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(71) **Applicant** *(for all designated States except US)*: **EXXONMOBIL UPSTREAM RESEARCH COMPANY** [US/US]; CORP-URC-SW359, P.O. Box 2189, Houston, TX 77252-2189 (US).

(72) **Inventors; and**
(71) **Applicants** *(for US only)*: **LAWSON, Michael** [GB/US]; 2221 West Dallas St. Apt. 469, Houston, TX 77019 (US). **POTTORF, Robert, J.** [US/US]; 1455 D Springrock Lane, Houston, TX 77055 (US). **DREYFUS, Sebastien, L.** [FR/US]; 1029 Arlington Street, Houston, TX 77008 (US).

(74) **Agents**: **BELL, Annora, A.** et al.; Exxonmobil Upstream Research Company, CORP-URC-SW359, P.O. Box 2189, Houston, TX 77252-2189 (US).

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— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*

— *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

[Continued on next page]

(54) Title: METHOD FOR DETERMINING THE VOLUME OF A SUBSURFACE HYDROCARBON ACCUMULATION PRE-DRILL

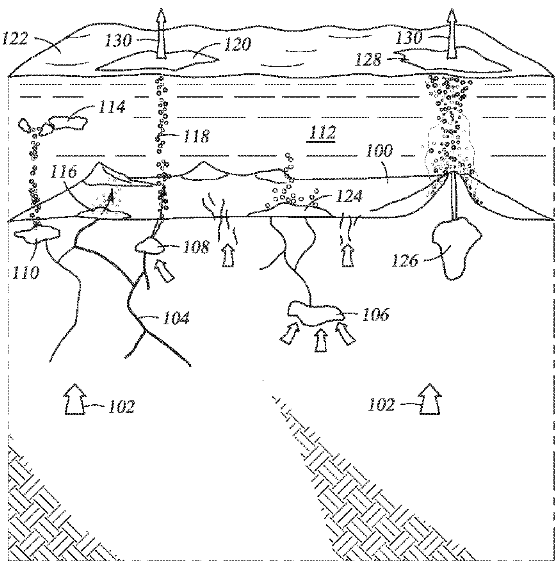

Fig. 1

(57) Abstract: A method is disclosed for determining a type, quality and/or volume of hydrocarbons associated with a subsurface hydrocarbon accumulation from a seeped hydrocarbon sample thereof. An initial concentration of atmospheric noble gases present in formation water in contact with the accumulation is either measured or modeled and modified by accounting for ingrowth of radiogenic noble gases during residence time of the formation water. Concentrations and isotopic ratios of noble gases present in the seep sample are measured and compared to the measured or modified modeled concentrations of the formation water for a plurality of exchange processes. An atmospheric noble gas signature measured in a hydrocarbon phase is compared with the modified concentration of the atmospheric noble gases in the formation water for the plurality of exchange processes. A type, quality, hydrocarbon/water volume ratio, and/or volume of hydrocarbons associated with the subsurface accumulation is determined.

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METHOD FOR DETERMINING THE VOLUME OF A SUBSURFACE HYDROCARBON ACCUMULATION PRE-DRILL

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims the benefit of U.S. Provisional Patent Application 61/616,813 filed March 28, 2012 entitled METHOD FOR DETERMINING THE PRESENCE AND VOLUME OF A SUBSURFACE HYDROCARBON ACCUMULATION, the entirety of which is incorporated by reference herein.

FIELD OF THE INVENTON

[0002] Embodiments of the present disclosure relate generally to the field of geochemistry. More particularly, the present disclosure relates to systems and methods for estimating the volume of subsurface hydrocarbon accumulations pre-drill from the sampling and analysis of seeped hydrocarbons. Furthermore, this present disclosure provides systems capable of determining the type of hydrocarbon present (oil versus (vs.) gas) and quality (density) and de-risking the presence of associated non-hydrocarbon gases in any subsurface hydrocarbon accumulation identified pre-drill through analysis of seeped hydrocarbons.

BACKGROUND

[0003] This section is intended to introduce various aspects of the art, which may be associated with exemplary embodiments of the present disclosure. This discussion is believed to assist in providing a framework to facilitate a better understanding of particular aspects of the disclosed methodologies and techniques. Accordingly, it should be understood that this section should be read in this light, and not necessarily as admissions of prior art.

[0004] The major components required for the presence of subsurface hydrocarbon accumulations in a sedimentary basin are (1) the generation and expulsion of liquid and/or gaseous hydrocarbons from a source rock, (2) migration of hydrocarbons to an accumulation in a reservoir, (3) a trap and a seal to prevent significant leakage of hydrocarbons from the reservoir.

[0005] At present, reflection seismic is the dominant technology for the identification of hydrocarbon accumulations pre-drill. This technique has been successful in identifying structures that may host hydrocarbon accumulations, and in some cases has been used to image the hydrocarbon fluids within subsurface accumulations. However, in some cases this technology lacks the required fidelity to provide an assessment of the volume of subsurface hydrocarbon accumulations due to poor imaging of the subsurface. Additionally, it is challenging to differentiate the types of hydrocarbons from other fluids in the subsurface by remote measurements.

[0006] Current pre-drill non-seismic hydrocarbon detection technologies do not improve the ability to determine the volume and fluid quality/type of subsurface hydrocarbon accumulations. For example, seepage of hydrocarbons at the sea floor or on land provides some indication of a working hydrocarbon system where hydrocarbons have been generated and expulsed during the thermal maturation of a source rock at depth, and have migrated via more or less complex migration pathways to the surface. However, it is difficult from current non-seismic technologies to determine whether such hydrocarbon seepages migrated directly from a source rock or from a hydrocarbon accumulation.

[0007] Furthermore, in the absence of suitable pre-drill reflection seismic data or post-drill measurements of hydrocarbon saturation using geophysical logging tools, there currently exist no additional pre-drill technologies capable of estimating the volume of subsurface hydrocarbon accumulations or technologies capable of determining the type (oil vs. gas) or quality (density) of hydrocarbon present in an accumulation.

[0008] Finally, the presence of non-hydrocarbon gases associated with a hydrocarbon accumulation has significant implications for the economic value of this accumulation. Such non-hydrocarbon gases may include carbon dioxide, nitrogen, noble gases and/or hydrogen sulfide that were generated on or off-structure via various physical and chemical processes. There are no current direct pre-drill methods available to allow for the de-risking of non-hydrocarbon gases.

[0009] As such, there is a need for additional techniques that can more effectively determine the volume and characterize the fluid type and quality of subsurface hydrocarbon accumulations pre-drill. In particular, a relatively inexpensive and rapid pre-drill method for determining the type, quality and volume of a subsurface hydrocarbon accumulation and associated non-hydrocarbon gas is required. This invention provides a valuable tool that may be used in hydrocarbon exploration at various business stage maturity levels, from frontier exploration to extension of proven plays to high-grading prospects within proven plays.

SUMMARY

[0010] In one aspect, a method is disclosed for determining the type, quality and/or volume of a subsurface hydrocarbon accumulation from a seep sample related thereto. An initial concentration of atmospheric noble gases present in formation water in contact with the subsurface hydrocarbon accumulation is measured or modeled. The modeled initial concentration is modified by accounting for ingrowth of radiogenic noble gases during residence time of the formation water. A seep sample related to the subsurface hydrocarbon accumulation is obtained. Concentrations and isotopic ratios of noble gases present in the sample are measured. The measured concentrations and isotopic ratios of the atmospheric noble gases and the radiogenic noble gases present in the sample are compared to the measured/modified modeled concentrations of the formation water for a plurality of exchange processes. An atmospheric noble gas signature measured in the hydrocarbon phase is compared with the measured/modified modeled concentration of the atmospheric noble gases in the formation water for the plurality of exchange processes. At least one of a type of hydrocarbons in the subsurface accumulation, a quality of hydrocarbons in the subsurface accumulation, a hydrocarbon/water volume ratio associated with the subsurface accumulation prior to escape to the surface, and a volume of the subsurface accumulation is determined. In this context, a hydrocarbon/water volume ratio is the volume of hydrocarbon within an accumulation relative to the total volume of water the oil has encountered during emplacement in the accumulation. This may include but is not limited to water in contact with the hydrocarbon accumulation and water present in the reservoir drainage area down dip of the accumulation.

[0011] In another aspect, a method is disclosed for determining a type, quality and volume of a subsurface hydrocarbon accumulation based on analysis of a seep sample related thereto. The sample is analyzed to determine a geochemical signature of the sample. An initial concentration of atmospheric noble gases present in formation water in contact with the subsurface hydrocarbon accumulation is determined. Ingrowth of radiogenic noble gases is modeled to modify the initial concentration for given formation water residence times. A residence time of the formation water is determined. An extent of interaction with a hydrocarbon phase is determined. At least one of a type, quality and hydrocarbon/water volume ratio for a sample associated with a hydrocarbon accumulation is determined. From the hydrocarbon/water volume ratio, the volume of the hydrocarbon accumulation is determined.

[0012] In another aspect, a method is disclosed for determining a type, quality and volume of a subsurface hydrocarbon accumulation from a seeped hydrocarbon sample thereof. An initial concentration of atmospheric noble gases in formation water and for a sample of a hydrocarbon phase in contact with a formation water is determined. A range of expected concentrations of atmospheric and radiogenic noble gases present in the sample is modeled for a range of residence times and for various extents of interaction between formation water and a hydrocarbon phase. Concentrations and isotopic ratios of noble gases present in the sample are measured. The measured noble gas concentrations are compared with the modeled range of expected concentrations of atmospheric and radiogenic noble gases. From the measured noble gas concentrations and the modeled range of expected concentrations of atmospheric and radiogenic noble gases, the type and quality of hydrocarbons in the subsurface accumulation and the hydrocarbon/formation water volume ratio of the subsurface accumulation are estimated. The estimated type and quality of hydrocarbons in the subsurface accumulation and the hydrocarbon/formation water volume ratio associated with the subsurface accumulation are integrated with seismic reflection constraints on a volume of water, thereby determining the volume of the subsurface hydrocarbon accumulation.

[0013] In still another aspect, a system is disclosed for determining a type, quality and volume of a subsurface hydrocarbon accumulation from a hydrocarbon seep sample thereof. The system includes a processor and a tangible, machine-readable storage medium that stores machine-readable instructions for execution by the processor. The machine-readable instructions include code for determining expected concentrations of noble gases present in formation waters pre-hydrocarbon charge, code for measuring concentrations of noble gases present in the seep sample, code for comparing the measured concentrations of noble gases with the modeled concentrations of noble gases expected in the pre-hydrocarbon charge formation waters accounting for one or more exchange and fractionation processes between formation water and the hydrocarbon phase, code for determining, using said comparison, the type and quality of hydrocarbons present in the subsurface accumulation, code for determining, using said comparison, the hydrocarbon/water volume ratio associated with the accumulation of interest, and code for determining, using said comparison and integration with reflection seismic constraints on water volume, the volume and location of hydrocarbons present in a subsurface accumulation.

[0014] In still another aspect, A computer program product having computer executable logic recorded on a tangible, machine readable medium, the computer program product comprising: code for determining expected concentrations of noble gases present in formation waters pre-hydrocarbon charge, code for measuring concentrations of noble gases present in the seep sample, code for comparing the measured concentrations of noble gases with the modeled concentrations of noble gases expected in the pre-hydrocarbon charge formation waters accounting for one or more exchange and fractionation processes between formation water and the hydrocarbon phase, code for determining, using said comparison, the type and quality of hydrocarbons present in the subsurface accumulation, code for determining, using said comparison, the hydrocarbon/water volume ratio associated with the accumulation of interest, and code for determining, using said comparison and integration with reflection seismic constraints on water volume, the volume and location of hydrocarbons present in a subsurface accumulation.

[0015] In yet another aspect, the method of producing hydrocarbons is described. The method may include: determining a type, quality and/or volume of a subsurface hydrocarbon accumulation from a seeped hydrocarbon sample thereof, wherein the determining includes modeling an initial concentration of atmospheric noble gases present in formation water in contact with a subsurface hydrocarbon accumulation, modifying the modeled initial concentration by accounting for ingrowth of radiogenic noble gases during residence time of the formation water, obtaining a hydrocarbon sample from a seep, measuring concentrations and isotopic ratios of atmospheric, mantle derived and radiogenic noble gases present in the hydrocarbon sample, comparing the measured concentrations and isotopic ratios of the atmospheric noble gases and the radiogenic noble gases present in the hydrocarbon sample to the modified modeled concentrations of the formation water for a plurality of exchange processes, determining at least one of a type of hydrocarbons in the subsurface accumulation, a quality of hydrocarbons in the subsurface accumulation, a hydrocarbon/water volume ratio in the subsurface accumulation prior to escape to the surface, and a volume of the subsurface accumulation; and producing hydrocarbons using at least one of the determined type, quality, volume ratio, and volume of the subsurface accumulation.

