



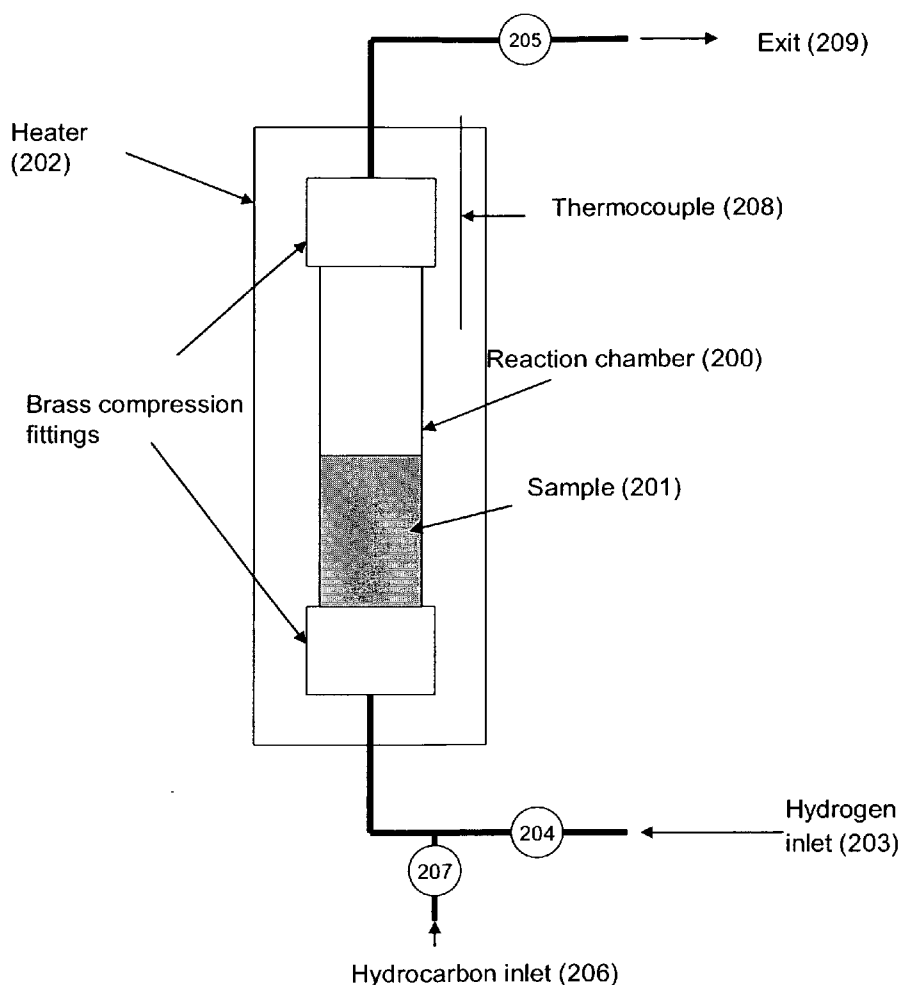
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(19) **United States**(12) **Patent Application Publication**
Mango(10) **Pub. No.: US 2006/0117841 A1**(43) **Pub. Date: Jun. 8, 2006**(54) **NOVEL WELL LOGGING METHOD FOR
THE DETERMINATION OF CATALYTIC
ACTIVITY****Related U.S. Application Data**(63) Continuation-in-part of application No. 11/006,159,
filed on Dec. 7, 2004.(75) Inventor: **Frank D. Mango**, Houston, TX (US)**Publication Classification**(51) **Int. Cl.**
E21B 49/00 (2006.01)(52) **U.S. Cl.** **73/152.11**

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HOUSTON, TX 77002 (US)(57) **ABSTRACT**

The present invention relates to assays for ascribing catalytic activity to rock samples by virtue of zero-valent transition metals potentially being present within the sample. Embodiments of the present invention are generally directed to novel assays for measuring intrinsic paleocatalytic activities (k) of sedimentary rocks for converting oil to gas and projecting the activities to the subsurface based on the measured linear relationship between $\ln(k)$ and temperature (T).

(73) Assignee: **Petroleum Habitats, L.L.C.**(21) Appl. No.: **11/168,778**(22) Filed: **Jun. 28, 2005**

