sources can be ruled out (e.g., Lehmann et al., 2003; Tolstikhin et al., 2011; Holland et al., 2013) or constrained (e.g., Solomon, 1996). However  $^{40}\text{Ar}^*$  is retained by the source minerals substantially better than  $^4\text{He}^*$  and an essential  $^{40}\text{Ar}^*$  fraction may have survived the weathering/sedimentation processes; therefore only partial loss of  $^{40}\text{Ar}^*$  atoms generates the time-bearing signal in the pore space. These complications make the respective time scales less certain; however, consideration of predicted  $^4\text{He}^*/^{21}\text{Ne}^*/^{136}\text{Xe}^*$  production (e.g. Holland et al., 2013) or the combined study of the host rocks (minerals) and related ground (pore) waters (e.g., Tolstikhin et al., 2011) allows the noble gas mobility and losses to be constrained and thus obtain a more reliable time estimates. Such studies should be considered as an important direction of our future efforts in understanding time scales related to ground water flow, hydrocarbon production rates and hydrocarbon accumulation and evolution.

### 1.1. Relating in-situ noble gas production rates to ASW noble gases

For relatively young ( $< 300$  Ma old) rocks the radiogenic  $^4\text{He}^*$  produced and released into the pore water,  $^4\text{He}^*_{\text{PS}}$  [ $\text{mol cm}^{-3}$ ] and the residence time  $T$  [years], during which He has accumulated in the pore water ( $\phi$  is the porosity) via the decay of U and Th [ $\mu\text{g g}^{-1}$ ] in a host rock with the rock density  $\rho$  [ $\text{g cm}^{-3}$ ] are related as (e.g., Zartman et al., 1961)

$$^4\text{He}^*_{\text{PW}} \approx (5.40 \times 10^{-18}\text{U} + 1.28 \times 10^{-18}\text{Th}) \times T \times L \times \rho \times (1 - \phi)/\phi \quad (1a)$$

Values of the “Loss” coefficient  $L$  (defined above) are presented in the Footnotes to Table 1.

For ancient samples with an age exceeding  $\approx 300$  Ma, the exponential decay of the parent isotopes should be taken into account. For U-Th- $^4\text{He}^*$  systematic Eq. (1a) is translated into

$$^4\text{He}^*_{\text{PW}} = [8 \times ^{238}\text{U}(\text{Exp}(\lambda_{238}T)-1) + 7 \times ^{235}\text{U}(\text{Exp}(\lambda_{235}T)-1) + 6 \times ^{232}\text{Th}(\text{Exp}(\lambda_{232}T)-1)] \times L \times \rho \times (1 - \phi)/\phi \quad (1b)$$

In Eq. (1b) the U, Th concentrations are  $\text{mol cm}^{-3}$  of rock and  $^4\text{He}^*_{\text{PS}}$  is in units of  $\text{mol cm}^{-3}$  of pore space. The exponential term should also be included in Eqs. (2)–(4) for K-Ar and other systematics in case of the ancient rock-water system.

Ground water flow and noble gas diffusion in a rock-water system cause mixing of the radiogenic and atmospheric noble gases (e.g., Ballentine et al., 1996; Ballentine and Sherwood Lollar, 2002), therefore concentrations of radiogenic species in ground water can be restored from the radiogenic/air-derived isotope ratios and the ASW concentrations (hereafter subscript ASW defines concentrations of air-derived noble gases in air-saturated waters). Because of the similar solubility of He and Ne, especially in the case of saline waters (Smith and Kennedy, 1983), air-derived  $^{20}\text{Ne}$  is the best proxy for  $^4\text{He}^*$ . Therefore it is possible to modify Eqs. (1a), (1b) by dividing its left and right sides by  $^{20}\text{Ne}_{\text{ASW}} = 8.5 \times 10^{-12} \text{ mol ml}^{-1}$  (solubility for  $10^\circ\text{C}$ , fresh water):

$$\begin{aligned} (^4\text{He}^*/^{20}\text{Ne}_{\text{ASW}})_{\text{PW}} &= (6.35 \times 10^{-7}\text{U} + 1.51 \times 10^{-7}\text{Th}) \times T \times L \times \rho \\ &\times (1 - \phi)/\phi \end{aligned} \quad (2)$$