[0016] These and other features and advantages of the present disclosure will be readily apparent upon consideration of the following description in conjunction with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0017] Advantages of the present techniques may become apparent upon reviewing the following detailed description and the accompanying drawings in which:

Figure 1 is a side elevational view of a seafloor;

Figure 2 is a flow diagram of a method in accordance with disclosed methodologies and techniques;

Figure 3 is a block diagram of a computer system according to disclosed methodologies and techniques;

Figure 4 is a block diagram representing machine-readable instructions according to disclosed methodologies and techniques;

Figure 5 is a side elevational view of a hydrocarbon reservoir; and

Figure 6 is a flowchart of a method according to disclosed methodologies and techniques.

DETAILED DESCRIPTION

[0018] Various terms as used herein are defined below. To the extent a term used in a claim is not defined below, it should be given the definition persons in the pertinent art have given that term in the context in which it is used.

[0019] As used herein, “a” or “an” entity refers to one or more of that entity. As such, the terms “a” (or “an”), “one or more”, and “at least one” can be used interchangeably herein unless a limit is specifically stated.

[0020] As used herein, the terms "comprising," "comprises," "comprise," “comprised,” "containing," "contains," "contain," "having," "has," "have," "including," "includes," and "include" are open-ended transition terms used to transition from a subject recited before the term to one or more elements recited after the term, where the element or elements listed after the transition term are not necessarily the only elements that make up the subject.

[0021] As used herein, “exemplary” means exclusively “serving as an example, instance, or illustration.” Any embodiment described herein as exemplary is not to be construed as preferred or advantageous over other embodiments.

[0022] As used herein “hydrocarbons” are generally defined as molecules formed primarily of carbon and hydrogen atoms such as oil and natural gas. Hydrocarbons may also include other elements or compounds, such as, but not limited to, halogens, metallic elements, nitrogen, oxygen, sulfur, hydrogen sulfide (H_2S) and carbon dioxide (CO_2).

Hydrocarbons may be produced from hydrocarbon reservoirs through wells penetrating a hydrocarbon containing formation. Hydrocarbons derived from a hydrocarbon reservoir may include, but are not limited to, petroleum, kerogen, bitumen, pyrobitumen, asphaltenes, tars, oils, natural gas, or combinations thereof. Hydrocarbons may be located within or adjacent to mineral matrices within the earth, termed reservoirs. Matrices may include, but are not limited to, sedimentary rock, sands, silicates, carbonates, diatomites, and other porous media.

[0023] As used herein, “hydrocarbon production” or “producing hydrocarbons” refers to any activity associated with extracting hydrocarbons from a well or other opening. Hydrocarbon production normally refers to any activity conducted in or on the well after the well is completed. Accordingly, hydrocarbon production or extraction includes not only primary hydrocarbon extraction but also secondary and tertiary production techniques, such as injection of gas or liquid for increasing drive pressure, mobilizing the hydrocarbon or treating by, for example chemicals or hydraulic fracturing the wellbore to promote increased flow, well servicing, well logging, and other well and wellbore treatments.

[0024] As used herein the term “noble gases” refers to a series of chemically inert elements that exhibit similar properties. The six noble gases that occur naturally are helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe) and radon (Rn). The noble gases considered in this disclosure are He, Ne, Ar, Kr and Xe.

[0025] As used herein the term “isotope” refers to one of two or more atoms with the same atomic number but with different numbers of neutrons. Each element of the noble gases has at least two isotopes. For example, helium can be present as one of two stable isotopes: ^{3}He, which has 2 protons and 1 neutron (shown herein as ^{3}He); and, ^{4}He, which has 2 protons and 2 neutrons.

[0026] As used herein the term "signatures” refers to the relative abundances, concentrations and/or ratios of various elements and isotopes of a given species.

[0027] As used herein the term “formation water” refers to any water that resides within the subsurface that may be present in a reservoir rock including water in the porous media within the accumulation or immediately below, but in contact with the hydrocarbon accumulation (e.g., the water leg). This may derive from a) meteoric origin, b) recharge of surface waters, such as rain water or seawater, that then migrates through permeable rock within the subsurface, and/or c) water trapped in the sediment during burial and remaining in place.

[0028] As used herein the term “residence time” refers to the time period that formation water has been present within the subsurface, and can be considered the age of the formation water.

[0029] As used herein the term “radiogenic” refers to generation or creation of a substance through radioactive decay of another substance. Radiogenic noble gases include ^{4}He, ^{21}Ne, ^{40}Ar, ^{82}Kr, ^{86}Kr, ^{129}Xe, ^{130}Xe and ^{136}Xe.

[0030] As used herein the term “thermogenic” refers to hydrocarbons generated from kerogen that is currently/has in the past been subjected to high temperature and pressure.

[0031] As used herein the term “de-risk” refers to an assessment of the possibility that undesirable species such as H_2S, CO_2 are present at concentrations that makes production or refining of hydrocarbons more difficult or reduce the value of produced hydrocarbons.

[0032] As used herein, the term "computer component" refers to a computer-related entity, either hardware, firmware, software, a combination thereof, or software in execution. For example, a computer component can be, but is not limited to being, a process running on a processor, a processor, an object, an executable, a thread of execution, a program, and/or a computer. One or more computer components can reside within a process and/or thread of execution and a computer component can be localized on one computer and/or distributed between two or more computers.

[0033] As used herein, the terms "computer-readable medium” or “tangible machine-readable medium” refer to any tangible storage that participates in providing instructions to a processor for execution. Such a medium may take many forms, including but not limited to, non-volatile media, and volatile media. Non-volatile media includes, for example, NVRAM, or magnetic or optical disks. Volatile media includes dynamic memory, such as main memory. Computer-readable media may include, for example, a floppy disk, a flexible disk, hard disk, magnetic tape, or any other magnetic medium, magneto-optical medium, a CD-ROM, any other optical medium, a RAM, a PROM, and EPROM, a FLASH-EPROM, a solid state medium like a holographic memory, a memory card, or any other memory chip or cartridge, or any other physical medium from which a computer can read. When the computer-readable media is configured as a database, it is to be understood that the database may be any type of database, such as relational, hierarchical, object-oriented, and/or the like. Accordingly, exemplary embodiments of the present techniques may be considered to include a tangible storage medium or tangible distribution medium and prior art-recognized equivalents and successor media, in which the software implementations embodying the present techniques are stored.

[0034] Some portions of the detailed description which follows are presented in terms of procedures, steps, logic blocks, processing and other symbolic representations of operations on data bits within a computer memory. These descriptions and representations are the means used by those skilled in the data processing arts to most effectively convey the substance of their work to others skilled in the art. In the present application, a procedure, step, logic block, process, or the like, is conceived to be a self-consistent sequence of steps or instructions leading to a desired result. The steps are those requiring physical manipulations of physical quantities. Usually, although not necessarily, these quantities take the form of electrical or magnetic signals capable of being stored, transferred, combined, compared, and otherwise manipulated in a computer system.

[0035] It should be borne in mind, however, that all of these and similar terms are to be associated with the appropriate physical quantities and are merely convenient labels applied to these quantities. Unless specifically stated otherwise as apparent from the following discussions, it is appreciated that throughout the present application, discussions using the terms such as “modeling”, “modifying”, “measuring”, “comparing”, “determining”, “analyzing”, “outputting”, “displaying”, “estimating”, “integrating”, or the like, refer to the action and processes of a computer system, or similar electronic computing device, that transforms data represented as physical (electronic) quantities within the computer system's registers and memories into other data similarly represented as physical quantities within the computer system memories or registers or other such information storage, transmission or display devices. Example methods may be better appreciated with reference to flow diagrams.

[0036] While for purposes of simplicity of explanation, the illustrated methodologies are shown and described as a series of blocks, it is to be appreciated that the methodologies are not limited by the order of the blocks, as some blocks can occur in different orders and/or concurrently with other blocks from that shown and described. Moreover, less than all the illustrated blocks may be required to implement an example methodology. Blocks may be combined or separated into multiple components. Furthermore, additional and/or alternative methodologies can employ additional, not illustrated blocks. While the figures illustrate various serially occurring actions, it is to be appreciated that various actions could occur concurrently, substantially in parallel, and/or at substantially different points in time.

[0037] In the following section, specific embodiments of the disclosed methodologies and techniques are described in connection with disclosed aspects and techniques. However, to the extent that the following description is specific to a particular aspect, technique, or a particular use, this is intended to be for exemplary purposes only and is not limited to the disclosed aspects and techniques described below, but rather include all alternatives, modifications, and equivalents falling within the scope of the appended claims.

[0038] According to disclosed aspects and methodologies, a system and method are provided for estimating/determining the hydrocarbon (gas or oil) / water volume ratio from analysis of hydrocarbon and/or gas samples.

[0039] According to disclosed aspects and methodologies, a method of determining a type, quality and volume of a subsurface hydrocarbon accumulation from a sample of naturally occurring substance is disclosed. The sample includes any seep sample. According to the method, an initial concentration of atmospheric noble gases present in formation water in contact with a subsurface hydrocarbon accumulation is either (i) measured when a formation water sample can be obtained from the location of the accumulation or within close proximity to the sampled location, or (ii) modeled to reflect the salinity of the fluid and temperature of exchange during recharge / exchange with the atmosphere. The ingrowth of radiogenic noble gases then modifies this initial composition reflecting the formation water residence time. A sample is collected from a hydrocarbon seep. The concentration and isotopic ratios of the noble gases present in a hydrocarbon sample collected from a seep is measured. The measured concentrations and isotopic ratios of atmospheric and radiogenic noble gases present in the sample are compared to the measured/modeled concentrations of the formation water for different exchange processes. The exchange of atmospheric and radiogenic noble gases between formation water and both the oil and/or gaseous hydrocarbon phase can occur through various processes. These processes can be modeled and may comprise (i) known equilibrium solubility laws that reflect in reservoir conditions, in particular reservoir temperature, pressure, formation water salinity and oil density, (ii) Rayleigh style fractionation to represent the de-gassing of an oil phase, and/or (iii) gas stripping to represent enrichment in the gas phase. The atmospheric noble gas signature measured in the hydrocarbon phase is compared with the modeled concentration of atmospheric noble gases in formation water for various exchange processes. The type, quality and hydrocarbon/water volume ratio in the subsurface accumulation prior to escape to the surface is determined. A volume of the subsurface accumulation is determined.

[0040] Also according to disclosed methodologies and techniques, a method of determining the type, quality and volume of a subsurface hydrocarbon accumulation is provided. According to the method, a hydrocarbon sample is obtained from a seep. The hydrocarbon sample is analyzed to determine its geochemical signature. The analyzing includes measuring the concentrations of noble gases co-transported with the hydrocarbon species present in the seep sample. An initial concentration of atmospheric noble gases present in formation water in contact with a subsurface hydrocarbon accumulation is determined. The ingrowth of radiogenic noble gases is modeled to modify this initial composition for given formation water residence times. A residence time of the formation water and extent of interaction with the hydrocarbon phase is determined. A type, quality and hydrocarbon/water volume ratio is determined for the accumulation associated with the hydrocarbon seep sample. From the hydrocarbon/water volume ratio, the volume of the hydrocarbon accumulation is determined.

[0041] According to methodologies and techniques disclosed herein, a method is provided for determining a type, quality and volume of a subsurface hydrocarbon accumulation from a sample of naturally occurring substance. According to the method, the initial concentration of atmospheric noble gases present alongside a hydrocarbon species is determined. A range of expected concentrations of atmospheric and radiogenic noble gases present in the sample is modeled for a range of residence times and for various extents of interaction between the formation water and hydrocarbon phase. The concentrations and isotopic ratios of noble gases present in the seep sample are measured. The measured noble gas signature is compared with the modeled concentrations of noble gases. From the measured noble gas signature and modeled formation water signature, the type and quality of hydrocarbon is estimated and the hydrocarbon/formation water volume ratio of the subsurface accumulation is estimated. The integration of this with seismic reflection constraints on the volume of the hydrocarbon field and volume of water present in said field thereby allows determination of the location and volume of hydrocarbon present in a subsurface accumulation.