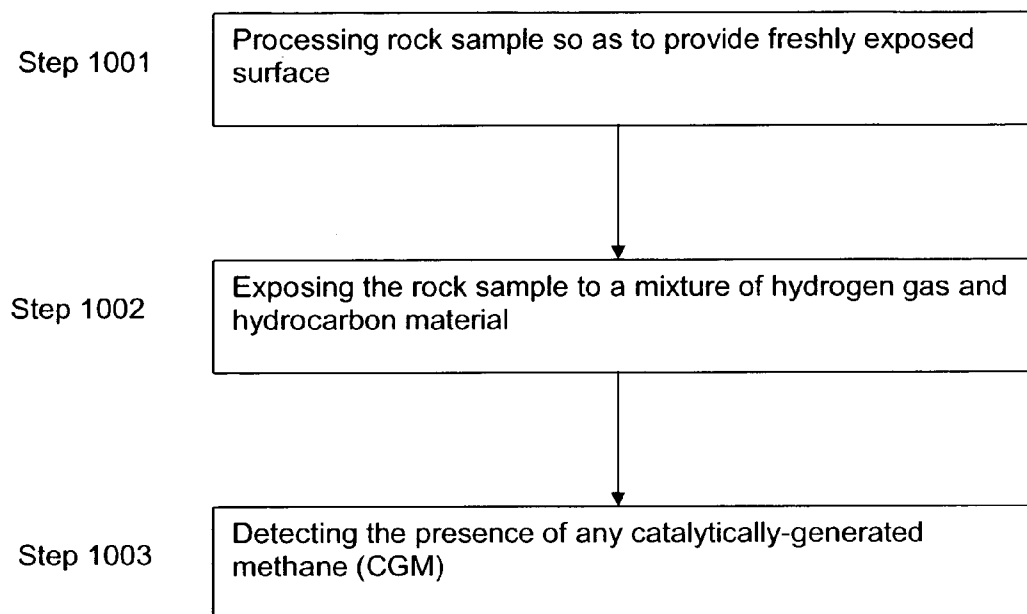


Fig. 1

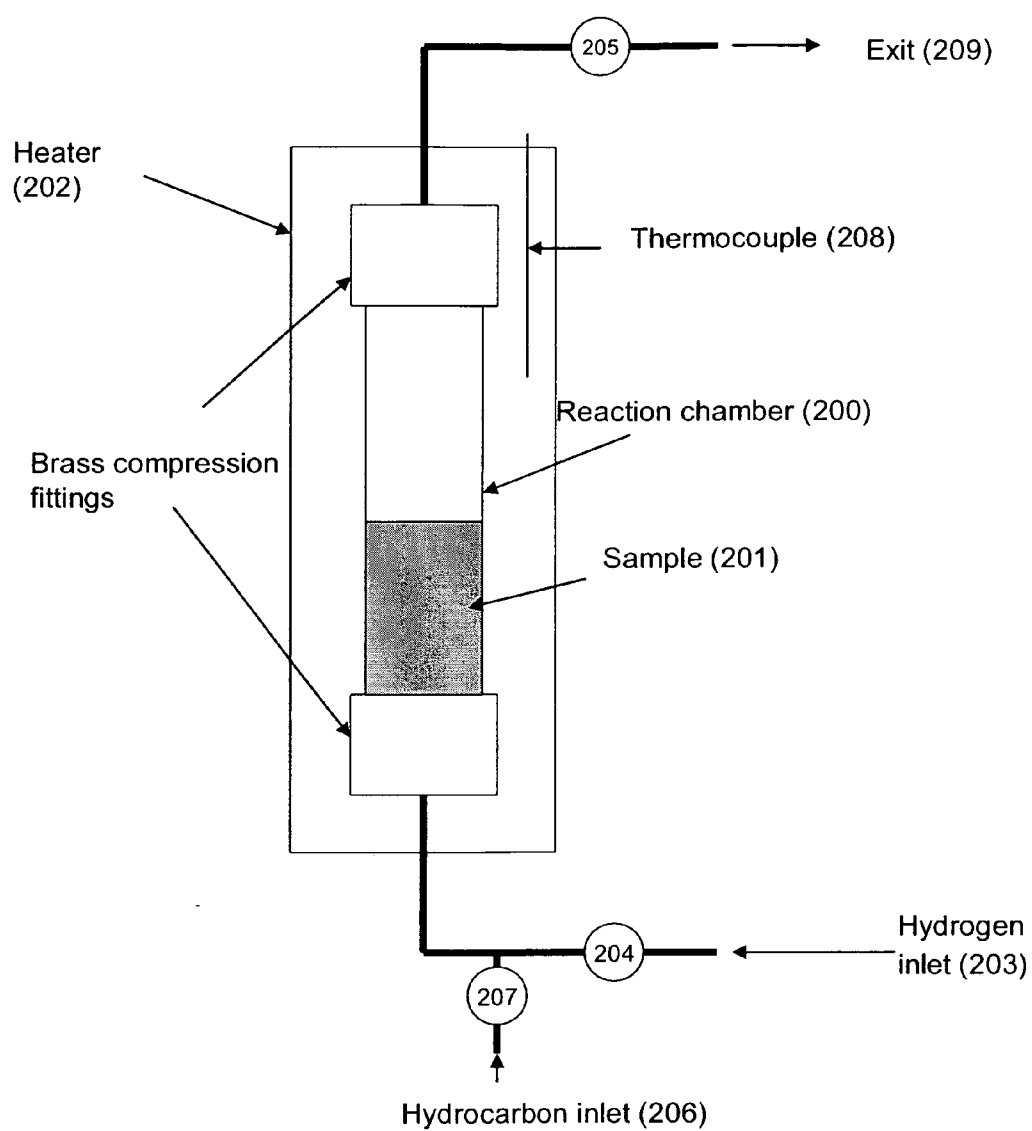


Fig. 2

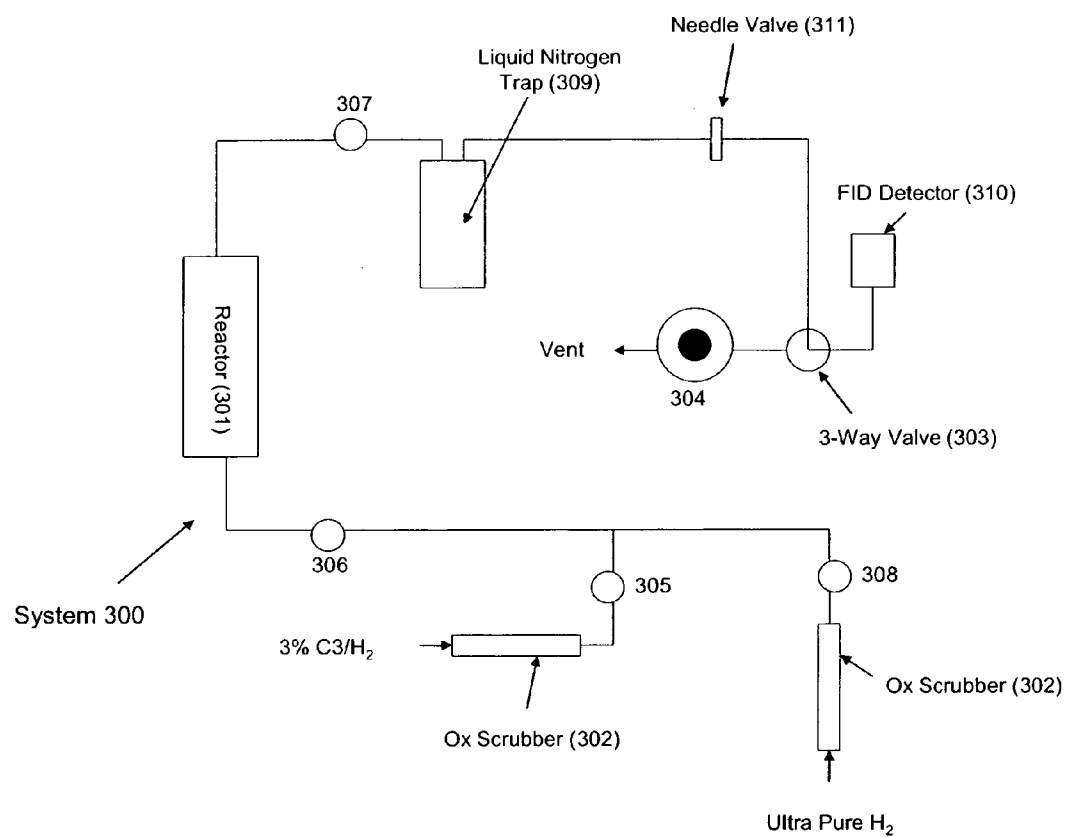


Fig. 3

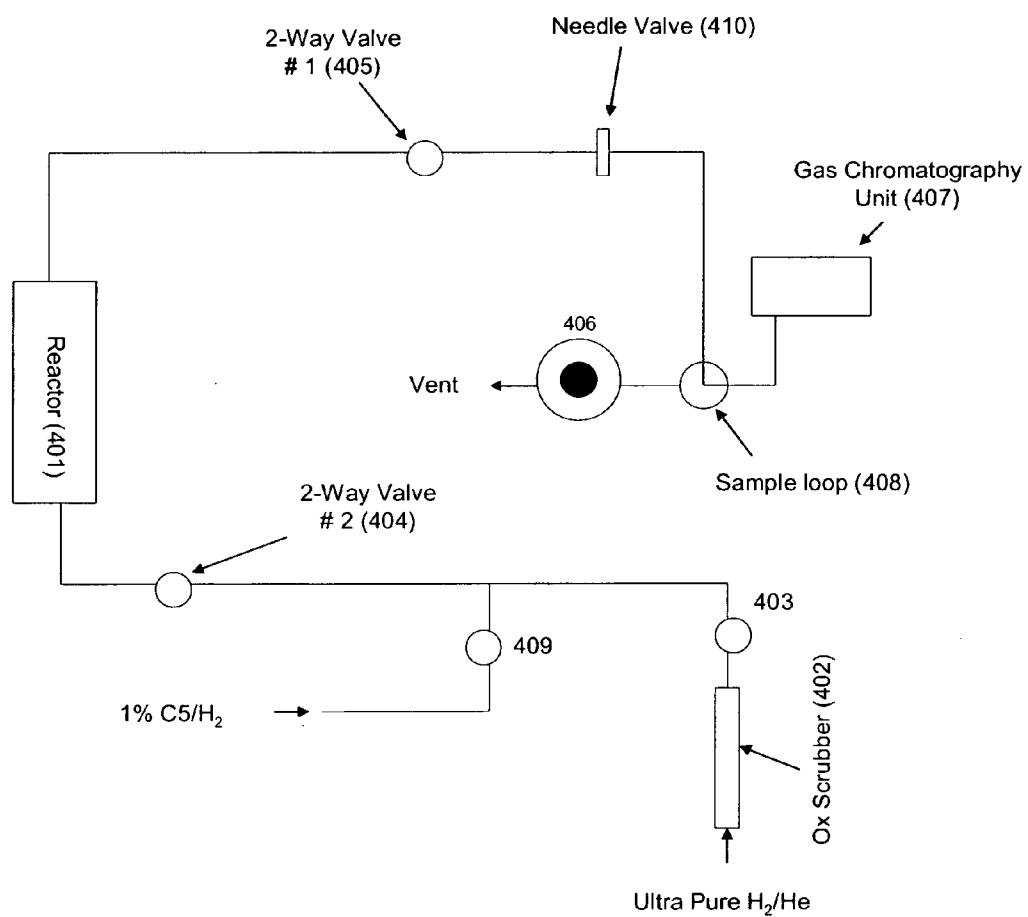
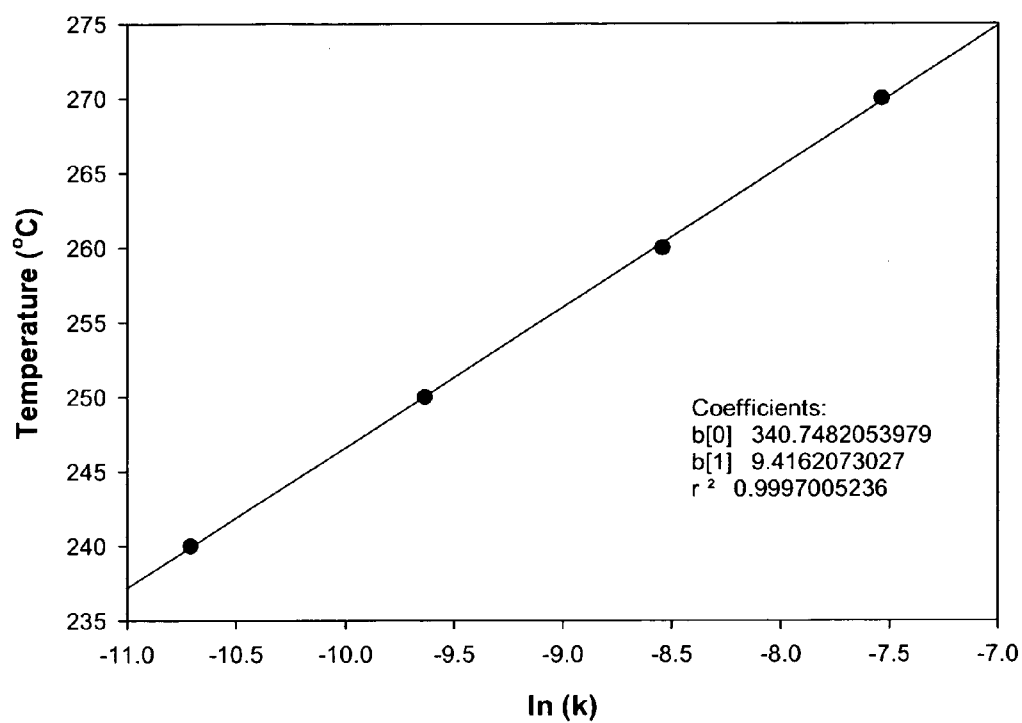