The solubility of He and Ne vary within  $\pm 10\%$  and  $\pm 20\%$ , respectively, depending on temperature (from  $10$  to  $40^\circ\text{C}$ ) and salinity (from fresh to sea water). As discussed below, other factors, which affect the  $^4\text{He}^*$  time scales, are more significant. Therefore for the estimates presented below we neglect: (i) variations of He and Ne solubility and treat them as constants and (ii) fractionation related to noble gas partitioning between gas (oil) and water phases, i.e.,  $(^4\text{He}^*/^{20}\text{Ne}_{\text{ASW}})_{\text{GAS}} \equiv (^4\text{He}^*/^{20}\text{Ne}_{\text{ASW}})_{\text{PW}}$ . A similar equation is available for  $^{21}\text{Ne}^*/^{21}\text{Ne}_{\text{ASW}}$  and  $^4\text{He}^*/^{40}\text{Ar}_{\text{ASW}}$  ratios, in which case the two coefficients in Eq. (2) should be replaced by  $9.78 \times 10^{-12}$  and  $2.32 \times 10^{-12}$  (for  $^{21}\text{Ne}^*/^{21}\text{Ne}_{\text{ASW}}$ ) and  $3.15 \times 10^{-10}$  and  $7.45 \times 10^{-11}$  (for  $^4\text{He}^*/^{40}\text{Ar}_{\text{ASW}}$ ) respectively, providing fresh  $10^\circ\text{C}$  water at recharge. It should be noted that Ar solubility could vary by a factor of  $\approx 2$ ; this should be taken into account when  $^4\text{He}^*/^{40}\text{Ar}_{\text{AIR}}$  and/or  $^{40}\text{Ar}^*/^{40}\text{Ar}_{\text{AIR}}$  ratios are used for the time scale estimates (Section 3, Figs. 3, 4).

Similar to Eqs. (1a), (1b), concentration of  $^{40}\text{Ar}^*$  in pore water [ $\text{mol ml}^{-1}$ ] can be calculated for a given K concentration [ $\text{g g}^{-1}$ ] following Zartman et al. (1961):

$$^{40}\text{Ar}^*_{\text{PW}} = 1.79 \times 10^{-16}\text{K} \times T \times L \times \rho \times (1 - \phi)/\phi. \quad (3)$$

Substituting the average parent element concentrations in the upper crust,  $\text{K} = 0.023 \text{ g g}^{-1}$ ,  $\text{U} = 2.7 \mu\text{g g}^{-1}$ ,  $\text{Th} = 10.5 \mu\text{g g}^{-1}$  (Rudnick and Gao, 2003), hereafter referred to as the average crustal concentration, in Eqs. (1a), (3) gives the present-day crustal  $^4\text{He}^*/^{40}\text{Ar}^*$  production ratio of 6.7. Fig. 3 below presents a comparison of this value with those observed in hydrocarbon accumulations.

Assuming the gas phase was produced by degassing of pore water and substituting  $^{40}\text{Ar}_{\text{ASW}} = 1.72 \times 10^{-8} \text{ mol ml}^{-1}$  (solubility for  $10^\circ\text{C}$ , fresh water) into Eq. (3) gives:

$$\begin{aligned} (^{40}\text{Ar}^*/^{40}\text{Ar}_{\text{ASW}})_{\text{GAS}} &\equiv (^{40}\text{Ar}^*/^{40}\text{Ar}_{\text{ASW}})_{\text{PW}} = 1.04 \times 10^{-8} \times \text{K} \times T \times L \\ &\times \rho \times (1 - \phi)/\phi. \end{aligned} \quad (4)$$

In the course of hydrocarbon formation the atmospheric and radiogenic noble gases are partitioning between the water and the hydrocarbon phase(s). To discuss this episode in noble gas evolution we consider only partitioning between water and gas: the mass balance of the two phases includes the ASW “initial” concentrations of air-derived isotopes  $^i\text{C}_{\text{ASW}}$  and those after gas/water separation,  $^i\text{C}_{\text{GAS}}$ ,  $^i\text{C}_{\text{WAT}}$  [ $\text{mol m}^{-3}$ ], as well as the volumes of the two phases, water,  $W$ , and gas,  $G$  [ $\text{m}^3$ ], as discussed by Zartman et al. (1961):

$$^i\text{C}_{\text{ASW}} W = ^i\text{C}_{\text{GAS}} G + ^i\text{C}_{\text{WAT}} W \quad (5)$$

Assuming thermodynamic equilibrium between the two phases (both at recharge and in the course of gas phase formation at depths) and using the dimensionless expression of the Henry solubility constant  $^i\text{H}_{\text{SOL}}$  ( $\text{mol m}^{-3} \text{ H}_2\text{O}/(\text{mol m}^{-3} \text{ gas})$ , at 1 atm then  $^i\text{C}_{\text{WAT}} = ^i\text{H}_{\text{SOL}} ^i\text{C}_{\text{GAS}}$ . Substituting this into Eq. (5) gives the gas/water ratio under STP conditions:

$$^i\text{G}/^i\text{W} = ^i\text{C}_{\text{ASW}}/^i\text{C}_{\text{GAS}} - ^i\text{H}_{\text{SOL}} \quad (6)$$

$^i\text{G}/^i\text{W}$  ratios, calculated from  $^{36}\text{Ar}$  and  $^{84}\text{Kr}$  concentrations, correlate

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