[0042] According to disclosed methodologies and techniques, A computer system is provided that is configured to determine a type, quality and volume of a subsurface hydrocarbon accumulation from a seep sample of naturally occurring substance. The computer system includes a processor and a tangible, machine-readable storage medium that stores machine-readable instructions for execution by the processor. The machine-readable instructions include: code for determining the expected concentrations of noble gases present in formation waters; code for measuring the concentration of noble gases present in the sample; code for modeling various exchange and fractionation processes that may include but is not restricted to solubility equilibrium, Rayleigh fractionation or gas stripping models, the expected concentrations and/or isotopic ratios of noble gases present in the sample; code for comparing the measured concentration or isotopic ratios of noble gases with the modeled concentration and isotopic ratios of noble gases of formation waters for a plurality of exchange processes; code for determining, using said comparison, the type and quality of hydrocarbons present and the hydrocarbon/formation water volume ratio of the subsurface accumulation is estimated. The integration of this with seismic reflection constraints on the volume of the hydrocarbon field and volume of water present in said field thereby allows determination of the location and volume of hydrocarbon present in a subsurface accumulation.

[0043] According to aspects of the disclosed methodologies and techniques, the noble gas signature of hydrocarbons and/or water can be used to (i) determine the type, quality and hydrocarbon/water volume ratio of a subsurface hydrocarbon accumulation, (ii) through integration with other isotopic and molecular geochemistry techniques, de-risk the presence of non-hydrocarbon gases associated with a subsurface hydrocarbon accumulation, and (iii) place constraints on the age of hydrocarbon accumulations in the subsurface. With further integration with conventional geophysical techniques such as seismic reflection, the precise location and volume of the subsurface hydrocarbon accumulation can be determined within the subsurface.

[0044] The methodologies and techniques disclosed herein are based on the fundamental concept that noble gases provide a conservative record of the presence, interaction and origin of fluids with which they come into contact. Various processes in the early earth's history resulted in the formation of three regions - the earth's atmosphere, its crust and its mantle – that are distinct in both their isotopic composition and relative elemental abundance patterns, as noted above. As a result, fluids or gases that originate from these different sources carry a resolvable fingerprint.

[0045] In the context of oil and gas exploration, these properties mean that the relative abundances and isotopic ratios of noble gases may be modified in a system with multiple fluids, and this is particularly evident in oil-water, gas-water or gas-oil-water systems. This is because when two or more fluids interact, the physical chemistry of the noble gases results in the exchange, or partitioning, of noble gases between the fluids. Natural gases and oils are initially devoid of noble gases, but can acquire them following interaction with formation water (*See, e.g.*, Bosch, A., and Mazor, E. Natural Gas Association with water and oil as depicted by atmospheric noble gases: case studies from the southeastern Mediterranean Coastal Plain. *Earth and Planetary Science Letters*, **87**, 338-346, 1988). The impact of this interaction on isotopic ratios and absolute concentrations of noble gases is a function of only three variables: (i) the initial concentration and isotopic signature of noble gases in the water phase, (ii) the solubility of noble gases in water and oil, and (iii) the ratio of the volumes of oil/water, gas/water or gas/oil/water. The noble gas signature of produced hydrocarbons has been used previously to determine the hydrocarbon/water volume ratio for oil-water systems (*See, e.g.*, Ballentine, C.J., O'Nions, R.K., Coleman, M.L. A Magnus Opus: Helium, neon, and argon isotopes in a North Sea oilfield. *Geochemica et Cosmochimica Acta*, **60**(5), 831-849, 1996; Bosch, A., and Mazor, E. Natural Gas Association with water and oil as depicted by atmospheric noble gases: case studies from the southeastern Mediterranean Coastal Plain. *Earth and Planetary Science Letters*, **87**, 338-346, 1988; Pinti, D.L. and Marty, B. Noble gases in crude oils from the Paris Basin: Implications for the origin of fluids and constraints on oil-was-gas-interactions. *Geochemica et Cosmochimica Acta*, **59**(16), 3389-3404, 1995) and gas-water systems (Bosch, A., and Mazor, E. Natural Gas Association with water and oil as depicted by atmospheric noble gases: case studies from the southeastern Mediterranean Coastal Plain. *Earth and Planetary Science Letters*, **87**, 338-346, 1988; Zaikowski, A., and Spangler, R.R. Noble gas and methane partitioning from ground water: An aid to natural gas exploration and reservoir evaluation. *Geology*, 18, 72-74, 1990; Zartman, R.E., Wasserburg, G.J., and Reynolds, J.H. Helium, argon, and carbon in some natural gases. *Journal of geophysical research*, **66**(1), 227-306, 1961).

[0046] In addition to the determination of hydrocarbon/water volume ratios from noble gas signatures of produced hydrocarbons, noble gases have also been utilized to identify the presence of a subsurface accumulation through the sampling of hydrocarbon seeps. This derives from the fact that hydrocarbons that migrate directly from a source rock to a seep have a shorted residence in the subsurface than hydrocarbons that migrate from a subsurface accumulation to a seep (*See, e.g.,* Battani, A., Prinzhofer, A., Deville, E., Ballentine, C.J. Trinidad Mud Volcanoes: The origin of the gas. *Shale Tectonics: AAPG Bulletin Memoir*, **93**, 225-238 2010). This difference in residence time of the hydrocarbons is identified through comparison of their radiogenic noble gas concentrations. While the initial concentration and isotopic signature of noble gases in water can be accurately measured or modeled, the solubility of noble gases is well known. The solubility of noble gases in water for a range of different temperatures has been determined (*See e.g.,* Crovetto, R., Fernandez-Prini, R., Japas, M.L. Solubilities of inert gases and methane in H_2O and D_2O in the temperature range of 300 to 600 K. *The Journal of Chemical Physics*, **76**, 1077-1086, 1982; Smith, S.P. Noble gas solubilities in water at high temperature. *EOS Transactions of the American Geophysical Union*, **66,** 397, 1985), whilst the solubility of noble gases in oils of two different densities and composition (or quality) has also been determined (*See, e.g.,* Kharaka, Y.K. and Specht, D.K. The solubility of noble gases in crude oil at 25-100°C. *Applied Geochemistry*, **3**, 137-144, 1988). The interaction of water with oil and/or natural gas results in predictable, but very different, isotopic and elemental fractionation patterns in both the water and oil/natural gas phases. The different signatures that arise as a result of this interaction have previously been investigated in produced hydrocarbons from a wellbore to determine the type of hydrocarbon present within the subsurface (*See, e.g.,* Bosch, A., and Mazor, E. Natural Gas Association with water and oil as depicted by atmospheric noble gases: case studies from the southeastern Mediterranean Coastal Plain. *Earth and Planetary Science Letters*, **87**, 338-346, 1988; also cited in Pinti, and Ballentine, C.J., Burgess, R., and Marty, B. Tracing fluid origin, transport and interaction in the crust. In: *Reviews in Mineralogy and Geochemistry*, **47**, 2002 and references therein).

[0047] In this disclosure, a method is provided to analyze seeped hydrocarbons for hydrocarbon exploration. Based on the fractionation pattern, it is therefore possible to determine the hydrocarbon phases that interacted (e.g. water with oil and/or natural gas) from the analysis of hydrocarbons that have escaped from a subsurface accumulation to a seep. The noble gases therefore provide a conservative tracer of the hydrocarbon type present within the subsurface (oil vs. gas). If the hydrocarbon phase is determined to be oil, it is possible to estimate the quality of the oil phase based on traditional molecular geochemical indicators of source facies and maturity. Given that two of the three variables that control the exchange of noble gases between water and hydrocarbons is known or can be modeled, it is now possible to place constraints on the hydrocarbon/water volume ratio within the system from the noble gas signature of seeped hydrocarbons. If constraints on the oil quality cannot be determined, constraints can be placed on hydrocarbon/water volume ratios for a range of hydrocarbon qualities. As a result of this aspect, it is possible to quantitatively predict the volume of hydrocarbon present within a subsurface accumulation.

[0048] Figure 1 is a diagram illustrating the numerous subsurface sources and migration pathways of hydrocarbons present at or escaping from seeps on the ocean floor 100. Hydrocarbons 102 generated at source rock (not shown) migrate upward through faults and fractures 104. The migrating hydrocarbons may be trapped in reservoir rock and form a hydrocarbon accumulation such as a gas 106, oil and gas 108, or a gas hydrate accumulation 110. Hydrocarbons seeping from the gas hydrate accumulation may dissolve into methane in the ocean 112 as shown at 114, or may remain as a gas hydrate on the ocean floor 100 as shown at 116. Alternatively, oil or gas from oil/gas reservoir 108 may seep into the ocean, as shown at 118, and form an oil slick 120 on the ocean surface 122. A bacterial mat 124 may form at a gas seep location, leaking from gas reservoir 106, and may generate biogenic hydrocarbon gases while degrading thermogenic wet gas. Still another process of hydrocarbon seepage is via a mud volcano 126, which can form an oil slick 128 on the ocean surface. Oil slicks 120 and 128 or methane gas 130 emitted therefrom are signs of hydrocarbon seepage that are, in turn, signs of possible subsurface hydrocarbon accumulation. The signatures measured from each of these seeps may be interrogated according to disclosed methodologies and techniques herein to discriminate between the different origins of hydrocarbons encountered at these seeps. In particular, methodologies and techniques disclosed herein discriminate between hydrocarbons that have migrated directly to the surface without encountering a trap within which they can be accumulated (source 1) and hydrocarbons that have leaked from a subsurface accumulation (source 2). If the presence and volume of such a hydrocarbon accumulation can be identified, it is possible the hydrocarbons from such an accumulation can be extracted.

[0049] Figure 2 depicts a flow diagram of a method 200 for determining from a seep sample the (i) type, (ii) quality and volume of a subsurface hydrocarbon accumulation, (iii) constraints on the residence time of the associated hydrocarbon, and (iv) the risk of encountering significant non-hydrocarbon gases in the associated accumulation. A sample can comprise any surface seep sample. According to the method, at block 202 the concentration and isotopic signature of noble gases in formation water is measured, modeled or otherwise determined. The isotopic signature can be modeled by making assumptions, at time of reservoir rock deposition, for the salinity of the fluid during dissolution of noble gases from the atmosphere to the water phase and the temperature of exchange. The modeling method of block 202 incorporates two linked algorithms. The first of these algorithms models the initial concentration of noble gases for any given temperature and water salinity. The initial concentration of noble gases in the water phase prior to interaction with any hydrocarbons can be estimated because noble gases dissolve in water during recharge from meteoric waters or at the air/water boundary for seawater. This initial signature is therefore dominated by atmospheric noble gases, namely ^{20}Ne, ^{36}Ar, ^{84}Kr and ^{132}Xe. The amount of noble gases that dissolve into the water phase obeys Henry's Law, which states that the amount of noble gases dissolved in water is proportional to the partial pressure of the noble gases in the atmosphere (which varies as a function of altitude for meteoric water recharge). The Henry's constant is directly related to the salinity of the water phase and the ambient temperature during the transfer of noble gases to the water. Formation waters recharged from meteoric waters at the air/soil interface may have an additional component of atmospheric derived noble gases from that which are expected purely from equilibrium, "excess air", which displays some fractionation to increased concentrations of heavier noble gases relative to the light noble gases (*See, e.g.,* Heaton, T.H.E and Vogel, J.C. 'Excess air' in groundwater. *Journal of Hydrology*, 50, 201-216, 1981. 1981). However, correction schemes are available to account for this (e.g. Aeschbach-Hertig, W., Peeters, F., Beyerle, U., Kipfer, R. Palaeotemperature reconstruction from noble gases in ground water taking into account equilibrium with entrapped air. Nature, 405, 1040-1044, 2000), and can be applied to models of initial formation water compositions. The resulting signature therefore lies between air-saturated water (ASW), air-saturated seawater (ASS) and air-saturated brine (ASB) for any given temperature. The second algorithm is used to model the ingrowth and accumulation of radiogenic noble gases produced by the radioactive decay of crustal minerals into the formation water. The concentration of the radiogenic noble gases typically increases with increasing formation water residence time (or age). This process results in an evolution in the isotopic ratios of noble gases within the formation water, in particular the ^{3}He/^{4}He and ^{40}Ar/^{36}Ar ratios, towards more "crustal" signatures. This evolving noble gas signature in the water phase now only significantly changes as a result of mixing and interaction with other fluids.