Fig. 4

*Fig. 5*

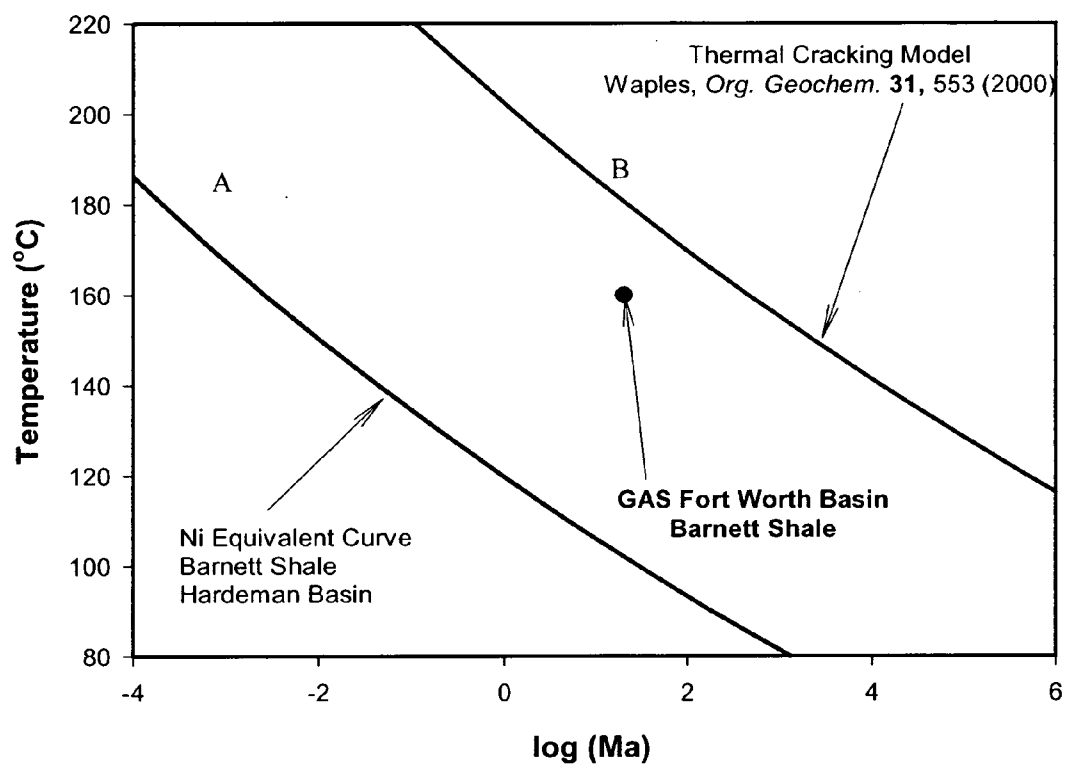


Fig. 6

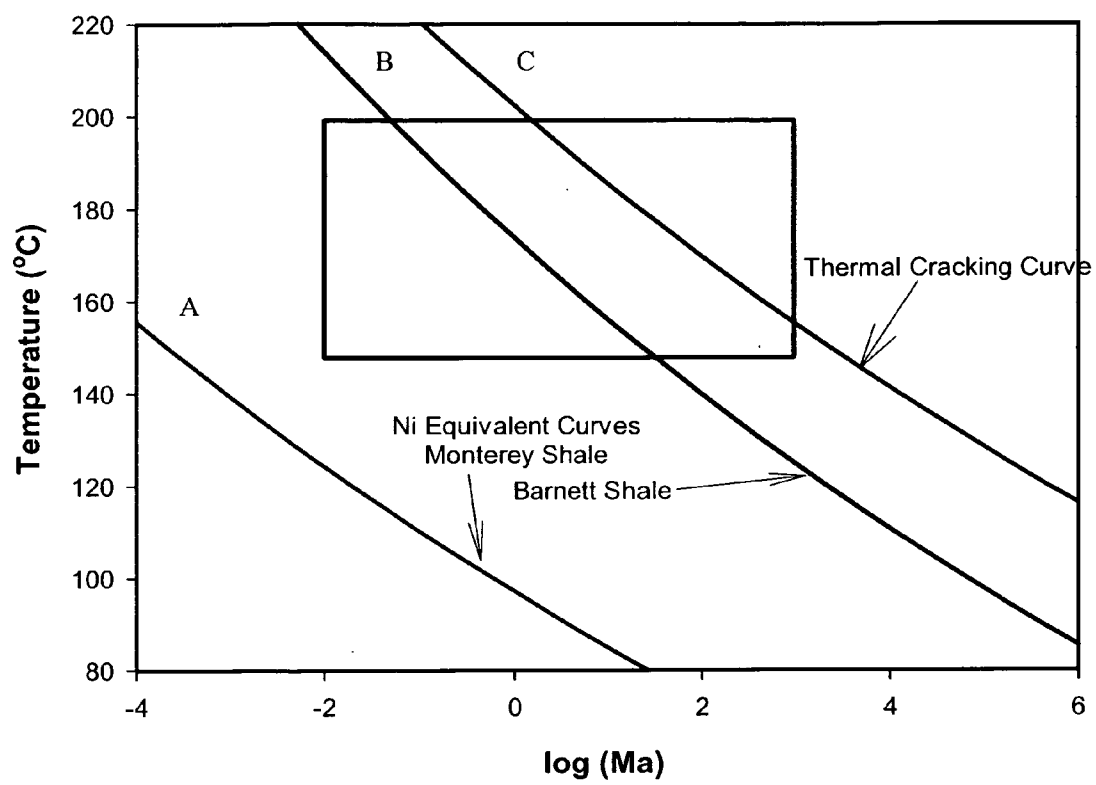


Fig. 7

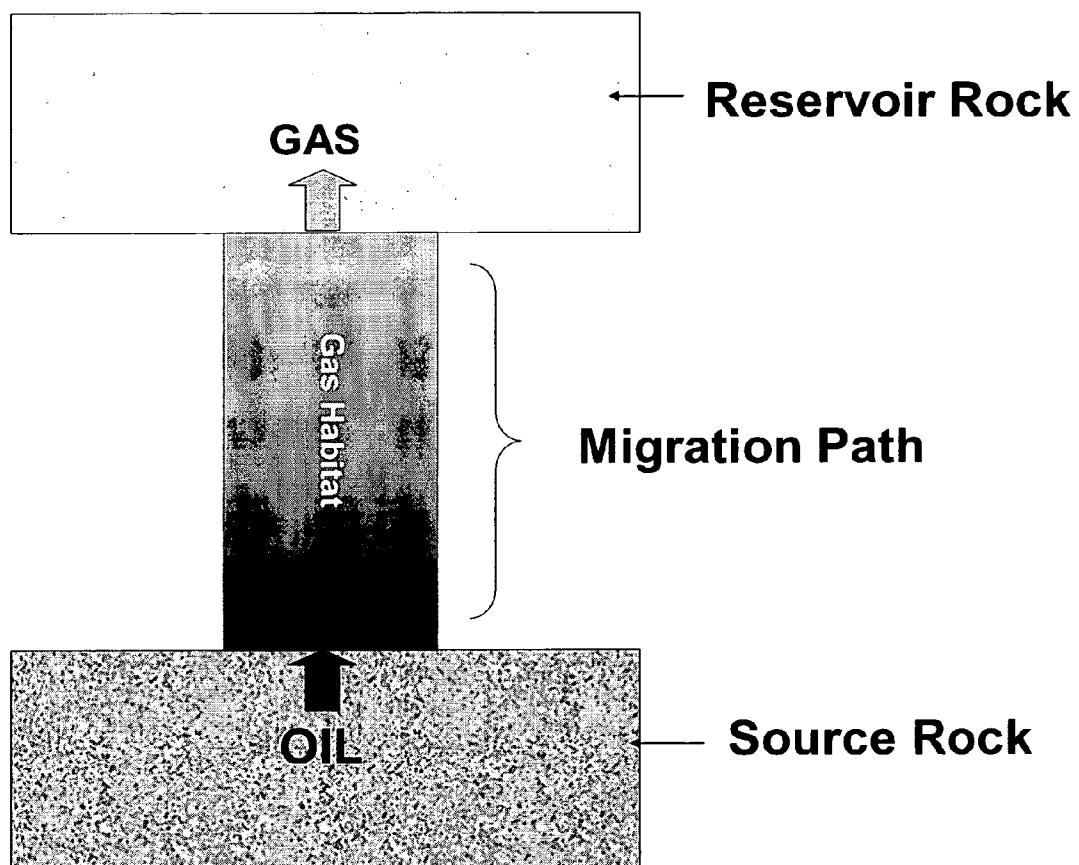


Fig. 8

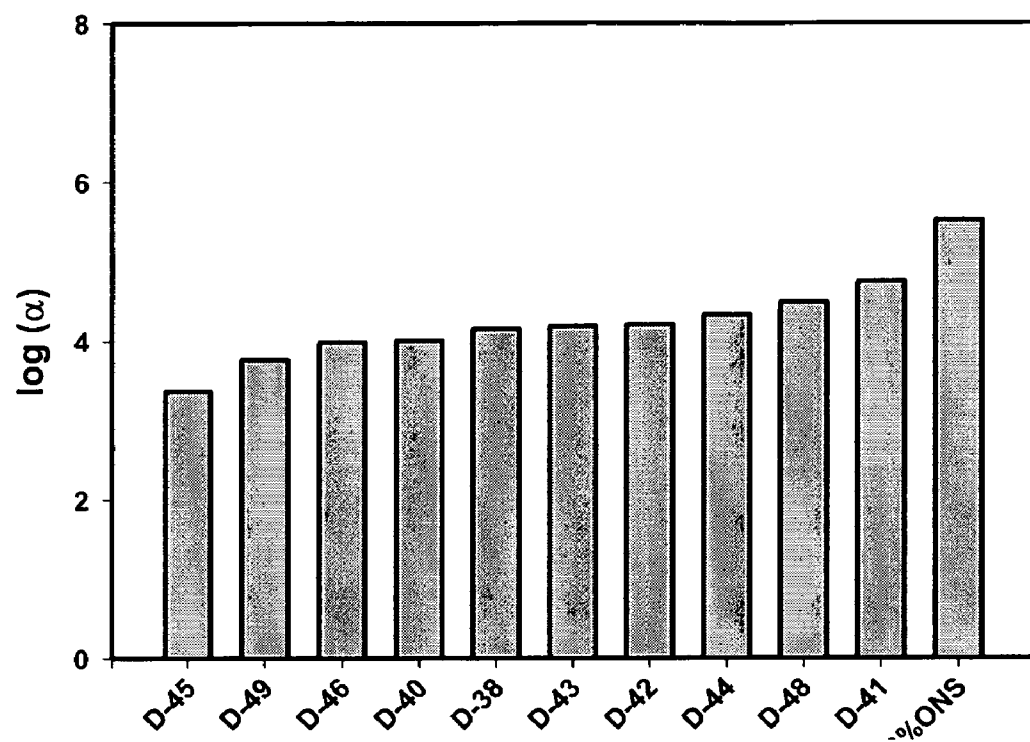


Fig. 9

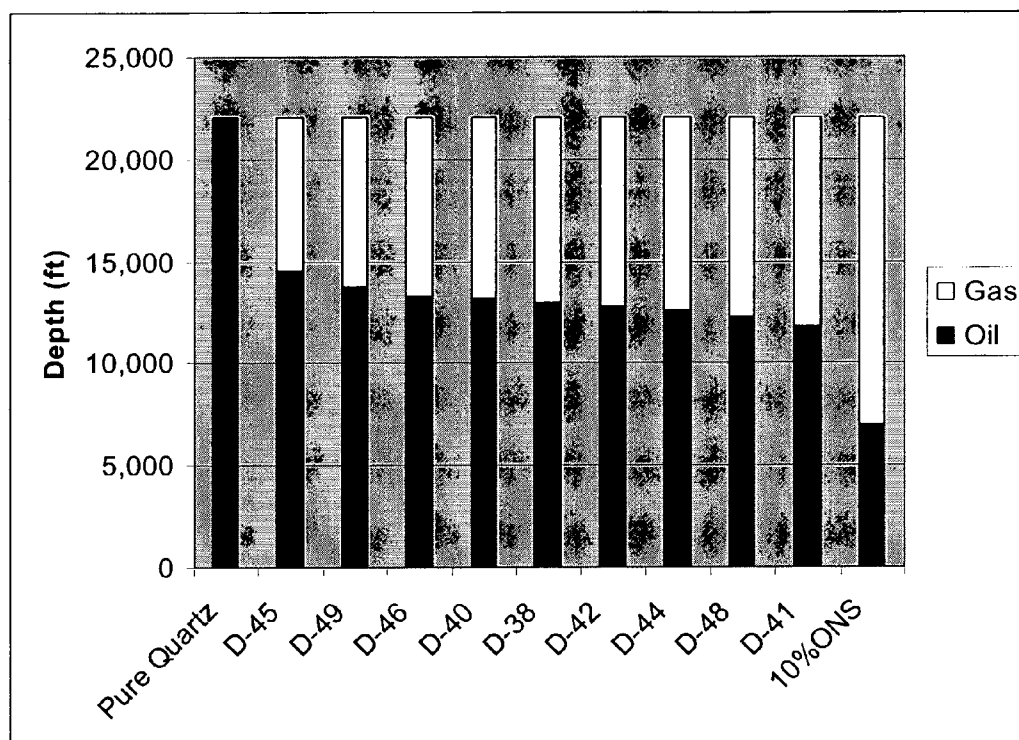


Fig. 10

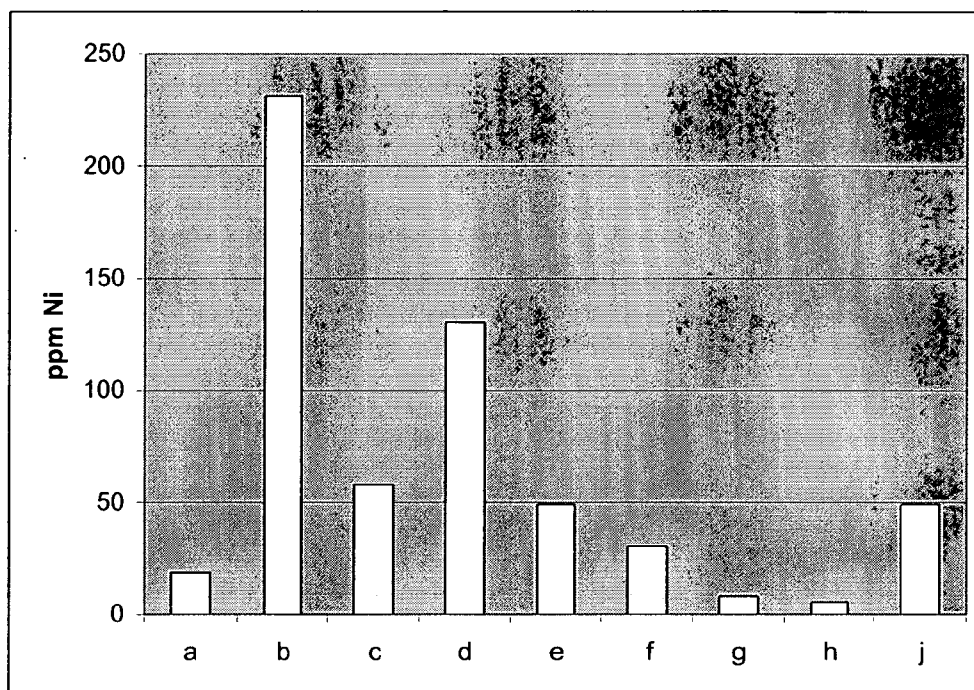


Fig. 11

NOVEL WELL LOGGING METHOD FOR THE DETERMINATION OF CATALYTIC ACTIVITY

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This Application is a continuation-in-part of U.S. patent application Ser. No. 11/006,159, filed Dec. 7, 2004.

TECHNICAL FIELD

[0002] The present invention relates generally to well logging, and specifically to assays for ascribing catalytic activity to rock samples, during the course of well logging, by virtue of zero-valent transition metals potentially being present within the sample. An understanding of such catalytic activity is useful in predicting the distribution of oil and gas in sedimentary basins and thus has revolutionary potential in oil and gas exploration.

BACKGROUND INFORMATION

[0003] Oil progresses to natural gas in deep sedimentary basins. This process, hereafter referred to as "oil-to-gas," is believed to be the major source of natural gas in the earth (Hunt, *Petroleum Geochemistry and Geology*, 2nd ed., W. H. Freeman, New York., Chapter 7, 1996). Knowing when and how this process occurs is the key to predicting the distribution of oil and gas with depth. The conventional view is that oil thermally cracks to gas (thermal gas) at temperatures between 150° C. and 200° C., the observed temperature range where most oil-to-gas occurs. Various kinetic models (thermal models) based on this theory have had only marginal success, however, and there are glaring contradictions. Oil, for example, is found in deep reservoirs (>20,000 ft) at temperatures where it should not exist (Paine et al., "Geology of natural gas in South Louisiana," American Association of Petroleum Geologists, Memoir 9, Volume 1, Natural Gases of North America, Beebe, B. W., Editor, 376-581, 1968; Price, "Thermal stability of hydrocarbons in nature: Limits, evidence, characteristics, and possible controls," *Geochimica et Cosmochimica Acta*, 57:3261-3280, 1993), and giant deposits of so-called thermal gas exist in shallow reservoirs that cannot be explained by the thermal model without invoking long-range migration from deeper horizons (Littke et al., "Gas generation and accumulation in the West Siberian basin," *AAPG Bull.*, 83:1642-1665, 1999).