[0050] Returning to Figure 2, at block 204, the absolute abundance of each isotope of each of the noble gases present in the seep sample is measured. This may include measuring the concentrations and isotopic ratios of each of the noble gases. The sample of interest may comprise water, oil, natural gas, sediments or other type of rock, or fluids present in sediments, pores, or trapped in fluid inclusions. The sampling methods used to collect the samples of interest include gravity or piston drop core sampling, the use of manned submersibles or remotely operated vehicles (ROV's) with coring sampling devices, and gas sampling apparatus (including pinch of valves and sombreros). Noble gas isotopes may also be sampled and measured within the water, oil, gas, or gas fluid inclusions trapped within cements of the reservoir rocks. The temperature and water salinity of the inclusions at the time of trapping can be determined through microthermometry. This information, when combined with a burial history model for the reservoir rock, provides a mechanism to determine the time of inclusion trapping. If water inclusions and oil or gas inclusions are trapped at the same time, the pressure at the time of trapping can also be estimated (*See, e.g.,* Narr, W.M. and Burruss, R.C. Origin of reservoir fractures in Little Knife Field, North Dakota. *American Association of Petroleum Geologists Bulletin*, 68, 1087-1100, 1984).

Similarly, the methane peak shift from Raman analysis of water or gas inclusions is another technique that measures trapping pressure. Combining these techniques, the isotopic composition of noble gases and their evolution through time as a function of temperature and pressure can be determined. These measurements serve to constrain modeled processes whereby noble gases are partitioned between water, oil and gas. Measurement of the abundance of each isotope can be conducted following standard extraction techniques using mass spectrometry.

[0051] At block 206 the measured concentrations and isotopic ratios of noble gases in the seep sample of interest is compared with the previously determined (e.g., modeled) noble gas concentrations and isotopic ratios of the formation water considering a variety of different exchange processes. The exchange of atmospheric noble gases between formation water and both the oil and/or gaseous hydrocarbon phase can occur through various processes, and the extent of fractionation induced by each of these processes give rise to different signatures in the different phases. These processes can be modeled and may comprise equilibrium solubility, Rayleigh style fractionation and gas stripping. During equilibrium solubility partitioning, interaction of an oil phase with water results in the oil phase developing an enrichment –e.g., an increase – in the ratio of ^{84}Kr and ^{132}Xe to ^{36}Ar (^{84}Kr/^{36}Ar and ^{132}Xe/^{36}Ar) and depletion – e.g., a decrease – in the ^{20}Ne to ^{36}Ar ratio (^{20}Ne/^{36}Ar) relative to an air-saturated water phase. This is because of the greater solubility of the heavier noble gases in oil than in water. In contrast, the interaction of a gas phase with water results in the gas phase becoming relatively enriched in the lighter noble gases (e.g., ^{20}Ne/^{36}Ar) relative to the air-saturated water phase signature and depleted in the ratios of the heavier noble gases (^{84}Kr/^{36}Ar and ^{132}Xe/^{36}Ar). The magnitude of this fractionation changes depending upon the exchange process operating during partitioning of the noble gases between the different phases and also on the density of the oil phase for oil-water partitioning. The solubility of noble gases increases with decreasing oil density (or increasing API gravity). A gas phase that exsolves from oil during migration from a source rock/accumulation in the subsurface preserves the noble gas signature of the oil phase (Ballentine, C.J., O'Nions, R.K., Coleman, M.L. A Magnus Opus: Helium, neon, and argon isotopes in a North Sea oilfield. *Geochemica et Cosmochimica Acta*, **60**(5), 831-849, 1996). These signatures are preserved and therefore provide a conservative tracer of which hydrocarbon phase(s) underwent exchange in the subsurface (oil-water, gas-water or gas-oil-water). Knowledge of the solubility of noble gases as a function of oil density further allows an estimate to be made of the oil quality when the hydrocarbon present is determined to be oil.

[0052] The following are examples of some of the different noble gas signatures that may arise in water, oil and gas as a result of different exchange processes following interaction of fluids in the subsurface.

[0053] The first example is a two phase system with only thermogenic gas and formation water whose noble gas signatures approach equilibrium following the equilibrium solubility model. The presence of a thermogenic gas accumulation result in predictable changes in both the formation water and gas phase noble gas signatures.

[0054] The solubility of noble gases is proportional to their mass, with lighter noble gases being less soluble than heavier noble gases. As such, any formation water sampled from a seep that has interacted with a subsurface gas accumulation should display a characteristic noble gas elemental fractionation pattern that is depleted in Ne relative to Ar and enriched in Kr and Xe relative to Ar, which indicates phase interaction with thermogenic gas. The extent of this fractionation depends on the gas/water volume ratio. With increasing gas/water volume ratio, the ^{20}Ne/^{36}Ar ratio of the water phase decreases from an initial formation water composition, that plots between either ASW or ASB for any given temperature and pressure, along a trajectory of decreasing atmospheric noble gas content (given by increasing 1/^{36}Ar in Zaikowski and Spangler, 1990, for example). Addition of atmosphere to the water (through excess air contributions during recharge for example) results in an evolution in the noble gas signature of the formation water to increasing values of Ne/^{36}Ar.

[0055] Samples of thermogenic gas can be obtained routinely from seeps and preserve a noble gas signature indicative of phase interaction within a subsurface accumulation. Thermogenic gas in contact with formation water that follows the equilibrium solubility model results in the exchange of noble gases from the water phase to the gas phase, and produces a signature that is enriched in the light (less soluble) noble gases He and Ne and relatively depleted in the heavier (more soluble) noble gases Kr and Xe. The extent of this fractionation is again controlled by the gas/water volume ratio that prevails within the subsurface. Placing constraints on the volume of water present within the subsurface formation allows quantitative volume estimates to be placed on the associated subsurface thermogenic gas accumulation.

[0056] Given that the noble gas signature of formation water can be estimated and thermogenic gas may be devoid initially of noble gases, the equilibrium partitioning of noble gases following gas-water exchange can be described by the following equation (e1):

$$V_{water}(i/^{36}Ar)^{AS(W/B)} = V_{water}(i/^{36}Ar)^{w} + V_{gas}(i/^{36}Ar)^{g} \qquad (e1)$$

where V_{water} is the volume of water, V_{gas} is the volume of gas, i is Ne, Kr or Xe, AS(W/B) is air-saturated water or brine, and ratios superscripted by w and g represent noble gas ratios in the water and gas phases, respectively. This equation (e1) is modified from Ballentine et al. (*See, e.g.,* Ballentine, C.J., O'Nions, R.K., Coleman, M.L. A Magnus Opus: Helium, neon, and argon isotopes in a North Sea oilfield. *Geochemica et Cosmochimica Acta,* **60**(5), 831-849, 1996). The solubility of noble gases at the temperatures and pressures relevant to the location of oil and gas accumulations can be assumed to obey Henry's Law. As such, the equation (e2) is:

$$(i/^{36}Ar)^{g} = (i/^{36}Ar)^{w} \text{ x } (K_i^{w}/K_{Ar}^{w}) \qquad (e2)$$

where K_i^{w} is the Henry's constant for noble gas i in water at a given temperature, pressure, and salinity.

[0057] Combining equations (e1) and (e2), equation (e3) is:

$$(i/^{36}Ar)^{g} = (i/^{36}Ar)^{ASW} \text{ x } [(V_{gas}/V_{water})+1/K_{Ar}^{w}] \,/\, [(V_{gas}/V_{water})+1/K_i^{w}] \qquad (e3)$$

From equation (e3), it can be deduced that, as the gas/water volume ratio increases, the ratio of any noble gas to ^{36}Ar in the gas phase, $(i/^{36}Ar)^{g}$, approaches that of an air-saturated water signature, $(i/^{36}Ar)^{ASW}$. In contrast, if the gas/water volume ratio is small, and as such represents a case where no subsurface accumulation is present, then the ratio of any noble gas to ^{36}Ar in the gas phase, $(i/^{36}Ar)^{g}$, approaches the product of the air-saturated water signature with the Henry's constant for that noble gas relative to argon, $(i/^{36}Ar)^{ASW}.(K_i^{w}/K_{Ar}^{w})$.

[0058] Another example is a two phase system with oil and water. As with the previous example of gas-water interaction, when formation water comes in to contact with an oil phase (which initially is devoid of noble gases), the noble gases partition from the water phase to the oil phase to reflect the differences in solubility of the noble gases in oil compared to water. The extent to which these noble gases partition in to the oil phase again depends on the relative solubility of noble gases in oil and water, the initial concentration of noble gases in the water phase (which can modeled) and the oil/water volume ratio. As such, the equations (e4) and (e5) are:

$$V_{water}(i/^{36}Ar)^{AS(W/B)} = V_{oil}(i/^{36}Ar)^{oil} + V_{water}(i/^{36}Ar)^{w} \qquad (e4)$$

$$(i/^{36}Ar)^{oil}\,(K_i^{oil}/K_{Ar}^{oil}) = (i/^{36}Ar)^{w} \text{ x } (K_i^{w}/K_{Ar}^{w}) \qquad (e5)$$

where V_{oil} is the volume of oil, K_i^{oil} is the Henry's constant for noble gas i in oil, and ratios superscripted by oil represent the noble gas signature or ratio in the oil phase. By combining equations (e4) and (e5), the oil/water volume ratio can then be determined by equation (e6):

$$V_{oil}/V_{water} = (i/^{36}Ar)^{AS(W/B)}/(\, i/^{36}Ar)^{oil} - (K_{Ar}^{oil}/K_{Ar}^{water})/\, (K_i^{oil}/K_i^{water}) \qquad (e6)$$

[0059] As with the previous gas-water exchange, this allows constraints to be placed on the noble gas signature of oils and water that arises as a result of different oil/water volume ratios. As the oil/water volume ratio increases, the ratios of noble gas i to ^{36}Ar in oil, $(i/^{36}Ar)^{oil}$, approaches the ratio of an air-saturated water or brine signature, $(i/^{36}Ar)^{ASW/B}$. In contrast, as the oil/water volume ratio approaches zero (and hence no significant oil accumulation is present) the ratios of noble gas i to ^{36}Ar in oil, approaches the product of the ratio of noble gas i to ^{36}Ar in oil and Henry's constant of noble gas i in oil relative to the Henry's constant in water, $(i/^{36}Ar)^{oil} \times (K^{i}_{oil}/K^{i}_{water})$.

[0060] A third example is where all three phases – gas, oil and water – are present. When phase separation or noble gas exchange between the three phases occurs during interaction under equilibrium conditions, the processes described in equations (e1) to (e6) serves as a structure for a three phase model. In this case, the total atmospheric noble gas inventory initially supplied during exchange with the atmosphere is shared among the three phases and is described by equation (e7):

$$V_{water}(i/^{36}Ar)^{AS(W/B)} = V_{water}(i/^{36}Ar)^{w} + V_{oil}(i/^{36}Ar)^{oil} + V_{gas}(i/^{36}Ar)^{g} \qquad (e7)$$

[0061] In this system, measured concentrations of noble gases in two of the three phases provide a mechanism to calculate oil/water, gas/water and oil/gas volume ratios. Iterative methods, such as the Newton-Raphson method, can use the equations described above to converge on a solution for each volume ratio. The oil/water, gas/water and gas/oil volume ratios calculated from the processes above are integrated with reflection seismic data and calculations of water volume to determine the hydrocarbon volumes present in the subsurface accumulation.

[0062] Returning again to Figure 2, at block 208, the type and/or quality of hydrocarbons in the subsurface accumulation, the hydrocarbon/water volume ratio in the subsurface accumulation prior to escape to the surface, and/or the volume of the subsurface accumulation is determined. Hydrocarbons can then be produced if feasible. As an example, reflection seismic data may be utilized to determine constraints for a volume of water associated with subsurface accumulation. From this constraint and the hydrocarbon/water ratio, a volume of the subsurface accumulation is determined, and more specifically, the volume of hydrocarbons within the subsurface accumulation is determined. As an alternative example, certain regions may have multiple wellbores to subsurface accumulations and have determined hydrocarbon/water volume ratio and the hydrocarbon volume in the subsurface accumulations associated with the wellbores. In these regions, a statistical technique may be utilized to determine a hydrocarbon volume for an accumulation associated with a hydrocarbon seep, which may be based on the hydrocarbon/water volume ratio of the accumulations associated with wellbores within the region.

[0063] Another aspect of disclosed methodologies and techniques is characterizing the non-hydrocarbon gas risk associated with a subsurface hydrocarbon accumulation. The results of previous portions of the method may be integrated with known geochemical and isotopic proxies, such as the isotopic systems of carbon ($\delta^{13}C$), nitrogen ($\delta^{15}N$), or sulfur ($\delta^{34}S$). These traditional isotopic systems provide information on the potential source of these non-hydrocarbon gases, which when considered with concentration data and integrated with the noble gases that further constrain gas origin, place constraints on the origin of the non-hydrocarbon gases that may be present in subsurface accumulations during the early stages (pre-drill) of exploration.