[0004] There is now mounting scientific evidence against the thermal models. From a series of laboratory experiments under realistic conditions (Domine et al., "Towards a new method of geochemical kinetic modeling: implications for the stability of crude oils," *Organic Geochemistry*, 28:597-612, 1998; Domine et al., "Up to what temperature is petroleum stable? New insights from 5200 free radical reaction model," *Organic Geochemistry*, 33:1487-1499, 2002), evidence now suggests that oil should not crack to gas over geologic time at temperatures between 150° C. and 200° C., the range within which most so-called thermal gas is formed, a conclusion supported by numerous other studies (Mallinson et al., "Detailed chemical kinetics study of the role of pressure in butane pyrolysis," *Industrial & Engineering Chemistry, Research*, 31:37-45, 1992; Burnham et al., "Unraveling the kinetics of petroleum destruction by using 1,2-¹³C isotopically labeled dopants," *Energy & Fuels*, 9:190-191, 1995; Jackson et al., "Temperature and pressure depen-

dence of n-hexadecane cracking," *Organic Geochemistry*, 23:941-953, 1995). Moreover, the gas produced in oil cracking is severely depleted in methane and does not resemble natural gas as it is distributed in the earth (Mango, "The origin of light hydrocarbons," *Geochimica et Cosmochimica Acta*, 64:1265-1277, 2001).

[0005] Catalysis by transition metals is an alternative explanation for oil-to-gas (Mango, "Transition metal catalysis in the generation of petroleum and natural gas," *Geochimica et Cosmochimica Acta*, 56:553-555, 1992), and there is experimental evidence supporting it. Crude oils are converted to gas over zero-valent transition metals (ZVTM) (e.g., Ni, Co, and Fe) under moderate laboratory conditions (150-200° C.) and the products are identical to natural gas in molecular and isotopic composition (Mango and Hightower, "The catalytic decomposition of petroleum into natural gas," *Geochimica et Cosmochimica Acta*, 61:5347-5350, 1997; Mango and Elrod, "The carbon isotopic composition of catalytic gas: A comparative analysis with natural gas," *Geochimica et Cosmochimica Acta*, 63:1097-1106, 1998; Mango, "The origin of light hydrocarbons," *Geochimica et Cosmochimica Acta*, 64:1265-1277, 2000).

[0006] The above-described experiments are highly relevant to the generation of natural gas in sedimentary basins. Transition metals are common in sedimentary rocks (Boggs, S., Jr., *Principles of Sedimentology and Stratigraphy*, 2nd ed., Prentice-Hall, Inc., NJ, pages 165 & 195, 1995), and could become catalytically active (i.e., reduced to zero-valencies) given the reducing conditions of petroleum habitats (Mango, "The light hydrocarbons in petroleum: a critical review," *Organic Geochemistry*, 26:417-440, 1997; Mango, "The origin of light hydrocarbons," *Geochimica et Cosmochimica Acta*, 64:1265-1277, 2000; Medina et al., "Low temperature iron- and nickel-catalyzed reactions leading to coalbed gas formation," *Geochimica et Cosmochimica Acta*, 64:643-649, 2000; Seewald, "Organic-inorganic interactions in petroleum-producing sedimentary basins," *Nature*, 426:327-333, 2003). All requisites are in place: transition metal oxides in sufficient amounts to promote the reaction and enough hydrogen to activate them to zero-valencies and drive the reaction at subsurface temperatures (Mango, "The origin of light hydrocarbons," *Geochimica et Cosmochimica Acta*, 64:1265-1277, 2000).

[0007] Catalysis may be the source of the huge gas deposits in the Gulf Coast geosyncline of south Louisiana (Paine et al., "Geology of natural gas in South Louisiana," American Association of Petroleum Geologists, Memoir 9, Volume 1, Natural Gases of North America, Beebe, B. W., Editor, 376-581, 1968). Oil is generally found at depths above 10,000 feet and gas is generally found below such depths, consistent with the thermal model. However, gas probabilities are also a strong function of reservoir composition: low in pure sandstone and high in sandstones interbedded with outer-neritic shales that are often enriched in transition metals (Mann and Stein, "Organic facies variations, source rock potential, and sea level changes in Cretaceous black shales of the Quebrada Ocal, Upper Magdalena Valley, Colombia," *American Association of Petroleum Geologists Bulletin*, 81:556-576, 1997; Cruickshank and Rowland, "Mineral deposits at the shelfbreak," SEPM Special Publication No. 33, 429-436, 1983).

[0008] Given high enough temperatures and hydrogen partial pressures at depth, transition metals in outer-neritic shales could attain zero-valencies. Thus activated, in-reservoir catalytic oil-to-gas would commence. In this instance, the important factor for predicting oil or gas in reservoir rocks is the presence of ZVTM in sufficient concentrations to promote catalytic oil-to-gas. A rock assay specific to ZVTM in outcrop rocks, cuttings, or core samples would thus be a powerful exploration tool for reservoirs that either preserve oil (no ZVTM) or convert it to gas (with ZVTM).

[0009] Other than commonly assigned co-pending U.S. patent application Ser. No. 10/830,266, Applicant is unaware of any practical tests for trace amounts (i.e., ppb or less) of ZVTM in sedimentary rocks. Most rock methods use spectroscopic techniques, such as atomic absorption (AA) spectroscopy or inductively-coupled plasma atomic emission spectroscopy (ICP-AES), that do not differentiate between oxidation states. Nickel valency speciation has been achieved by X-ray absorption fine-structure spectroscopy using the National Synchrotron Light Source at Brookhaven National Laboratory (NY) and with anodic stripping voltammetry (Galbreath et al., "Chemical speciation of Nickel in residual oil ash," *Energy & Fuels*, 12:818-822, 1998), but the complexities of these methods preclude their use in routine rock analysis.

[0010] In addition to the above, a convenient assay for the direct determination of intrinsic paleocatalytic activity within sedimentary rock, for the purpose of making predictions in oil and gas exploration, particularly during the course of well logging, would also be highly desirable. Applicant is unaware of any assays that measure the intrinsic catalytic activity of rocks to convert oil to gas under subsurface conditions.

BRIEF DESCRIPTION OF THE INVENTION

[0011] Embodiments of the present invention are generally directed to novel assays for measuring intrinsic paleocatalytic activities (k) of sedimentary rocks for converting oil to gas and projecting the activities to the subsurface based on the measured linear relationship between $\ln(k)$ and temperature (T), and to well logging protocols employing such assays. Sedimentary rocks sufficiently catalytic to convert 90+% of their contained oil to gas at temperature T for oil residence time t are designated "gas habitats." Sedimentary rocks that cannot convert 90% of their oil to gas in time t are designated "oil habitats." Some embodiments of the present invention include approximating the intrinsic paleocatalytic activity $k(T)$ of an un-drilled reservoir at temperature T from the linear relationship between $\ln k$ and T for a drilled reservoir rock that is genetically similar to the un-drilled reservoir rock. Some embodiments of the present invention enable the prediction of oil or gas in an un-drilled reservoir at temperature T for residence time t based on an approximation of its intrinsic paleocatalytic activity $k(T)$ taken from the $\ln k$ vs T curve for a genetically related reservoir distal from the undrilled reservoir. Some embodiments of the present invention provide oil-gas habitat maps of stratigraphic rock units contouring the interface between oil and gas habitats based on the intrinsic paleocatalytic activities $k(T)$ or their approximations at various locations in a basin. Some embodiments of the present invention enable prediction of the distribution of oil and gas in various reservoirs within a stratigraphic rock unit based on the

oil-gas habitat map of that rock unit. Some embodiments of the present invention enable prediction of the distribution of oil and gas in various reservoirs in a stratigraphic rock unit proximal to a stratigraphic source rock unit within which oil and gas is generated and expelled into reservoirs within the proximal rock unit based on the oil-gas habitat map of the source rock unit. Some embodiments of the present invention enable the prediction of the conversion of oil to gas within a conduit rock along an oil migration pathway based on its intrinsic paleocatalytic activity $k(T)$ or an approximation thereof at temperature T and the residence time t that migrating oil remains in the conduit.

[0012] Assays of the present invention typically comprise the following general steps: 1) processing rock sample potentially comprising zero-valent transition metal (ZVTM) so as to provide freshly exposed surface under conditions that preserve intrinsic catalytic activity; 2) exposing the rock sample to a mixture of hydrogen gas and hydrocarbon material under appropriate conditions such that the hydrocarbon material undergoes catalytic decomposition yielding catalytically-generated methane (CGM) if ZVTM is present; and 3) detecting the presence of any CGM. The presence of CGM confirms intrinsic catalytic activity imparted by ZVTM present in the sample. Generally, such rock samples are sedimentary rock samples, and processing (e.g., grinding) to provide freshly exposed surface is generally carried out in an inert, non-oxidizing atmosphere. Similarly, the exposure of such rock samples to hydrogen and hydrocarbon reactants is typically carried out in an inert, non-oxidizing atmosphere.

[0013] Depending on the embodiment, such above-described methane detection can provide qualitative and/or quantitative analysis of the sample. In some embodiments, when assaying a rock as described above, the qualitative analysis of catalytically-generated methane is sufficient to make predictive assessments as to the content (i.e., primarily oil or primarily gas) of the reservoir from where the analyzed sample was extracted (source reservoir) or of any other reservoir that is genetically similar to the source reservoir. Two reservoirs are genetically similar if their overall organic and inorganic compositions are similar and if their genetic depositional environments are similar. In the Louisiana gas fields cited above, for example (Paine et al., "Geology of natural gas in South Louisiana," American Association of Petroleum Geologists, Memoir 9, Volume 1, Natural Gases of North America, Beebe, B. W., Editor, 376-581, 1968), the various reservoirs comprising interbedded sandstone and outer-neritic shales are genetically related, as defined here, for they share a common outer-neritic depositional environment. Outer-neritic environments include deposition along shelf breaks that are often highly reducing, organic rich sediments with high concentrations of transition metals (Cruickshank, M. J., and Roland, T. J. Jr., "Mineral deposits at the Shelfbreak," *SEPM Special Publication No. 33*, 429-436, 1983). Sandstone reservoirs interbedded with outer-neritic shale are not genetically similar to sandstone reservoirs interbedded with inner-neritic shale because outer-neritic and inner-neritic depositional environments are dissimilar, particularly with respect to metal concentrations and, therefore, their respective catalytic activities. In some or other embodiments, a more quantitative analysis provides greater insight into the content of such a source reservoir.

[0014] In some embodiments, upon quantitatively and/or qualitatively analyzing the catalytically-generated methane, the rock sample is ascribed an intrinsic catalytic activity. Such an intrinsic catalytic activity can then be projected onto the reservoir from where the sample was extracted (i.e., the source reservoir) or any other genetically similar reservoirs, to determine whether the intrinsic catalytic activity is sufficient to enable significant oil-to-gas conversion over geologic timescales and under environmental conditions within the reservoir. By processing the rock samples under inert conditions and exposing the processed rock samples to reactants under non-oxidizing conditions, the intrinsic catalytic activity so determined is equatable with the native catalytic activity in the reservoir.

[0015] Accordingly, the present invention, and the knowledge of catalytic activity gained thereby, is useful in predicting whether a particular reservoir will be likely to contain predominantly oil or predominantly gas.

[0016] In some embodiments, an analysis of the amount of methane produced under a given set of conditions and in a given timeframe generates a rate constant, k , for such a reaction at a particular reaction temperature. If such rate constants are determined for two or more such reaction temperatures, a linear plot of $\ln k$ versus T ($\ln k$ vs. T plot) can be generated. Such $\ln k$ vs. T plots can be extrapolated to yield a rate constant for the source reservoir that is indicative of its paleocatalytic activity. With such a source reservoir rate constant, it is possible to determine the extent and significance of oil-to-gas processes within said reservoir under sub-surface conditions over geologic timescales by integrating $k dt$ over the temperature interval in the subsiding basin.

[0017] The foregoing has outlined rather broadly the features of the present invention in order that the detailed description of the invention that follows may be better understood. Additional features and advantages of the invention will be described hereinafter which form the subject of the claims of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

[0018] For a more complete understanding of the present invention, and the advantages thereof, reference is now made to the following description taken in conjunction with the accompanying drawings, in which:

[0019] **FIG. 1** is a flow diagram depicting the steps involved in a rock assay in accordance with embodiments of the present invention;

[0020] **FIG. 2** depicts an exposure chamber, operable for both static and flow exposures, in accordance with some embodiments of the present invention;

[0021] **FIG. 3** depicts a reaction system in accordance with some embodiments of the present invention;

[0022] **FIG. 4** depicts another reaction system in accordance with some embodiments of the present invention;

[0023] **FIG. 5** is a $\ln(k)$ vs. T curve generated in accordance with some embodiments of the present invention;

[0024] **FIG. 6** is a plot of an application in which gas is correctly predicted in one basin based on a rock assay from

a genetically similar reservoir rock from a different basin in accordance with some embodiments of the present invention;

[0025] **FIG. 7** is a plot of the differences between thermal cracking and the current invention in their capacities to explain oil-to-gas as seen in sedimentary basins;

[0026] **FIG. 8** illustrates a scenario wherein oil converts to gas while migrating from source rock to reservoir rock through conduits constituting gas habitats;

[0027] **FIG. 9** shows, graphically, data for the samples in Table 1, wherein rate acceleration index A ($\log(\alpha)$) for the 10 rock samples and the synthetic sample representing a sandstone associated with 10% outer-neritic Monterey shale (% ONS), is provided;

[0028] **FIG. 10** depicts hydrocarbon composition as a function of depth within the various reservoirs shown in Table 1; and

[0029] **FIG. 11** depicts nickel concentrations in various sandstones from North America.

DETAILED DESCRIPTION OF THE INVENTION

[0030] In the following description, specific details are set forth such as specific quantities, sizes, etc. so as to provide a thorough understanding of embodiments of the present invention. However, it will be apparent to those skilled in the art that the present invention may be practiced without such specific details. In many cases, details concerning such considerations and the like have been omitted inasmuch as such details are not necessary to obtain a complete understanding of the present invention and are within the skills of persons of ordinary skill in the relevant art.

[0031] Referring to the drawings in general, it will be understood that the illustrations are for the purpose of describing a particular embodiment of the invention and are not intended to limit the invention thereto.

[0032] The present invention concerns paleocatalysis, a new field concerning catalysis proceeding over geologic time. Because these reactions are orders of magnitude slower than traditional catalytic reactions, they present formidable analytical challenges. A typical sedimentary rock can have as little as parts-per-billion (ppb) levels of zero-valent transition metal (ZVTM) and be effective paleocatalysts in the subsurface. In contrast, typical industrial catalyst have metal concentrations in the parts-per-hundred range. Industrial catalytic reactions will take minutes where paleocatalytic reactions will take millions of years. The analytical challenge is this: a reservoir rock that converts oil to gas in two million years at 150° C., will generate only $\sim 7 \times 10^{-7}$ g gas/(g rock hr) at 280° C. In one embodiment of the invention disclosed herein, this problem is addressed by sending 100% of the product (catalytic methane) directly into the analytical detector, typically a flame ionization detector (FID), to maximize accuracy and sensitivity. Using such techniques, it is possible to accurately measure paleo-activities as low as 10^{-9} g gas/(g rock hr) at reasonable laboratory temperatures. In another embodiment of the invention, unusually stable light hydrocarbons (ethane and propane, for example) are used as reactants so that high-temperature assays can be employed to boost product yield

without contaminating the product with thermal cracking products. In still other embodiments, the present invention is directed at using such techniques in concert with well logging. The Applicant is unaware of other analytical procedures for determining paleocatalytic activities with this degree of sensitivity and accuracy. The Applicant is also unaware of other analytical procedures for determining intrinsic catalytic activities of reservoir rocks, activities that realistically project to subsurface activities under natural conditions. The Applicant is also unaware of methods for predicting oil or gas in various reservoirs based on their intrinsic catalytic activities.

[0033] While most of the terms used herein will be recognizable to those of skill in the art, the following definitions are nevertheless put forth to aid in the understanding of the present invention.

[0034] "Sedimentary rock," as defined herein, refers generally to rock formed by the accumulation and cementation of mineral grains transported by wind, water, or ice to the site of deposition or chemically precipitated at the depositional site. The sedimentary rocks specific to this invention include reservoir rocks, source rocks, and conduit rocks. Reservoir rocks are rocks that trap and sequester migrating fluids. "Source rocks" are rocks within which petroleum is generated and either expelled or retained. "Conduit rocks", as defined herein, are rocks through which petroleum migrates from its source to its final destination. A "sedimentary basin," as defined herein, is an accumulation of a large thickness of sediment, as in sedimentary rock. "Outcrop rocks," as defined herein, generally refers to segments of bedrock exposed to the atmosphere.

[0035] A "target reservoir", as defined herein, refers to a drilling prospect in a sedimentary basin comprising a sedimentary rock believed to be a reservoir containing economic quantities of oil or gas.

[0036] A "gas habitat," as defined herein, refers to a "sedimentary rock" within a sedimentary basin that is sufficiently catalytic to convert 90% or more of its contained oil to gas over the specified time-temperature residence interval, typically 10 million years (Ma) for basins where subsidence rates place reservoirs at temperature T_r ($\pm 10^\circ \text{C}$.) for 10 Ma. The rate of oil-to-gas conversion at T , $k(T)$, is determined from the linear $\ln k$ vs. T equation, like that shown in the plot of FIG. 5 determined for a rock from multiple rock assays at different temperatures. Alternatively, $k(T)$ can be approximated from a single rock assay from the Arrhenius equation in Mango, "Transition metal catalysis in the generation of natural gas," *Organic Geochemistry*, 24:977-984, 1996, assuming Ni is equivalent to ZVTM. A temperature vs. time t plot, T vs $\log(\text{Ma})$, like the "Ni Equivalent" curves in FIGS. 6 & 7, define the gas habitat field to the right of the temperature-time curve. These curves, or curves for genetically similar reservoir rocks, define where in time-temperature space a given rock will have a high probability of containing gas.

[0037] An "oil habitat," as defined herein, refers to a "sedimentary rock" within a sedimentary basin that is not sufficiently catalytic at a specified basin temperature T to convert 90% or more of its contained oil to gas over a specified period of geologic time t . The temperature-time curve for a specified rock defines the oil habitat field for that reservoir rock to the left of the curve. Thus, there is a high

probability of finding gas in a reservoir targeted for drilling designated a "gas habitat" and oil in a reservoir targeted for drilling designated an "oil habitat." See commonly assigned co-pending U.S. patent application Ser. No. 10/830,266. Conversely, such ZVTM content can be inferred indirectly through a determination of intrinsic catalytic activity.

[0038] "Oil-to-gas," as defined herein, refers to geological processes in which crude oil (higher molecular weight hydrocarbons) converts into natural gas (lower molecular weight hydrocarbons). In the "thermal model," as defined herein, which is the generally accepted but imperfect model, oil-to-gas proceeds through thermal cracking and is thus a function of reservoir temperature and geologic time. Oil-to-gas in the "catalytic model," as defined herein, refers to a newer, but experimentally confirmed process, whereby oil is catalytically converted to gas with the aid of ZVTM. See Mango et al., "Role of transition-metal catalysis in the formation of natural gas," *Nature*, 368:536-538, 1994. The reservoir rock in the catalytic model is an active agent in oil-to-gas and a passive agent in the thermal model. Concentrations of ZVTM control oil-to-gas rates in the catalytic model and the kinetic parameters associated with thermal cracking control oil-to-gas rates in the thermal model. The two models have profoundly different predictive powers in oil and gas exploration.

[0039] An "active reservoir," as defined herein and in accordance with the oil-to-gas catalytic model, refers to a reservoir in which the surrounding sedimentary rock comprises at least a critical concentration of ZVTM as defined above. An "inactive reservoir," as defined herein and in accordance with the oil-to-gas catalytic model, refers to a reservoir with a less than critical concentration of ZVTM.

[0040] "Transition metal," as defined herein, refers to metals comprised of elements of the "d-block" of the Periodic Table. Specifically, these include elements 21-29 (scandium through copper), 39-47 (yttrium through silver), 57-79 (lanthanum through gold), and all known elements from 89 (actinium) on. Iron (Fe), cobalt (Co), and nickel (Ni) all have special relevance, however, due to their established catalytic activity. See Mango and Hightower, "The catalytic decomposition of petroleum into natural gas," *Geochimica et Cosmochimica Acta*, 61:5347-5350, 1997.

[0041] "Zero-valent transition metal(s)," as used herein, are transition metals in their zero-oxidation (i.e., neutral) state. This includes metal compounds in which a fraction of the metal in the compound retains valence electrons. For example, nickel does not retain valence electrons in NiO and NiS by this definition because it surrenders both of its valence electrons to oxygen and sulfur, respectively, but compounds like Ni_xO and Ni_yS , in which x and y are >1 , are potentially catalytic because a fraction of Ni (i.e., $(x-1)$ and $(y-1)$, respectively) retains valence electrons and thus a fraction of the Ni in these compounds is zero-valent. The transition metals in the minerals pentlandite ($(\text{Fe,Ni})_9\text{S}_8$), skutterudite ($(\text{Co,Ni})\text{As}_3$), and ullmannite (NiSbS) are viewed as containing zero-valent metals by this definition and are, therefore, potentially catalytic.

[0042] "Quantitative analysis," as defined herein, generally refers to the determination of species quantity and/or concentration with a high level of precision. In contrast, "qualitative analysis" generally describes a lower level of precision, but still at a level capable of being used for predictive determinations.

[0043] An “assay,” according to the present invention, generally refers to a quantitative or qualitative analysis (i.e., evaluation) of a sample. To assay a sample is to subject it to quantitative or qualitative analysis.

[0044] “Catalytically-generated methane,” abbreviated “CGM” and as used herein, refers to methane generated via the catalytic decomposition of hydrocarbon material. Such catalytic decomposition, in the assays of the present invention, is induced via the catalytic activity of rock samples comprising ZVTM, and in accordance with the catalytic oil-to-gas model. Without such ZVTM present in the rock sample being assayed, no CGM will be produced.

[0045] “Catalytic activity,” as defined herein, refers to the propensity of a catalyst to catalyze the catalytic decomposition of hydrocarbons to form CGM. “Intrinsic catalytic activity” refers to an unadulterated catalytic activity (i.e., such activity has not been compromised by exposure to oxygen) of a rock sample (source rock) that is equitable to the native catalytic activity of the reservoir or reservoir region from where the sample was extracted.

[0046] “Genetically similar,” as defined herein, refers to rocks that are similar in overall organic and inorganic composition and which were deposited under similar depositional environments. Genetically similar rocks can be expected to contain similar concentrations of ZVTM and have similar levels of catalytic activity.

[0047] “Paleocatalysis,” as defined herein, refers to catalytic reactions that proceed over geologic time. The paleocatalytic reaction specific to this invention is the conversion of oil to natural gas catalyzed by ZVTM. Like conventional commercial catalysts, paleocatalysts will express different levels of catalytic activity depending on how they were synthesized. Thus, one rock possessing ZVTM need not be similar in catalytic properties to another rock possessing similar concentrations of ZVTM. Genetically similar rocks, on the other hand, having been naturally synthesized under similar circumstances, should be similarly catalytic.

[0048] “Habitat maps,” as defined herein, refers to maps of stratigraphic rock units showing the lines of intersection between oil and gas habitats as defined herein.

[0049] A “well log,” as defined herein, is a record of the measured or computed physical characteristics of the rock section encountered in a well, typically as a function of depth. See Dictionary of Geological Terms, 3rd edition, R. L. Bates and J. A. Jackson (eds.), Anchor Books, New York: 1984. “Well logging,” as defined herein, is the process of acquiring such well log(s).