[0064] Yet another aspect of the disclosed methodologies and techniques is to use the radiogenic noble gas concentrations in oils and gases sampled from seeps to place constraints on the residence time of the formation water with which they have been in contact, and thus place constraints on the age of the accumulation and timing of trap presence. This information can be integrated with basin models and used to calibrate timing of trap presence and hydrocarbon migration.

[0065] Still another aspect of the disclosed methodologies and techniques is to use the noble gas signature of waters, oils and gases in fluid inclusions to assess paleo-phase interaction. Noble gas signatures indicative of extensive exchange or partitioning of noble gases from formation water to hydrocarbons, when integrated with conventional fluid inclusion techniques, provide information on the presence of accumulations at the time of trapping that may no longer be present. Such information may be useful in assessments of how a paleo-accumulation has leaked, or provide an indication that an economic accumulation was located in close proximity to that particular location in the past.

[0066] The results of the method 200 may also be integrated with conventional exploration or prospect assessment technologies to confirm or de-risk the presence and/or volume of a hydrocarbon accumulation and to assess potential migration pathways from the source rock to the seep. Such technologies may include reflection seismic, high resolution seismic imaging, acoustic, basin modeling, and/or probabilistic or statistical assessments. By integrating these technologies, various characteristics of the accumulation may be estimated, such as hydrocarbon volume, hydrocarbon type (e.g., oil vs. gas), and the like. Once a hydrocarbon accumulation has been identified and located, the hydrocarbons therein may be extracted or otherwise produced using known principles of hydrocarbon management.

[0067] Figure 3 is a block diagram of a computer system 300 that may be used to perform any of the methods disclosed herein. A central processing unit (CPU) 302 is coupled to system bus 304. The CPU 302 may be any general-purpose CPU, although other types of architectures of CPU 302 (or other components of exemplary system 300) may be used as long as CPU 302 (and other components of system 300) supports the inventive operations as described herein. The CPU 302 may execute the various logical instructions according to disclosed aspects and methodologies. For example, the CPU 302 may execute machine-level instructions for performing processing according to aspects and methodologies disclosed herein.

[0068] The computer system 300 may also include computer components such as a random access memory (RAM) 306, which may be SRAM, DRAM, SDRAM, or the like. The computer system 300 may also include read-only memory (ROM) 308, which may be PROM, EPROM, EEPROM, or the like. RAM 306 and ROM 308 hold user and system data and programs, as is known in the art. The computer system 300 may also include an input/output (I/O) adapter 310, a communications adapter 322, a user interface adapter 324, and a display adapter 318. The I/O adapter 310, the user interface adapter 324, and/or communications adapter 322 may, in certain aspects and techniques, enable a user to interact with computer system 300 in order to input information.

[0069] The I/O adapter 310 preferably connects a storage device(s) 312, such as one or more of hard drive, compact disc (CD) drive, floppy disk drive, tape drive, etc. to computer system 300. The storage device(s) may be used when RAM 306 is insufficient for the memory requirements associated with storing data for operations of embodiments of the present techniques. The data storage of the computer system 300 may be used for storing information and/or other data used or generated as disclosed herein. The communications adapter 322 may couple the computer system 300 to a network (not shown), which may enable information to be input to and/or output from system 300 via the network (for example, the Internet or other wide-area network, a local-area network, a public or private switched telephony network, a wireless network, any combination of the foregoing). User interface adapter 324 couples user input devices, such as a keyboard 328, a pointing device 326, and the like, to computer system 300. The display adapter 318 is driven by the CPU 302 to control, through a display driver 316, the display on a display device 320. Information and/or representations of one or more 2D canvases and one or more 3D windows may be displayed, according to disclosed aspects and methodologies.

[0070] The architecture of system 300 may be varied as desired. For example, any suitable processor-based device may be used, including without limitation personal computers, laptop computers, computer workstations, and multi-processor servers. Moreover, embodiments may be implemented on application specific integrated circuits (ASICs) or very large scale integrated (VLSI) circuits. In fact, persons of ordinary skill in the art may use any number of suitable structures capable of executing logical operations according to the embodiments.

[0071] Figure 4 depicts a representation of machine-readable logic or code 400 that, when executed, performs a method of determining a presence, type, quality, and/or volume of a subsurface hydrocarbon accumulation from a sample related thereto. Code 400 may be used or executed with a computing system such as computing system 300. At block 402, code is provided for determining expected concentrations of noble gases present in formation waters. At block 404, code is provided for measuring concentrations of noble gases present in the hydrocarbon seep sample. At block 406, code is provided for modeling one or more exchange and fractionation processes in the expected concentrations of noble gases present in a hydrocarbon sample taken from a hydrocarbon seep. At block 408, code is provided for comparing the measured concentrations of noble gases with the determined concentrations of noble gases in the formation waters (e.g., modeled concentrations). At block 410, code is provided for determining, using said comparison, a type and a quality of hydrocarbons present in the hydrocarbon sample. At block 412, code is provided for determining, using said comparison, a hydrocarbon/water volume ratio present in the sample. The determination of hydrocarbon volume in the subsurface accumulation through the characterization of a seep sample may be used to decrease the uncertainty of accumulation presence and size provided through reflection seismic technology. That is, the seismic data may be verified by the integration of the determination with the seismic data. Alternatively, a statistical technique may be utilized to determine a hydrocarbon volume for an accumulation associated with a hydrocarbon seep, wherein the hydrocarbon/water volume ratio of the accumulation is associated with wellbores within the region. At block 414 code is provided for determining, using said comparison and constraints provided by reflection seismic on water volume, a volume of a subsurface hydrocarbon accumulation. Alternatively or in addition, this code may be based on statistical technique in other embodiments. Code for effectuating or executing other features of the disclosed aspects and methodologies may be provided as well. This additional code is represented in Figure 4 as block 416, and may be placed at any location within code 400 according to computer code programming techniques.

[0072] Aspects disclosed herein may be used to perform hydrocarbon production activities such as extracting hydrocarbons from a subsurface formation, region, or reservoir, which is indicated by reference number 502 in Figure 5. A method 600 of producing hydrocarbons from subsurface reservoir 502 is shown in Figure 6. At block 602, the volume of hydrocarbons in the subsurface region is predicted according to methodologies and techniques disclosed herein. At block 604 hydrocarbon production is conducted to remove and/or otherwise produce hydrocarbons from the subsurface region, which may be accomplished by drilling a well 504 using oil drilling equipment 506 (Figure 5). Other hydrocarbon management activities may be performed according to known principles.

[0073] Illustrative, non-exclusive examples of methods and products according to the present disclosure are presented in the following non-enumerated paragraphs. It is within the scope of the present disclosure that an individual step of a method recited herein, including in the following enumerated paragraphs, may additionally or alternatively be referred to as a "step for" performing the recited action.

A. A method of determining a type, quality, hydrocarbon/water volume ratio and/or volume of a subsurface hydrocarbon accumulation from a seep sample related thereto, the method comprising:

measuring or modeling an initial concentration of atmospheric noble gases present in formation water in contact with the subsurface hydrocarbon accumulation;

modifying the measured/modeled initial concentration by accounting for ingrowth of radiogenic noble gases during residence time of the formation water;

obtaining a seep sample related to a potential subsurface hydrocarbon accumulation;

measuring concentrations and isotopic ratios of atmospheric noble gases and radiogenic noble gases present in the sample;

comparing the measured concentrations and isotopic ratios of the atmospheric noble gases and the radiogenic noble gases present in the sample to the measured/modified modeled concentrations of the formation water for a plurality of exchange processes;

comparing an atmospheric noble gas signature measured in the hydrocarbon phase with the measured/modified modeled concentration of the atmospheric noble gases in the formation water for the plurality of exchange processes; and

determining at least one of

a type of hydrocarbons in the subsurface accumulation,

a quality of hydrocarbons in the subsurface accumulation, a hydrocarbon/water volume ratio in the subsurface accumulation prior to escape to the surface, and

a volume of the subsurface accumulation.

A1. The method according to paragraph A, wherein the plurality of exchange processes include at least one of

equilibrium solubility laws calibrated to reflect conditions in the subsurface accumulation,

Rayleigh-style fractionation to represent the de-gassing of an oil phase, and

gas stripping to represent enrichment in a gas phase.

A2. The method according to any of paragraphs A-A1, wherein the conditions include at least one of reservoir temperature, pressure, formation water salinity and oil density.

A3. The method according to any of paragraphs A-A2, wherein the noble gases include at least one of helium (He), neon (Ne), argon (Ar), krypton (Kr), and xenon (Xe).

A4. The method according to any of paragraphs A-A3, wherein the isotopic ratios include a ratio of Kr to Ar.

A5. The method according to paragraph A4, wherein the ratio of Kr to Ar is a ratio of ^{84}Kr/^{36}Ar.

A6. The method according to any of paragraphs A-A5, wherein the isotopic ratios include a ratio of Xe to Ar.

A7. The method according to paragraph A6, wherein the ratio of Xe to Ar is a ratio of ^{132}Xe/^{36}Ar.

A8. The method according to any of paragraphs A-A7, wherein the isotopic ratios include a ratio of Ne to Ar.

A9. The method according to paragraph A8, wherein the ratio of krypton to argon is a ratio of ^{20}Ne/^{36}Ar.

A11. The method according to any of paragraphs A-A10, further comprising producing hydrocarbons based on at least one of the determined type, quality, hydrocarbon/water volume ratio, and the volume of the subsurface accumulation.

A12. The method according to any of paragraphs A-A11, wherein the initial concentration is modeled to reflect a salinity of the fluid and temperature of exchange during recharge/exchange with atmosphere.

A13. The method according to any of paragraphs A-A12, wherein the sample comprises one of water, oil, natural gas, sediments, rock, fluids present in sediments, fluids from rock pores, and fluids trapped in fluid inclusions.

A14. The method according to any of paragraphs A-A13, further comprising characterizing non-hydrocarbon gas risk associated with the subsurface hydrocarbon accumulation.

A15. The method according to any of paragraphs A-A14, wherein the determination of hydrocarbon volume in the subsurface accumulation is utilized to lessen uncertainty of accumulation presence and size provided by integrating the determination with seismic measurements.

A16. The method of any one of paragraphs A-A15, wherein the determination of hydrocarbon volume in the subsurface accumulation is based on a comparison to seismic data to provide constraints on the water volume ratio.

A17. The method of one of paragraphs A-A16, wherein the determination of hydrocarbon volume in the subsurface accumulation is based on a statistical technique utilized to determine a hydrocarbon volume for an accumulation associated with a hydrocarbon seep, wherein the hydrocarbon/water volume ratio of the accumulation is associated with wellbores within the region.

B. A method of determining a type, quality and volume of a subsurface hydrocarbon accumulation based on analysis of a sample related thereto, comprising:

analyzing the sample to determine a geochemical signature of the sample;

determining an initial concentration of atmospheric noble gases present in formation water in contact with the subsurface hydrocarbon accumulation.

modeling ingrowth of radiogenic noble gases to modify the initial concentration for given formation water residence times.

determining a residence time of the formation water;

determining an extent of interaction with a hydrocarbon phase;

determining at least one of a type, quality and hydrocarbon/water volume ratio for a sample associated with a hydrocarbon accumulation; and

from the hydrocarbon/water volume ratio, determining the volume of the hydrocarbon accumulation.

B1. The method according to paragraph B, wherein the noble gases include at least one of helium (He), neon (Ne), argon (Ar), krypton (Kr), and xenon (Xe).

B2. The method according to paragraph B1, wherein the isotopic ratios include at least one of ^{84}Kr/^{36}Ar, ^{132}Xe/^{36}Ar, and ^{20}Ne/^{36}Ar.

C. A method for determining a type, quality and volume of a subsurface hydrocarbon accumulation from a hydrocarbon sample thereof, comprising:

determining an initial concentration of atmospheric noble gases present alongside a hydrocarbon species;

modeling a range of expected concentrations of atmospheric and radiogenic noble gases present in the sample for a range of residence times and for various extents of interaction between formation water and a hydrocarbon phase;

measuring concentrations and isotopic ratios of noble gases present in the sample.

comparing the measured noble gas concentrations with the modeled range of expected concentrations of atmospheric and radiogenic noble gases;

estimating, from the measured noble gas concentrations and the modeled range of expected concentrations of atmospheric and radiogenic noble gases, the type and quality of hydrocarbons in the subsurface accumulation and the hydrocarbon/formation water volume ratio of the subsurface accumulation; and

integrating the estimated type and quality of hydrocarbons in the subsurface accumulation and the hydrocarbon/formation water volume ratio of the subsurface accumulation with seismic reflection constraints on a volume of the hydrocarbon accumulation and a volume of water present in the hydrocarbon accumulation, thereby determining the volume of hydrocarbons present in the subsurface accumulation.

C1. The method according to paragraph C, wherein the noble gases include at least one of helium (He), neon (Ne), argon (Ar), krypton (Kr), and xenon (Xe).

C2. The method according to any of paragraphs C-C1, wherein the isotopic ratios include at least one of ^{84}Kr/^{36}Ar, ^{132}Xe/^{36}Ar, and ^{20}Ne/^{36}Ar.

D. A system for determining a type, quality and volume of a subsurface hydrocarbon accumulation from a hydrocarbon sample thereof, the system comprising:

a processor;

a tangible, machine-readable storage medium that stores machine-readable instructions for execution by the processor, wherein the machine-readable instructions include

code for determining expected concentrations of noble gases present in formation waters,

code for measuring concentrations of noble gases present in the seep sample,

code for modeling one or more exchange and fractionation processes in the expected concentrations of noble gases present in the sample,

code for comparing the measured concentrations of noble gases with the modeled concentrations of noble gases in the formation waters,

code for determining, using said comparison, the type and quality of hydrocarbons present in the subsurface.

E. A computer program product having computer executable logic recorded on a tangible, machine readable medium, the computer program product comprising:

code for determining expected concentrations of noble gases present in formation waters,

code for measuring concentrations of noble gases present in the hydrocarbon sample,

code for modeling one or more exchange and fractionation processes in the expected concentrations of noble gases present in a hydrocarbon sample taken from a hydrocarbon seep,

code for comparing the measured concentrations of noble gases with the modeled concentrations of noble gases in the formation waters,

code for determining, using said comparison, a type and a quality of hydrocarbons present in the hydrocarbon sample.

E1. The computer program product or system of one of paragraphs D and E further comprising wherein the computer program product comprises: code for determining hydrocarbon volume in the subsurface accumulation by integrating the determination with seismic measurements.

E2. The computer program product or system of one of paragraphs D and E further comprising wherein the computer program product comprises: code for determining hydrocarbon volume in the subsurface accumulation based on a comparison to seismic data to provide constraints on the water volume ratio.

E3. The computer program product or system of one of paragraphs D and E further comprising wherein the computer program product comprises: code for determining hydrocarbon volume in the subsurface accumulation based on a statistical technique utilized to determine a hydrocarbon volume for an accumulation associated with a hydrocarbon seep, wherein the hydrocarbon/water volume ratio of the accumulation is associated with wellbores within the region.

F. A method of producing hydrocarbons, comprising:

determining a type, quality and/or volume of a subsurface hydrocarbon accumulation from a hydrocarbon sample thereof, wherein the determining includes

modeling an initial concentration of atmospheric noble gases present in formation water in contact with a subsurface hydrocarbon accumulation,

modifying the modeled initial concentration by accounting for ingrowth of radiogenic noble gases during residence time of the formation water,

obtaining a hydrocarbon seep sample,

measuring concentrations and isotopic ratios of atmospheric noble gases and radiogenic noble gases present in the hydrocarbon sample,

comparing the measured concentrations and isotopic ratios of the atmospheric noble gases and the radiogenic noble gases present in the hydrocarbon sample to the modified modeled concentrations of the formation water for a plurality of exchange processes,

determining at least one of

a type of hydrocarbons in the subsurface accumulation,

a quality of hydrocarbons in the subsurface accumulation,

a hydrocarbon/water volume ratio in the subsurface accumulation prior to escape to the surface, and

a volume of the subsurface accumulation; and

producing hydrocarbons using at least one of the determined type, quality, hydrocarbon / water volume ratio, and volume of the subsurface accumulation.

[0074] It should be understood that the preceding is merely a detailed description of specific embodiments of the invention and that numerous changes, modifications, and alternatives to the disclosed embodiments can be made in accordance with the disclosure here without departing from the scope of the invention. The preceding description, therefore, is not meant to limit the scope of the invention. Rather, the scope of the invention is to be determined only by the appended claims and their equivalents. It is also contemplated that structures and features embodied in the present examples can be altered, rearranged, substituted, deleted, duplicated, combined, or added to each other. The articles “the”, “a” and “an” are not necessarily limited to mean only one, but rather are inclusive and open ended so as to include, optionally, multiple such elements.

CLAIMS

What is claimed is:

1. A method of determining a type, quality and/or volume of a subsurface hydrocarbon accumulation pre-drill from a seep sample related thereto, the method comprising:

measuring or modeling an initial concentration of atmospheric noble gases present in formation water in contact with the subsurface hydrocarbon accumulation;

modifying the measured/modeled initial concentration by accounting for ingrowth of radiogenic noble gases during residence time of the formation water;

obtaining a seep sample related to the subsurface hydrocarbon accumulation;

measuring concentrations and isotopic ratios of atmospheric noble gases and radiogenic noble gases present in the sample;

comparing the measured concentrations and isotopic ratios of the atmospheric noble gases and the radiogenic noble gases present in the sample to the measured/modified modeled concentrations of the formation water for a plurality of exchange processes;

comparing an atmospheric noble gas signature measured in the hydrocarbon phase with the measured/modified modeled concentration of the atmospheric noble gases in the formation water for the plurality of exchange processes; and

determining at least one of

a type of hydrocarbons in the subsurface accumulation,

a quality of hydrocarbons in the subsurface accumulation,

a hydrocarbon/water volume ratio associated with the subsurface accumulation prior to escape to the surface, and

a volume of hydrocarbons in the subsurface accumulation.

2. The method of claim 1, further comprising producing hydrocarbons based on at least one of the determined type, quality, hydrocarbon/water volume ratio, and the volume of the subsurface accumulation.

3. The method of claim 1, wherein the initial concentration is modeled to reflect a salinity of the fluid and temperature of exchange during recharge/exchange with atmosphere.

4. The method of claim 1, wherein the sample comprises one of water, oil, natural gas, sediments, rock, fluids present in sediments, fluids from rock pores, and fluids trapped in fluid inclusions.

5. The method of claim 1, further comprising characterizing non-hydrocarbon gas risk associated with the subsurface hydrocarbon accumulation.

6. The method of claim 1, wherein the determination of hydrocarbon volume in the subsurface accumulation is utilized to lessen uncertainty of accumulation presence and size provided by integrating the determination with seismic measurements.

7. The method of claim 1, wherein the determination of hydrocarbon volume in the subsurface accumulation is based on a comparison to seismic data to provide constraints on the water volume ratio.

8. The method of claim 1, wherein the determination of hydrocarbon volume in the subsurface accumulation is based on a statistical technique utilized to determine a hydrocarbon volume for an accumulation associated with a hydrocarbon seep, wherein the hydrocarbon/water volume ratio of the accumulation is associated with wellbores within the region.

9. A method of determining a type, quality and volume of hydrocarbons in a subsurface hydrocarbon accumulation pre-drill based on analysis of a seep sample related thereto, comprising:

analyzing the seep sample to determine a geochemical signature of the sample;

determining an initial concentration of atmospheric noble gases present in formation water in contact with the subsurface hydrocarbon accumulation.

modeling ingrowth of radiogenic noble gases to modify the initial concentration for given formation water residence times.

determining a residence time of the formation water;

determining an extent of interaction with a hydrocarbon phase;

determining at least one of a type, quality and hydrocarbon/water volume ratio of the hydrocarbon accumulation associated with the seep sample; and from the hydrocarbon/water volume ratio, determining the volume of the hydrocarbon accumulation.

10. A method for determining a type, quality and volume of hydrocarbon within a subsurface hydrocarbon accumulation from a seeped hydrocarbon sample thereof, comprising:

determining an initial concentration of atmospheric noble gases present alongside a hydrocarbon species;

modeling a range of expected concentrations of atmospheric and radiogenic noble gases present in the sample for a range of residence times and for various extents of interaction between formation water and a hydrocarbon phase;

measuring concentrations and isotopic ratios of noble gases present in the seep sample;

comparing the measured noble gas concentrations with the modeled range of expected concentrations of atmospheric and radiogenic noble gases;

estimating, from the measured noble gas concentrations and the modeled range of expected concentrations of atmospheric and radiogenic noble gases, the type and quality of hydrocarbons in the subsurface accumulation and the hydrocarbon/ water volume ratio associated with the subsurface accumulation; and

utilizing the estimated quality of hydrocarbons in the subsurface accumulation to quantify a hydrocarbon/ water volume ratio associated with the subsurface accumulation; and

integrating with seismic reflection constraints on a volume of water present in the hydrocarbon accumulation, thereby determining the volume of hydrocarbons present in the associated subsurface accumulation.

11. A system for determining a type, quality and volume of hydrocarbons within a subsurface hydrocarbon accumulation from a seeped hydrocarbon sample thereof, the system comprising:

a processor;

a tangible, machine-readable storage medium that stores machine-readable instructions for execution by the processor, wherein the machine-readable instructions include

code for determining expected concentrations of noble gases present in formation waters, code for measuring concentrations of noble gases present in the sample,

code for comparing the measured concentrations of noble gases with the modeled concentrations of noble gases in the formation waters accounting for one or more exchange and fractionation processes during hydrocarbon – water exchange,

code for determining, using said comparison, the type and quality of hydrocarbons associated with the subsurface, and

code for determining, using said comparison, the hydrocarbon/water volume ratio, associated with the subsurface accumulation, and

code for determining, using said comparison, the volume of the hydrocarbon accumulation associated with the subsurface hydrocarbon accumulation.

12. A computer program product having computer executable logic recorded on a tangible, machine readable medium, the computer program product comprising:

code for determining expected concentrations of noble gases present in formation waters,

code for modeling one or more exchange and fractionation processes in the expected concentrations of noble gases present in a hydrocarbon sample taken from a hydrocarbon seep,

code for measuring concentrations of noble gases present in the hydrocarbon sample,

code for comparing the measured concentrations of noble gases with the modeled concentrations of noble gases in the formation waters,

code for determining, using said comparison, a type and a quality of hydrocarbons associated with the hydrocarbon sample, and

code for determining, using said comparison, the hydrocarbon/water volume ratio associated with the subsurface accumulation, and

code for determining, using said comparison, the volume of hydrocarbons associated with the subsurface hydrocarbon accumulation.

13. A method of producing hydrocarbons, comprising:

determining a type, quality and/or volume of hydrocarbons within a subsurface hydrocarbon accumulation from a seeped hydrocarbon sample thereof, wherein the determining includes

modeling an initial concentration of atmospheric noble gases present in formation water in contact with a subsurface hydrocarbon accumulation, modifying the modeled initial concentration by accounting for ingrowth of radiogenic noble gases during residence time of the formation water,

obtaining a hydrocarbon seep sample,

measuring concentrations and isotopic ratios of atmospheric noble gases and radiogenic noble gases present in the hydrocarbon sample,

comparing the measured concentrations and isotopic ratios of the atmospheric noble gases and the radiogenic noble gases present in the hydrocarbon sample to the modified modeled concentrations of the formation water for a plurality of exchange processes,

comparing an atmospheric noble gas signature measured in the hydrocarbon phase with the modified modeled concentration of the atmospheric noble gases in the formation water for a plurality of exchange processes,

determining at least one of

a type of hydrocarbons associated with the subsurface accumulation,

a quality of hydrocarbons associated with the subsurface accumulation,

a hydrocarbon/water volume ratio associated with the subsurface accumulation prior to escape to the surface, and

a volume of hydrocarbons associated the subsurface accumulation; and

producing hydrocarbons using at least one of the determined type, quality, volume ratio, and volume of hydrocarbons associated with the subsurface accumulation.

14. A method of determining a type of hydrocarbons in subsurface hydrocarbon accumulation pre-drill from a seep sample related thereto, the method comprising:

measuring or modeling an initial concentration of atmospheric noble gases present in formation water in contact with the subsurface hydrocarbon accumulation;

modifying the measured/modeled initial concentration by accounting for ingrowth of radiogenic noble gases during residence time of the formation water;

obtaining a seep sample related to the subsurface hydrocarbon accumulation;

measuring concentrations and isotopic ratios of atmospheric noble gases and radiogenic noble gases present in the sample;

comparing the measured concentrations and isotopic ratios of the atmospheric noble gases and the radiogenic noble gases present in the sample to the measured/modified modeled concentrations of the formation water for a plurality of exchange processes;

comparing an atmospheric noble gas signature measured in the hydrocarbon phase with the measured/modified modeled concentration of the atmospheric noble gases in the formation water for the plurality of exchange processes; and

determining a type of hydrocarbons in the subsurface accumulation.