[0050] Embodiments of the present invention are generally directed to novel assays for ZVTM, and to methods of assaying rock samples potentially comprising ZVTM for intrinsic catalytic activity. The novel assays of the present invention are generally methods or processes for quantitatively and/or qualitatively evaluating the catalytic activity of, and the presence of ZVTM in, rock samples. Furthermore, application of such assays to oil and gas exploration provides for revolutionary advances in the predictability of oil and gas deposits based upon observed catalytic activity and/or the levels of ZVTM present in the surrounding sedimentary rock.

[0051] Referring to FIG. 1, assays of the present invention generally comprise the following steps: (Step 1001) pro-

cessing rock sample potentially comprising ZVTM so as to provide freshly exposed surface; (Step 1002) exposing the rock sample to a mixture of hydrogen gas and hydrocarbon material (reaction mixture) under appropriate conditions such that the hydrocarbon material undergoes decomposition yielding catalytically-generated methane if ZVTM is present; and (Step 1003) detecting the presence of any catalytically-generated methane (CGM). The presence of CGM confirms intrinsic activity imparted by ZVTM in the sample. Generally, such rock samples are sedimentary rock samples. Typically, a heat extraction step is carried out between Steps 1001 and 1002 to extract from the sample any non-catalytically produced hydrocarbons (including methane) that could contaminate the final catalytically-generated methane (CGM) product. In some embodiments, a separating step is carried out between Steps 1002 and 1003, wherein CGM is separated from other hydrocarbons. Additionally, in some embodiments, the amount of CGM generated in Step 1002 is measured and quantified.

[0052] Typically, the rock sample is obtained from a reservoir of interest such that information about said rock, acquired through the assays of the present invention, is equitable to the reservoir itself (the source reservoir) and any other genetically similar reservoir. There is great flexibility in the quantity of rock sample used in the assays of the present invention. Generally, the amount of rock sample used is between about 0.1 g and about 20 g, typically between about 0.5 g and about 10 g, and more typically between about 0.5 g and about 5 g. In some embodiments, “side wall” rock samples are selected for the assay because such samples are less likely to be contaminated by oxygen. In some embodiments, outcrop rock are selected for the assay because such samples, if sufficiently large (a few mm in diameter), retain an inner core uncontaminated by oxidation.

[0053] Processing rock sample potentially comprising ZVTM so as to provide freshly exposed surface generally comprises a grinding technique, wherein the rock sample is ground. Such grinding can be accomplished with mortar and pestle by hand or mechanically milling by placing the rock samples in a closed brass cylinder containing a brass ball and shaking the cylinder with a mechanical ‘paint shaker’ for a short period of time, typically 15 minutes. Mechanical rock crushing in brass prevents sample contamination by transition metals in steel cylinders and balls. Because mechanical rock crushing can generate heat, and thus promote the oxidation of ZVTM if mechanical crushing is carried out in air, it is best to seal the cylinder in an inert atmosphere free of oxygen.

[0054] There can be considerable variability in the mesh size and surface area of the particles of which the ground rock sample is comprised. In some embodiments, the ground sample is sieved to include or exclude particles of a particular size or range of sizes.

[0055] Generally, the above-described processing to provide freshly exposed surface is generally carried out in an inert, non-oxidizing atmosphere. Suitable inert, non-oxidizing atmospheres include, but are not limited to, inert gases like Ar, He, N₂, Kr, and combinations thereof. In some embodiments, the inert gases are scrubbed of oxygen (O₂) by passage through a special filter. Such filters typically comprise metals which reacts with the O₂.

[0056] Care is generally taken to ensure that the processed samples do not contact O₂ until after they have been exposed to hydrogen/hydrocarbon in the assay reaction. If such processed samples do come into contact with O₂, any zero-valent metals potentially present in such samples will be at least partially oxidized, and any catalytic activity that the rock might possess will be reduced below the native catalytic activity. This is because the catalytic oil-to-gas process is highly specific to zero-valent metals and the active sites on the surfaces of zero-valent metals are extremely sensitive to destruction by oxygen. Such oxidation will lead to catalytic activity determinations for the rock sample that are below that for the source reservoir. Consequently, any projection of such determined activity onto the source reservoir will be underestimated.

[0057] The step of exposing can be carried out in either a static or flow system. Referring to FIG. 2, in an exemplary static system, a rock sample 201 is placed in a reaction chamber 200 capable of being heated with a heating element 202. Hydrogen reactant gas is introduced through inlet 203 with valve 204 open and valve 205 open. Hydrocarbon reactant is introduced through inlet 206 with valve 207 open. With sufficient reactants in the reaction chamber 200, the system is closed by closing valves 204, 205 and 207. The closed chamber is then heated to the desired level (determined via thermocouple 208). After sufficient time, valves 204 and 205 are opened allowing hydrogen gas to pass through the reaction chamber 200 carrying the product gases, potentially comprising CGM, out of the reaction chamber through exit 209 to a separator that removes CGM from all higher hydrocarbons and sends it to a detector for analysis. Alternatively, such a system could be run in a flow mode, wherein valves 204, 205, and 207 are kept open. Such flow scenarios, however, generally require detection techniques with greater sensitivity than that required for the static systems.

[0058] Exposure duration, i.e., the time in which a reaction mixture is in contact with a processed rock sample, can vary considerably. Generally, such exposure duration is between about 1 minute and about 30 days, typically between about 1 minute and about 24 hours, and more typically between about 1 minute and about 1 hour.

[0059] Exposure conditions include variables such as temperature and pressure. The temperature at which the step of exposing is carried out is generally between about 150° C. and about 450° C., typically between about 200° C. and about 350° C., and more typically between about 220° C. and about 300° C. The hydrogen gas partial pressure at which the step of exposing is carried out is generally between about 1 torr and about 100 torr, typically between about 1 torr and about 50 torr, and more typically between about 1 torr and about 5 torr. These temperatures are generally above that typically found in source reservoirs.

[0060] Typically, when exposing a rock sample to a mixture of hydrogen gas and hydrocarbon material, the hydrocarbon to hydrogen gas ratio can be between about 1:1000 and about 1000:1, as determinable by their partial pressures. Because this catalytic reaction is zero-order, its rate is independent of reactant concentrations beyond sufficient concentrations to saturate the active sites dispersed over the rock surface. Reactant concentrations (partial pressures of hydrogen and hydrocarbon) are, therefore, critical only

below saturation concentrations. To obtain accurate assays, it is essential to maintain hydrogen and hydrocarbon concentrations above saturation. In some embodiments, one or both of the hydrocarbon material and hydrogen gas are optionally scrubbed of oxygen prior to being introduced into the reaction chamber. In some embodiments, the hydrocarbon material and hydrogen gas are pre-mixed prior to being introduced into the reaction chamber through inlet 207, while in other embodiments they are mixed within the reaction chamber by mixing the rock sample with hydrocarbon prior to placing the sample into the reaction chamber 200 or by injecting hydrogen through inlet 203 and hydrocarbon through inlet 206 separately.

[0061] The hydrocarbon material typically comprises one or more gaseous hydrocarbon species, but may also comprise liquid hydrocarbon material. In some embodiments, a quantity of a single hydrocarbon material is used, but mixtures of hydrocarbon species can also be employed. Typically, the hydrocarbon material comprises hydrocarbon species having between two and eighteen carbon atoms. Such hydrocarbon species can be aliphatic and/or aromatic and may contain one or more heteroatoms (e.g., O, N, S).

[0062] As mentioned above, in some embodiments, between the steps of exposing and detecting, a separating step is employed. Such separating steps can be used to separate any catalytically generated methane, potentially produced in the exposing step, from other hydrocarbon species. In some embodiments, this separation involves a cold trap (e.g., a liquid nitrogen trap) that condenses all other hydrocarbons, but allows methane to pass through and on to the detector/analyzer. In other embodiments, a chromatographic separation is employed. In such latter embodiments, a gas chromatographic column is usually employed, the column comprising any one of a number of suitable stationary phases suitable for the separation of methane from heavier hydrocarbons.

[0063] In some embodiments, detecting the presence of CGM in the above-described assay involves a detection device selected from the group consisting of a flame ionization detector (FID), a mass-selective detector, a spectroscopic detector, an electron capture detector, a thermal conductivity detector, a residual gas analyzer, and combinations thereof.

[0064] Depending on the embodiment, such above-described methane detection can provide qualitative and/or quantitative analysis. In some embodiments, when assaying a rock as described above, the qualitative analysis of catalytically-generated methane is sufficient to make predictive assessments as to the content (i.e., primarily oil or primarily gas) of a reservoir from where the analyzed rock was extracted. In some or other embodiments, a more quantitative analysis provides greater insight into the content of the source reservoir.

[0065] In some embodiments, oil or gas predictions can be made on a reservoir other than the source reservoir if the two reservoirs share a common depositional environment and thus can be expected to be similar in overall composition and ZVTM content. Such reservoirs are referred to here as "genetically similar" reservoirs. This application is particularly powerful because it can potentially predict oil or gas in an un-drilled reservoir based on analysis of rocks taken from drilled genetically similar reservoirs distal from the un-

drilled reservoir. In other embodiments, stratigraphic units can be mapped for catalytic activity by assaying representative rock samples covering the various depositional environments throughout the stratigraphic units. From the paleo-catalytic activities at depth and residence times, habitat maps can be constructed showing where in these units oil will convert to gas and where it should not, thus where in the basin the probability for oil is high (oil habitats) and where it is low (gas habitats). Habitat maps could be particularly useful in mapping sedimentary rocks that are particularly rich in transition metals such as the outer-neritic shales (Cruickshank, M. J., and Roland, T. J. Jr., "Mineral deposits at the Shelfbreak," SEPM Special Publication No. 33, 429-436, 1983; Mann, U., and Stein, R. "Organic facies variations, source rock potential, and sea level changes in Cretaceous black shales of the Quebrada Ocal, Upper Magdalena Valley, Colombia," *American Association of Petroleum Geologists, Bulletin* 81:556-576, 1997) and the so-called black shales (Rimmer, S. M., "Geochemical paleoredox indicators in Devonian-Mississippian black shales, Central Appalachian Basin (USA)," *Chemical Geology* 206:373-391, 2004.).

[0066] In some embodiments, upon quantitatively and/or qualitatively analyzing the catalytically-generated methane, the rock sample is ascribed an intrinsic catalytic activity. Such an intrinsic catalytic activity can then be projected onto the reservoir (from where the rock was extracted (i.e., the source reservoir), or a genetically similar reservoir, so as to determine whether the intrinsic catalytic activity is sufficient to enable significant oil-to-gas conversion over geologic timescales (e.g., eons) and under environmental conditions (temperatures and pressures) within the reservoir. By processing the rock samples under inert conditions, thereby precluding oxidation of the active sites in any ZVTM potentially present, the intrinsic catalytic activity so determined is equatable to the native activity within the reservoir.

[0067] The usefulness of many such above-described embodiments lies in using the knowledge of catalytic activity to predict whether a particular reservoir will be likely to contain predominantly oil or predominantly gas, based upon the catalytic activity of the reservoir, as determined from analyzing a rock sample obtained from said reservoir or a genetically similar reservoir, with an assay of the present invention. Such assays can permit the designation of a reservoir as being a gas habitat or an oil habitat, in accordance with the oil-to-gas model, with a direct measurement of the catalytic activity of source rock from said reservoir or from a genetically similar reservoir.

[0068] In some embodiments, an analysis of the amount of methane produced under a given set of conditions and a given timeframe permits the generation of a rate constant, k , for such a reaction for a particular reaction temperature. If such rate constants are determined for two or more such reaction temperatures, a plot of $\ln k$ versus T ($\ln k$ vs. T plot) can be generated. Such $\ln k$ vs. T plots can be extrapolated to yield a rate constant for the source reservoir or genetically similar reservoir. With such a source reservoir rate constant, it is possible to determine the extent and significance of oil-to-gas processes within said reservoir over geologic timescales.