15. A method of determining a quality of hydrocarbons in a subsurface hydrocarbon accumulation pre-drill from a seep sample related thereto, the method comprising:

measuring or modeling an initial concentration of atmospheric noble gases present in formation water in contact with the subsurface hydrocarbon accumulation;

modifying the measured/modeled initial concentration by accounting for ingrowth of radiogenic noble gases during residence time of the formation water;

obtaining a seep sample related to the subsurface hydrocarbon accumulation;

measuring concentrations and isotopic ratios of atmospheric noble gases and radiogenic noble gases present in the sample;

comparing the measured concentrations and isotopic ratios of the atmospheric noble gases and the radiogenic noble gases present in the sample to the measured/modified modeled concentrations of the formation water for a plurality of exchange processes;

comparing an atmospheric noble gas signature measured in the hydrocarbon phase with the measured/modified modeled concentration of the atmospheric noble gases in the formation water for the plurality of exchange processes; and

determining a quality of hydrocarbons in the subsurface accumulation.

16. A method of determining a hydrocarbon/water volume ratio of a subsurface hydrocarbon accumulation pre-drill from a seep sample related thereto, the method comprising:

measuring or modeling an initial concentration of atmospheric noble gases present in formation water in contact with the subsurface hydrocarbon accumulation;

modifying the measured/modeled initial concentration by accounting for ingrowth of radiogenic noble gases during residence time of the formation water;

obtaining a seep sample related to the subsurface hydrocarbon accumulation;

measuring concentrations and isotopic ratios of atmospheric noble gases and radiogenic noble gases present in the sample;

comparing the measured concentrations and isotopic ratios of the atmospheric noble gases and the radiogenic noble gases present in the sample to the measured/modified modeled concentrations of the formation water for a plurality of exchange processes;

comparing an atmospheric noble gas signature measured in the hydrocarbon phase with the measured/modified modeled concentration of the atmospheric noble gases in the formation water for the plurality of exchange processes; and

determining a hydrocarbon/water volume ratio associated with the subsurface accumulation prior to escape to the surface.

17. A method of determining a volume of a subsurface hydrocarbon accumulation pre-drill from a seep sample related thereto, the method comprising:

measuring or modeling an initial concentration of atmospheric noble gases present in formation water in contact with the subsurface hydrocarbon accumulation;

modifying the measured/modeled initial concentration by accounting for ingrowth of radiogenic noble gases during residence time of the formation water;

obtaining a seep sample related to the subsurface hydrocarbon accumulation;

measuring concentrations and isotopic ratios of atmospheric noble gases and radiogenic noble gases present in the sample;

comparing the measured concentrations and isotopic ratios of the atmospheric noble gases and the radiogenic noble gases present in the sample to the measured/modified modeled concentrations of the formation water for a plurality of exchange processes;

comparing an atmospheric noble gas signature measured in the hydrocarbon phase with the measured/modified modeled concentration of the atmospheric noble gases in the formation water for the plurality of exchange processes; and

determining a volume of hydrocarbons in the subsurface accumulation.

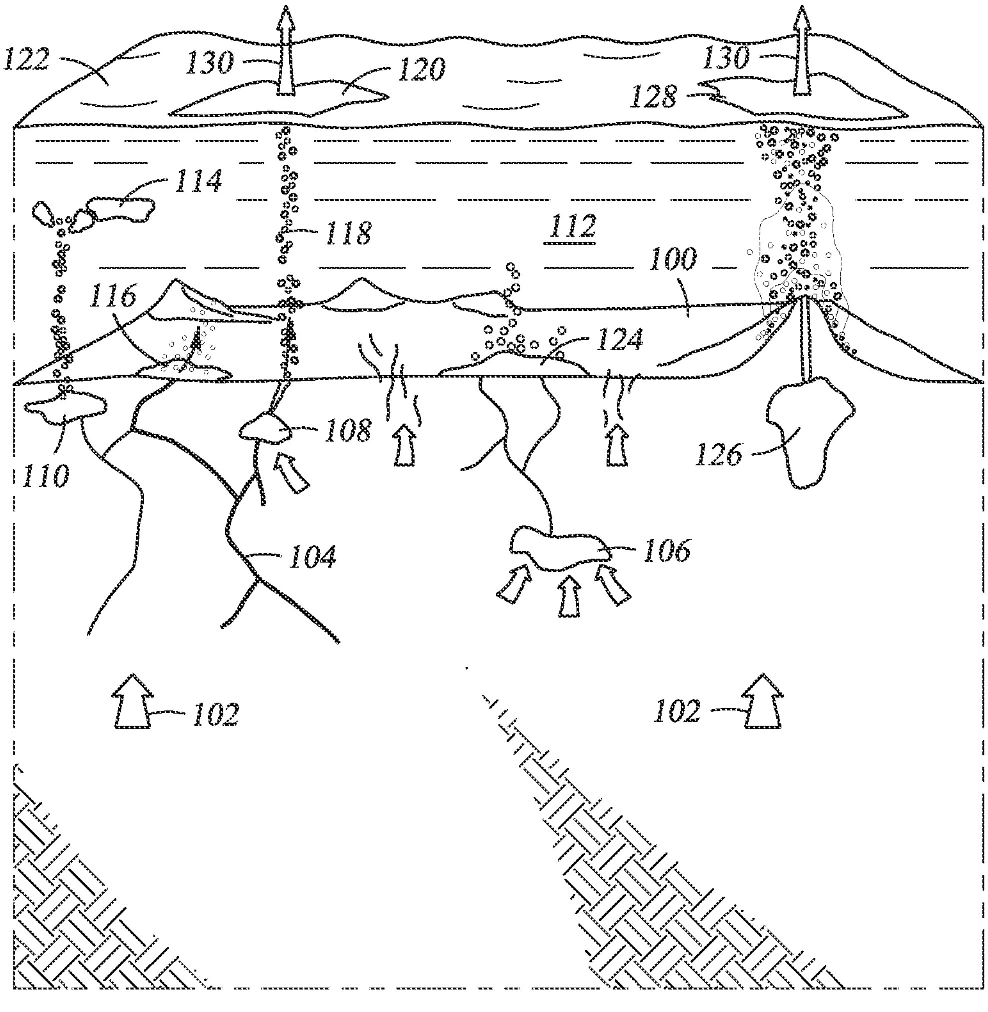
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Fig. 1

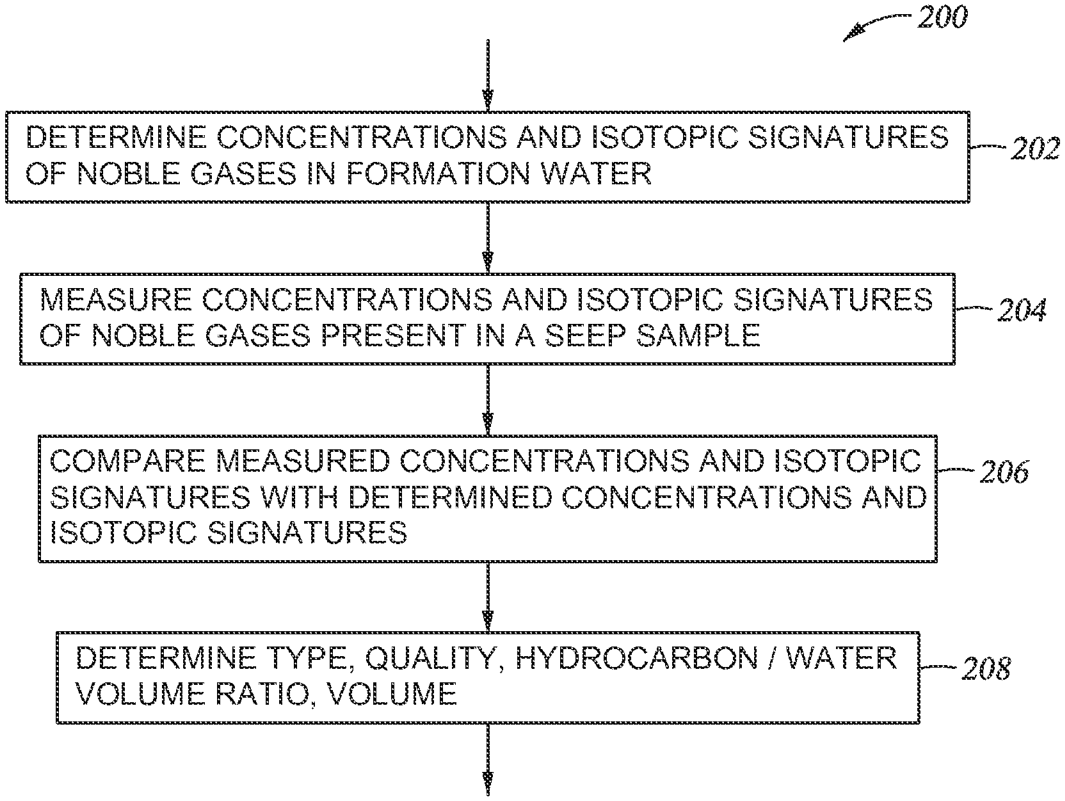
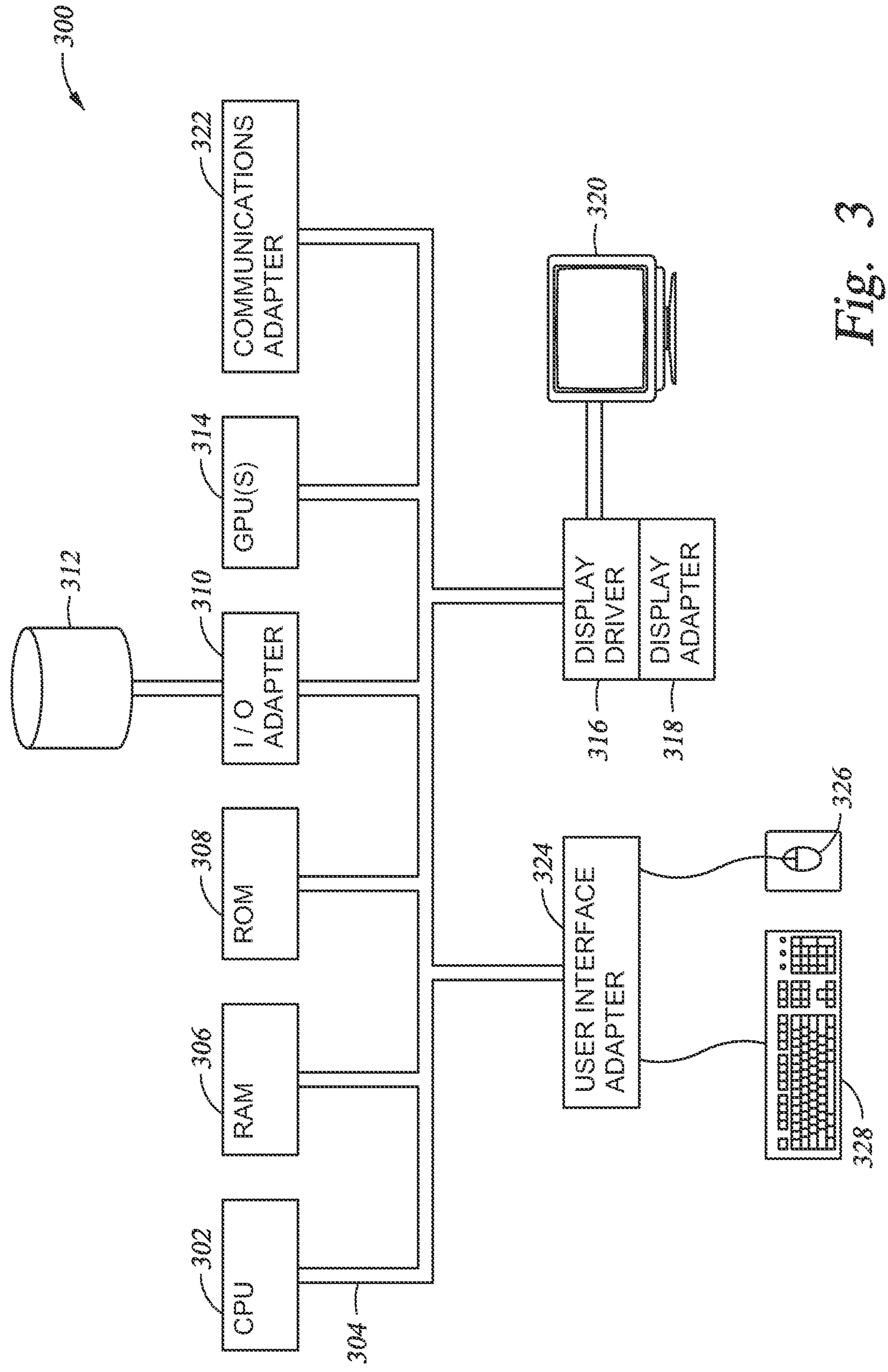