[0069] Predictive determinations of oil or gas in a reservoir are based upon the required presence of ZVTM for

catalytic conversion of heavier hydrocarbons to natural gas (Mango, "The origin of light hydrocarbon," *Geochimica et Cosmochimica Acta*, 64:1265-1277, 2000). For example, outer-neritic shales (black shales) are one of the richest sources of transition metals in sedimentary rocks, and reservoirs comprising such shales are much more likely to be active reservoirs, i.e., gas habitats as opposed to oil habitats. The present invention permits such predictive determinations to be made via direct evaluation of the intrinsic catalytic activity of source rock as opposed to determining whether such rock has a threshold concentration of ZVTM.

[0070] While not intending to be bound by theory, it is believed that interaction of the reaction mixture is primarily a surface phenomenon. In such cases, the levels of potential catalytic activity, relative to the surface area and/or surface area per unit mass of the sample, can be quantified. An exemplary method of determining surface area is by Brunauer, Emmet, and Teller (BET) analysis.

[0071] In some embodiments, one or more of the above-described processes may comprise one or more contamination control measures, wherein such contamination control measures are employed when handling samples prior to or during the assay process.

[0072] The ZVTM of significance with respect to the methods and processes of the present invention include all ZVTM that suitably catalyze the decomposition of hydrocarbons to yield catalytically-generated methane in accordance with the methods and processes of the present invention. For the purposes of oil and gas exploration, these include, but are not limited to, iron (Fe), cobalt (Co), and nickel (Ni).

[0073] While the discussions herein have focused primarily on catalytic activity afforded by ZVTM, the present invention is generally directed toward ascertaining intrinsic catalytic activity of rock samples for the purpose of ascertaining catalytic oil-to-gas conversion within reservoirs. As such, Applicant does not preclude the possibility that zero-valent metals other than transition metals may provide some catalytic activity. Thus, it is possible that rare earth metals, in their zero-valent state, can contribute to the oil-to-gas conversion, even if such contribution is small by virtue of their presence in trace amounts.

[0074] In some embodiments, the optional step of separating is coupled with the detection/analysis step. This is particularly well suited for embodiments employing chromatographic separation, and to gas chromatographic separations in particular. Suitable gas chromatographic (GC) methods, coupled with a detection/analysis technique, include, but are not limited to, gas chromatography-mass spectrometry (GC-MS), gas chromatography-electron capture detection (GC-ECD), gas chromatography-pulsed flame photometric detection (GC-PFPC), gas chromatography-Fourier transform infrared spectroscopy detection (GC-FTIR), and combinations thereof.

[0075] In some embodiments, any or all of the above-mentioned methods and assays can be used during the course of, or in concert with, well logging. Accordingly, such well logging can provide well logs with intrinsic catalytic activity of sedimentary rock as a function of well depth.

[0076] Most generally, the present invention is directed to methods of making predictive determinations whether a

reservoir is active or inactive, in accordance with the oil-to-gas catalytic model, by assaying the surrounding sedimentary rock for catalytic activity, and by consequence, ZVTM.

[0077] In economic terms, if a reservoir is sufficiently removed from natural gas markets, then the economic incentives for drilling in an oil habitat greatly outweigh those for drilling in a gas habitat. The present invention permits such determinations to be made inexpensively with a relatively high level of accuracy, helping to avoid significant and costly exploration processes in order to ascertain the reservoir content.

[0078] The following Examples are provided to demonstrate particular embodiments of the present invention. It should be appreciated by those of skill in the art that the methods disclosed in the Examples which follows merely represent exemplary embodiments of the present invention. However, those of skill in the art should, in light of the present disclosure, appreciate that many changes can be made in the specific embodiments described and still obtain a like or similar result without departing from the spirit and scope of the present invention.

EXAMPLE 1

[0079] This Example serves to illustrate an embodiment by which the present invention can be used to assay sedimentary rock for oil-to-gas catalytic activity via the detection of catalytically-generated methane produced when a gaseous hydrocarbon species is contacted with said rock in the presence of hydrogen and under static exposure conditions.

[0080] A one gram sample of source rock (Miocene Monterey formation, California, taken from an outcrop on Venice Beach) was ground to 60 mesh and mixed with 5 cubic centimeters (cc) of sand under argon, and then heat-extracted at 300° C. for 30 minutes in flowing purified H₂. Referring to reaction system 300 in FIG. 3, this mixture was sealed in a 10 cc brass reactor 301, then pressure vented five times at room temperature with a gas mixture of 97% H₂ and 3% propane (C3), the gases purified by passage through commercial O₂ scrubbers 302 (BOT-2 purchased from Agilent Technologies, Willington, Del.). Each pressure vent involved opening 3-way valve 303 to vent. With valve 304 closed, the reactor was then pressurized to 50 psig with the gas mixture (valve 305 open), then closed by closing valve 306. With valve 306 closed, valve 304 was opened slowly to allow the reactor to vent to atmospheric pressure. This was repeated five times to remove all oxygen from the sample particles, the reactor 301, and all associated tubing. Inside the closed reactor at 50 psig gas mixture (valves 306 & 307 closed), a mixture of rock sample, hydrogen, and propane, the hydrogen and propane above catalyst saturation partial pressures, was then heated to 260° C. for 30 minutes, then brought back to room temperature. With the reactor at 200° C., it was then opened (valves 306 & 307 open) to flowing H₂ gas (valve 305 closed and valve 308 opened) through a liquid nitrogen (LN₂) trap 309 and directly into a FID detector 310 (3-way valve 303 open to FID) at a flow rate of ~0.2 cc/min (adjusted via needle valve 311), the same rate used to calibrate the detector using a 3% propane/hydrogen mixture as a standard for calculating g CH₄/pA see (pA=pico amperes). An integrator attached to the FID detector inte-

grated the eluting methane signal which indicated a rock activity of ~3×10⁻⁵ g CH₄/(g rock hr).

EXAMPLE 2

[0081] This Example serves to illustrate an embodiment wherein the hydrocarbon material is a liquid and illustrates activity suppression by high concentrations of hydrocarbon and also illustrates the catalytic nature of the reaction.

[0082] A sample of Monterey rock (0.88 g) like that in Example 1, heat-extracted at 350° C. for 30 minutes in purified H₂, was saturated with 100 micro liters of n-nonane (C9) and placed in Reactor 301. After five pressure-vents, as described in Example 1 using ultra pure H₂ purified through oxygen scrubber 302 at room temperature, the reactor was closed (valves 306 and 307 closed) and heated to 240° C. for 30 minutes. The product, vented to FID (310) at 100° C. over about 30 minutes, indicated a catalytic activity of ~3×10⁻⁶ g CH₄/(g rock hr). The reaction was repeated without adding additional n-nonane. The second product was ~70 times that of the first with an activity of ~2×10⁻⁴ g CH₄/(g rock hr). These results illustrate activity suppression in the first reaction by excess liquid hydrocarbon suppressing hydrogen diffusion to the active sites. Similar suppressions were observed for pure nickel powder when a film of wax was dispersed over its surface. Because excess hydrocarbon was removed between the first and second reaction on venting to FID (310), hydrogen access to the active sites was unimpeded in the second reaction. The dramatic increase in methane yield between the first and second reactions also illustrates the catalytic nature of the reaction. If thermal cracking were the source of methane, the yield in the first reaction would be greater than that in the second, not less.

EXAMPLE 3

[0083] This Example serves to illustrate an embodiment wherein the products are separated by gas chromatography. It also illustrates 1) that sedimentary rocks are catalytic in their natural state without added hydrogen or hydrocarbon, 2) that catalytic activity increases by a factor of 20 with H₂ addition, 3) that catalytic activity is destroyed with the addition of oxygen-contaminated 1% pentane/hydrogen, and 4) that hydrocarbons in a natural source rock (and pentane) undergo insignificant thermal decomposition to thermal methane under reaction conditions. These results illustrate that sedimentary rocks are naturally catalytic in the conversion of hydrocarbons to natural gas.

[0084] Referring to FIG. 4, a Monterey source rock similar to those used above (0.25 g), except that it was not heat-extracted, was placed in reactor 401 and flushed with purified He (through oxygen scrubber 402) to vent (valves 403, 404, 405, and 406 open) as the reactor temperature was increased from room temperature to 280° C. Reactor 401 was then closed (valves 404 and 405 closed) for 23 hours. Opened to He flow (280° C.) (valves 404 and 405 opened), 100 micro liter aliquots were taken at time intervals selected to capture maximum product from the effluent stream and sent to the GC unit 407 through sample loop 408 for product separation and analysis. A typical product was 69% methane (wt % C1-C4) with a methane GC peak intensity of 43 pA sec. The above reaction was repeated (0.3 g rock) using purified H₂ (through scrubber 402) in place of He. The product extracted from the effluent stream and analyzed

under the same conditions showed significantly higher concentrations of methane: 350 pA sec. The composition of the product gas, corrected for olefins (thermal products), was 97% methane (C1-C4). A third reaction on the Monterey source rock under the same conditions except that the purified H₂ was replaced by a mixture of unpurified pentane (1%) in hydrogen (99%) (valve 409 open, valve 403 closed) showed only trace amounts of methane. This third reaction serves as a blank experiment in which the catalytic activity of the Monterey rock was destroyed by the unpurified gas. The experiment demonstrates that hydrocarbons (in the Monterey source rock and pentane) undergo minimal thermal decomposition to methane under these reaction conditions. Thus, the methane produced under the same conditions using purified gases was catalytic methane.

EXAMPLE 4

[0085] This Example serves to illustrate how a $\ln k$ vs. T plot can be generated and how such a plot can be extrapolated to yield k for reservoiric conditions.

[0086] Steady-state flow reactions were carried out using ultra-pure nickel powder (~1 g) obtained from Sigma-Aldrich, 203904-25 (99.99% Ni), 100 mesh. 1% n-Pentane in H₂ was passed through the oxygen scrubber 302 in FIG. 3 at a flow rate of 0.4 cc/sec directly to FID detector 310 (valves 305, 306, and 307 open and 3-way valve 303 directed to detector 310). The methane signal (pA) climbed smoothly from 240 to 270° C. The plot in FIG. 5 shows a perfect linearity between $\ln k$ vs. T , where k was calculated from a prior calibration using 3% C₃/H₂ ($k=(pA) \times 4.077 \times 10^{-11}$). The linearity in $\ln k$ vs. T and the independence between k and hydrogen and hydrocarbon concentrations (demonstrated in separate experiments) is consistent with zero-order kinetics.

EXAMPLE 5

[0087] This Example serves to illustrate an embodiment wherein the hydrocarbon material is a liquid dispersed on sand. It further illustrates an embodiment wherein the analysis of a rock from one basin correctly predicts gas in a genetically similar rock in an adjacent basin. A thermal cracking model incorrectly predicts oil.

[0088] n-Nonane (C₉) was dispersed on pure quartz sand by evaporating to dryness a slurry of 100 cc sand and 50 ml pentane containing 1 g n-nonane. A sidewall core sample of Barnett shale (Mississippian) from the Hardeman basin, Texas was ground to 60 mesh under Ar and heat-extracted at 350° C. in flowing purified H₂ for 30 minutes. The product (0.84 g) was mixed with 5 cc of the nonane-impregnated sand and the mixture placed in Reactor 301 (FIG. 3). The reactor was pressure-vented (50 psig) with ultra pure H₂ as described above. With the reactor closed at room temperature and 50 psig H₂ (valves 306 & 307 closed), the reactor was heated to 280° C. for 1 hour, then cooled to 200° C., then opened to FID unit 310 through valve 303 by opening valves 306 and 307. The integrated methane product indicated a rate constant $k \approx 1 \times 10^{-4}$ g CH₄/(g rock hr).