200
DETERMINE CONCENTRATIONS AND ISOTOPIC SIGNATURES OF NOBLE GASES IN FORMATION WATER
202
MEASURE CONCENTRATIONS AND ISOTOPIC SIGNATURES OF NOBLE GASES PRESENT IN A SEEP SAMPLE
204
COMPARE MEASURED CONCENTRATIONS AND ISOTOPIC SIGNATURES WITH DETERMINED CONCENTRATIONS AND ISOTOPIC SIGNATURES
206
DETERMINE TYPE, QUALITY, HYDROCARBON / WATER VOLUME RATIO, VOLUME
208

Fig. 2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CPU
304
306
RAM
308
ROM
310
I / O ADAPTER
312
314
GPU(S)
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COMMUNICATIONS ADAPTER
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DISPLAY DRIVER
DISPLAY ADAPTER
316
318
324
USER INTERFACE ADAPTER
326
328

Fig. 3

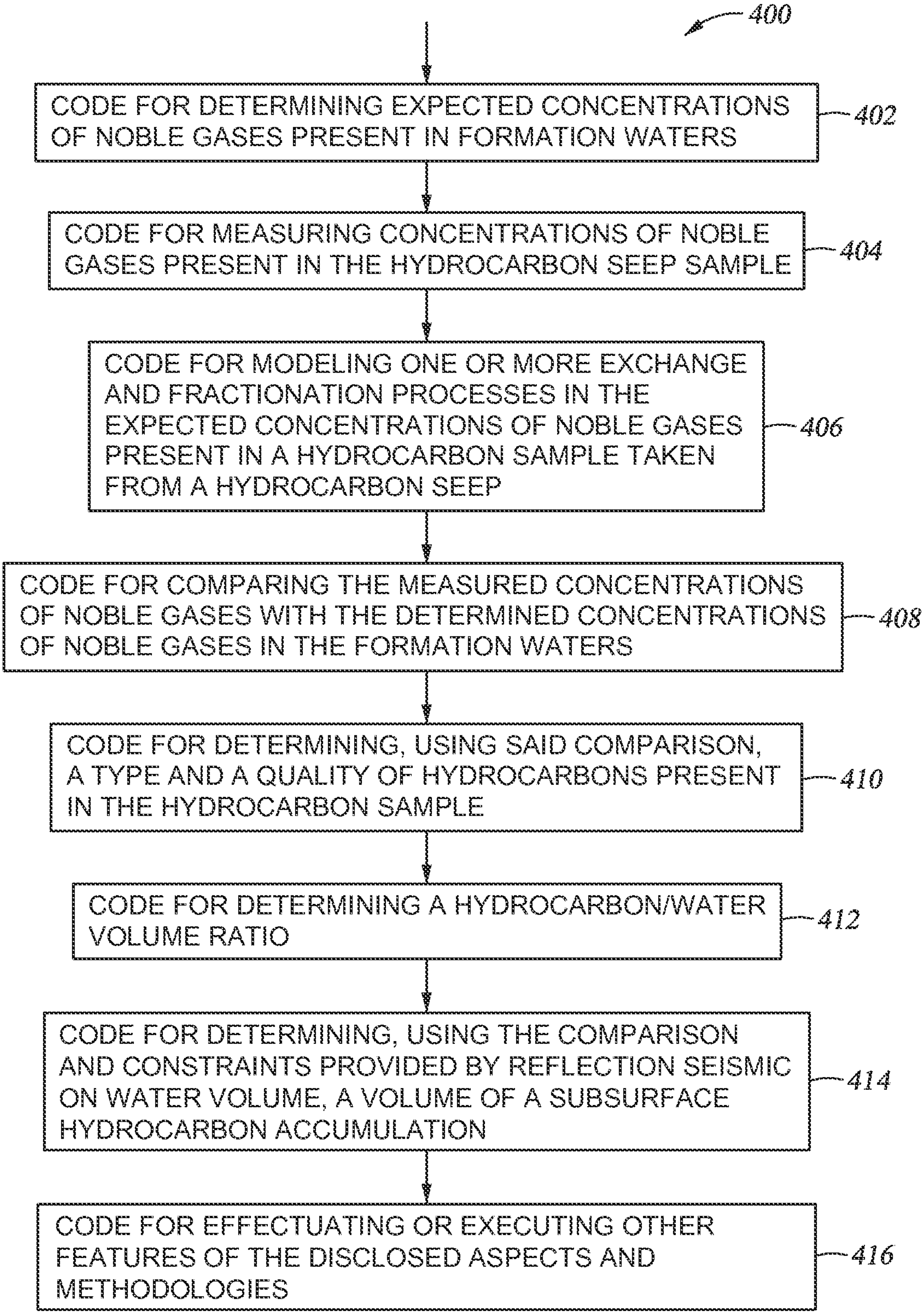
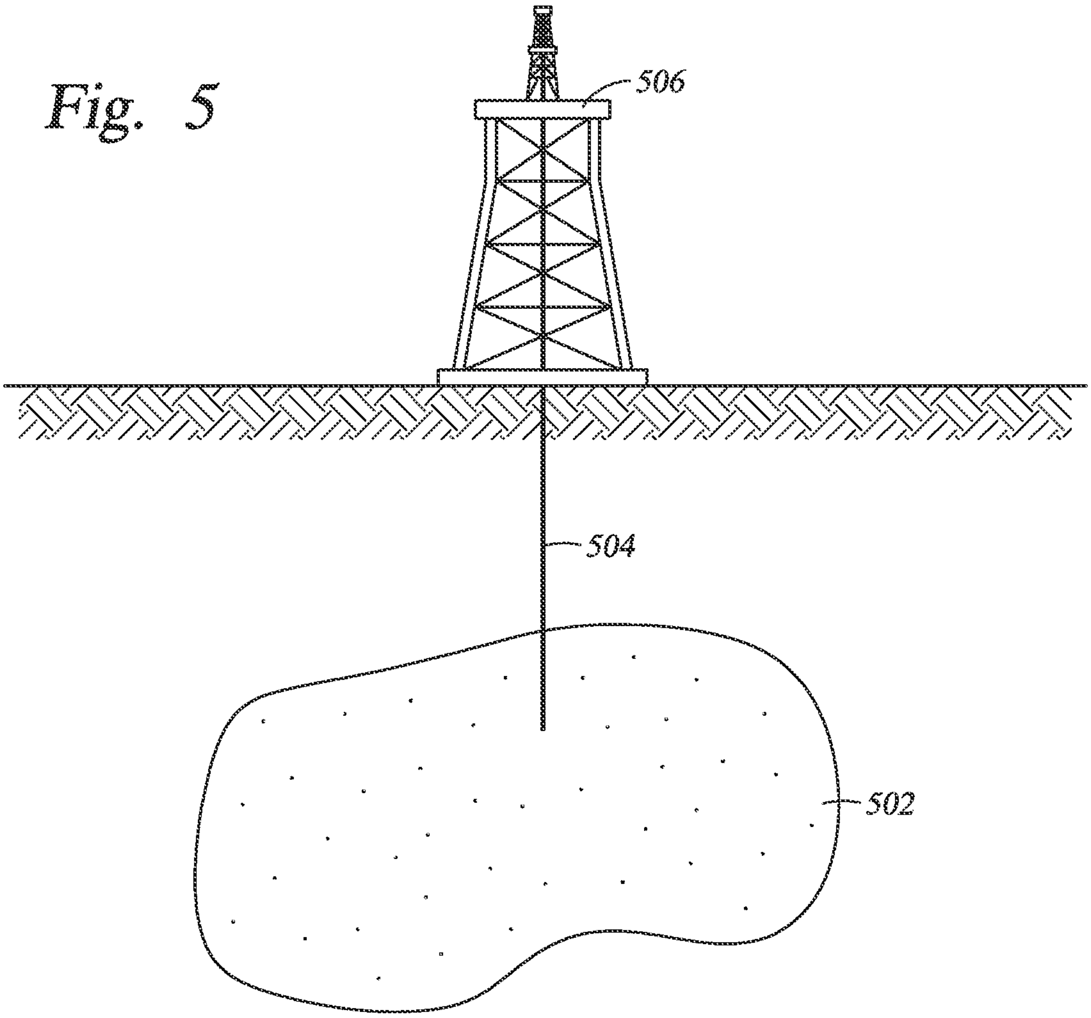

400
CODE FOR DETERMINING EXPECTED CONCENTRATIONS OF NOBLE GASES PRESENT IN FORMATION WATERS
402
CODE FOR MEASURING CONCENTRATIONS OF NOBLE GASES PRESENT IN THE HYDROCARBON SEEP SAMPLE
404
CODE FOR MODELING ONE OR MORE EXCHANGE AND FRACTIONATION PROCESSES IN THE EXPECTED CONCENTRATIONS OF NOBLE GASES PRESENT IN A HYDROCARBON SAMPLE TAKEN FROM A HYDROCARBON SEEP
406
CODE FOR COMPARING THE MEASURED CONCENTRATIONS OF NOBLE GASES WITH THE DETERMINED CONCENTRATIONS OF NOBLE GASES IN THE FORMATION WATERS
408
CODE FOR DETERMINING, USING SAID COMPARISON, A TYPE AND A QUALITY OF HYDROCARBONS PRESENT IN THE HYDROCARBON SAMPLE
410
CODE FOR DETERMINING A HYDROCARBON/WATER VOLUME RATIO
412
CODE FOR DETERMINING, USING THE COMPARISON AND CONSTRAINTS PROVIDED BY REFLECTION SEISMIC ON WATER VOLUME, A VOLUME OF A SUBSURFACE HYDROCARBON ACCUMULATION
414
CODE FOR EFFECTUATING OR EXECUTING OTHER FEATURES OF THE DISCLOSED ASPECTS AND METHODOLOGIES
416

Fig. 4

Fig. 5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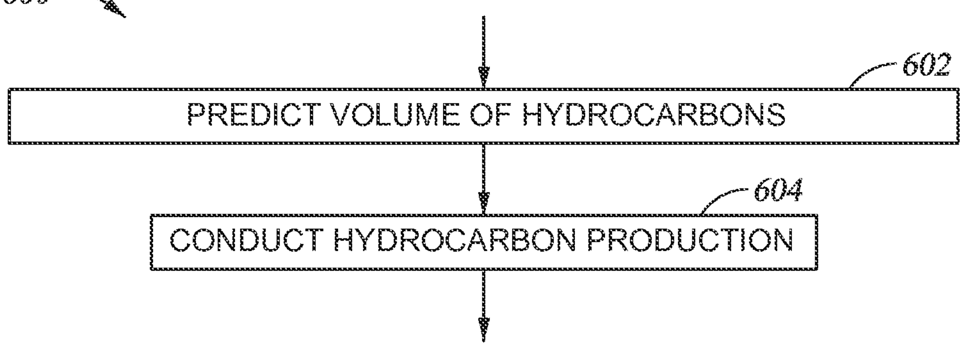
600
602
PREDICT VOLUME OF HYDROCARBONS
604
CONDUCT HYDROCARBON PRODUCTION

Fig. 6

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2013/033160

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - G01N 33/24 (2013.01)
USPC - 250/255
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC(8) - G01N 1/00, 1/10, 25/00, 30/00, 30/02, 33/00, 33/18, 33/24, 33/26; G01V 9/00; G21H 5/00, 5/02 (2013.01)
USPC - 73/19.1, 23.2, 23.35, 152.18, 152.19; 250/253, 255, 256, 261; 422/83, 89; 436/25, 29, 30

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
CPC - G01N 33/00, 33/24, 33/241; G01V 9/002, 9/007; G21H 5/00, 5/02 (2013.01)

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
PatBase, Google Patents, Google

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 3,571,591 A (BRADLEY et al) 23 March 1971 (23.03.1971) entire document	1-17
A	US 2,551,449 A (MENKE) 01 May 1951 (01.05.1951) entire document	1-17
A	US 5,286,651 A (SMITH) 15 February 1994 (15.02.1994) entire document	1-17
A	US 2007/0169540 A1 (STERNER et al) 26 July 2007 (26.07.2007) entire document	1-17
A	US 4,340,391 A (DEMAISON et al) 20 July 1982 (20.07.1982) entire document	1-17

☐ Further documents are listed in the continuation of Box C. ☐

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search 17 May 2013	Date of mailing of the international search report 06 JUN 2013
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-3201	Authorized officer: Blaine R. Copenheaver PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774