EXAMPLE 6

[0089] This Example serves to illustrate an embodiment wherein the reaction is carried out under static conditions from steady-state flow at constant temperature. It further

illustrates the embodiment wherein unusually stable light hydrocarbons are employed as reactants so that high-temperature assays (350+° C.) can be employed to boost reaction rates without contaminating the catalytic methane with thermal cracking methane. Propane, used in EXAMPLE 6, has a half-life at 200° C. of 800 million years (Laidler, K. J., Sagert, N. H., and Wojciechowske, B. W. "Kinetics and Mechanisms of the thermal decomposition of propane," *Proceedings of the Royal Society* A270, 242-253, 1962) while ethane has a half-life of 50 billion years at the same temperature (Laidler, K. J., and Wojciechowske, B. W. "Kinetics and Mechanisms of the thermal decomposition of ethane," *Proceedings of the Royal Society* A260, 91-102, 1961). Cycloalkanes are also unusually stable and can be employed for high-temperature assays without contaminating the catalytic methane product with thermal methane (Mango, F. D., "The origin of light cycloalkanes in petroleum," *Geochim. Cosmochim. Acta* 54, 23-27, 1990). This further illustrates an embodiment wherein a rock from one basin correctly predicts gas in a genetically similar rock in the same basin.

[0090] A sample (4.6 gm) of Barnett shale core (Ft Worth basin, Sims-2 well) ground to 60 mesh under Ar was placed in reactor 301 (FIG. 3), pressure-vented 5 times with 50 psig pure H₂ (oxygen-scrubbed through 302), then heat-extracted under purified H₂ flow (0.2 cc/sec) for 30 minutes at 350° C. The inlet gas was then switched to 3% propane in hydrogen (purified through 302) by closing valve 308 and opening valve 305. Gas flow to FID (0.2 cc/sec) was then continued at 350° C. until the FID signal was constant, whereupon the reactor was closed (valves 306 and 307 closed) for 5 minutes, then opened to FID. A catalytic methane peak emerged after about 10 minutes: $A=1.03 \times 10^5$ pA sec, corresponding to a catalytic activity of $k(350^\circ \text{C.})=1.1 \times 10^{-5}$ g C₁/(g rock hr). This rock would have a nickel-equivalent activity of 2.46×10^{-13} g C₁/(g rock hr) at 160° C. and would convert oil to gas in 6 Ma at this temperature (3% porosity filled with oil). Since the Barnett shale was at 160° C. for 20 Ma, genetically similar facies of Barnett shale would be designated gas habitats. After destroying all catalytic activity by injecting ~1 cc air with gas flow at temperature, a repeat of the reaction with 3% propane, 350° C., five minutes closed, showed no detectable amounts of methane, demonstrating the feasibility of high-temperature assay uncontaminated by thermal cracking.

[0091] FIG. 6 is a plot of temperature vs. residence time (in million of years, Ma) for the Barnett shale analyzed above (Example 5) showing where in time-temperature space this reservoir will contain oil (to the left of the Barnett curve, Curve A) and where it will contain gas (to the right of Curve A). The x axis is the log time, in millions of years (Ma), for 100% conversion of oil to gas in a rock with 3% porosity filled with oil (~0.013 g oil/g rock) at the indicated temperatures. Curve A, the Barnett curve (the 'Ni Equivalent Curve'), was constructed from the kinetic equation published by Mango (Mango, "Transition metal catalysis in the generation of natural gas," *Org. Geochem.* 24:977-984, 1996) for zero-valent nickel. A rate constant for Barnett at each temperature T (k_T) was calculated from the following equation, where k' is the rate constant for Ni published by Mango and k_T is the 'nickel-equivalent' rate constant for Barnett: $k_T=(k'_T/k'_{280}) \times 1E-04$. This curve is only an approximation of the true Barnett T vs time curve which is best constructed from multiple assays at multiple tempera-

tures to obtain an adequate linear relationship between $\ln k$ and T . It should be stressed that any 'true' Barnett curve thus obtained would need calibration to natural conditions where lower hydrogen partial pressures and retained hydrocarbons would serve to suppress the intrinsic activities measured in assays. Curve B, the thermal cracking curve, was constructed from the oil cracking kinetic data published by Waples for the same 3% porosity rock (Waples, D. W., "The kinetics of in-reservoir oil destruction and gas formation: constraints from experimental and empirical data, and from thermodynamics," *Org. Geochem.* 31:553-575, 2000). The data point represents the gas deposits in the Mississippian Barnett shale in the Ft Worth basin, Texas with an estimated residence time of 20 Ma at a temperature of $\sim 160^\circ\text{C}$. A thermal cracking model based on the Waples curve will incorrectly predict oil in the Ft Worth basin while the Barnett curve, from a rock assay of Barnett shale in a genetically similar reservoir in an adjacent basin (Hardeman basin), correctly predicts gas.

[0092] The box in **FIG. 7** encloses the time-temperature region where most oil-to-gas occurs in sedimentary basins according Hunt (Hunt, *Petroleum Geochemistry and Geology*, 2nd ed., W. H. Freeman, New York, Chapter 7, 1996). Thus, any method for predicting gas must be effective in this time-temperature region. The thermal cracking model published by Waples (Waples, "The kinetics of in-reservoir oil destruction and gas formation: constraints from experimental and empirical data, and from thermodynamics," *Organic Geochemistry*, 31:553-575, 2000), which is typical of most such models, can explain only $\sim 30\%$ of the observed cases. The catalytic model, as reflected in rock assays on Barnett and Monterey rocks described herein, will predict gas throughout the critical zone.

[0093] **FIG. 8** illustrates another application of the invention where oil converts to gas while migrating from source rock to reservoir rock through conduits constituting gas habitats. Consider, for reference, the examples of oil-to-gas reported by Paine (Paine et al., "Geology of natural gas in South Louisiana," American Association of Petroleum Geologists, Memoir 9, Volume 1, Natural Gases of North America, Beebe, B. W., Editor, 376-581, 1968) in the giant gas fields in southern Louisiana occurring in sandstone reservoirs interbedded with outer-neritic shales at depths usually greater than 10,000 ft. (temperatures $>140^\circ\text{C}$). Outer-neritic shales tend to be rich in transition metals like the Monterey source rock analyzed herein. The Monterey rock exhibits robust activity in assay which projects to very high paleoactivities at the temperatures indicated in the Paine publication (see **FIG. 7**). At 160°C ., for example, a sandstone reservoir interbedded with 1% Monterey shale would be a gas habitat at all residence times greater than 5,000 years—a tiny slice of geologic time. Migrating oil with a residence time greater than 5,000 years, at temperatures $\sim 160^\circ\text{C}$., would be converted to gas as indicated in **FIG. 8**. This concept, the conversion of oil to gas in migration, is new to oil and gas exploration. It provides a potentially powerful explanation for how oil from one reservoir (an oil habitat) becomes gas in a shallower reservoir, also an oil habitat. Gas habitats along migration pathways constitute gas conduits in an otherwise all oil plumbing system.

[0094] Thus, in light of the foregoing, the present invention provides extremely sensitive assays for determining the

catalytic activity of sedimentary rocks at levels as low as $0.01\ \mu\text{g CH}_4/(\text{g rock hr})$ based upon any ZVTM-induced catalytic decomposition of hydrocarbon material to generate methane. The fact that this activity is destroyed by oxygen points to a low valent-specific catalyst. That the catalytic action of pure zero-valent nickel is similarly destroyed by oxygen indicates that low-valent metals dispersed on the rock's surface are the active agents in sedimentary rocks. Furthermore, such catalytically-generated methane, if present, is indicative of the intrinsic catalytic activity of the rock sample. Assays at different temperatures yield a linear activity curve ($\ln k$ vs T) that is useful in predicting activities k at subsurface temperatures. Because subsurface conditions are different from laboratory conditions (hydrogen partial pressures, hydrocarbon concentrations and other unanticipated factors that might alter reaction rates) the activity curve should be calibrated on reservoirs for which residence time t , temperature T , and % oil conversion to gas are known, thus giving subsurface activity at temperature T , $k_s(T)$. A correction factor α ($\alpha = k_s(T)/k(T)$) thus converts the assay activity curve to the sub-surface curve: $\ln k_s$ vs. T . Such curves give the rate constants for source reservoirs and all genetically similar non-source reservoirs at all subsurface temperatures. The time for 90+% oil conversion to gas can then be calculated for all sub-surface temperatures. This yields a curve like the Ni equivalent curve in **FIG. 6** that divides temperature-time space into oil and gas habitats, regions where the subject reservoirs have a high probability of containing oil or gas, respectively.

EXAMPLE 7

[0095] This Example serves to illustrate the analysis of various deltaic reservoir rocks from the Bastian Bay and Lake Raccourci fields, and how such analysis can be useful in well logging procedures, in accordance with embodiments of the present invention. All rocks were found to be catalytic, accelerating rates of gas generation by factors ranging from 2000 to well over 50000. Rocks with interbedded shales were on average five times more active than rocks without interbedded shale. Based on their measured activities, reservoirs would convert oil to gas at depths between 8,000 and 11,000 ft, remarkably close to Paine's observation that reservoir rocks with interbedded shales usually contain gas at depths greater than 10,000 ft (Paine et al., "Geology of natural gas in South Louisiana," American Association of Petroleum Geologists, Memoir 9, Volume 1, Natural Gases of North America, Beebe, B. W., Editor, 376-581, 1968). Activities were surprisingly high and pervasive, covering essentially all of the deltaic rocks so analyzed. The results presented here explain, for the first time, the vast amounts of gas in reservoir rocks that have never reached thermal cracking temperatures. Pure sandstone reservoir rocks are clearly catalytic and this property is likely responsible for the erratic and unpredictable distribution of gas in sandstone reservoir rocks. Nickel, one of the more active transition metals in sedimentary rocks, varies substantially in sandstones, from 5 ppm to 230 ppm in the 9 sandstones cited in Boggs (Principles of Sedimentology and Stratigraphy, 2nd ed, Prentice Hall, Upper Saddle River, N.J., 1995, p. 165). Thus, the catalytic activities of different sandstone strata should similarly vary. At a given temperature, high-activity reservoir rocks should thus contain gas while low-activity reservoir rocks should contain oil. A well log that includes catalytic activity would thus be useful in

correlating stratigraphic units across a basin and uniquely powerful for predicting hydrocarbon composition (% gas) within different strata at various depths throughout a basin.

[0096] Bastian Bay and Lake Raccourci fields are 2 of 18 fields cited in Paine et al. (1968) as being representative of over 670 fields in south Louisiana producing oil and/or gas from that portion of the giant Gulf Coast geosyncline as of 1962. Bastian Bay is located about 55 miles southeast of New Orleans in Plaquemines Parish. There are 133 Bastian Bay wells produced from Upper Miocene *Textularia articulate* sandstone. Bastian Bay was the largest gas-producing field in south Louisiana in 1962 yielding about 7.2 thousand bbl crude oil, 3.3 million bbl condensate, 1.5 billion scf solution and associated gas, and 100 billion scf of non-associated gas, or about 90% gas (oil equivalent). Lake Raccourci field is located in Lafourche and Terrebonne Parishes, approximately 42 miles south-southwest of New Orleans. Forty-eight wells produce from the Upper Miocene Eponides (*Buccella*) mansfieldi sandstones.

[0097] A Pan American Petroleum Corporation Bastian Bay core (13,298 to 13,606 ft.; API 1707501617) from well # A-17 (L. L. & E) was obtained from the Bureau of Economic Geology, Houston Research Center (11611 West Little York, Tex. 77041). It was mostly clean sandstone with intervals of sandstone with thin laminae of interbedded shale. A side-wall core from Lake Raccourci field (16,128 ft., Amco Production S/L 4599 #10, API 17-057-22201) was also obtained from the Bureau of Economic Geology.

[0098] Ten samples constitute the database described here: eight from Bastian Bay, one from Lake Raccourci, and the last sample a synthetic rock constructed to reflect genuine outer-neritic shale with 90% pure sandstone and 10% outer-neritic shale from the Monterey formation (Miocene) (Piper, D. Z., and Isaacs, C. M. (2001) "The Monterey Formation: Bottom-water redox conditions and photic-zone primary productivity," *From Rocks to Molecules*, Eds. C. M. Isaacs and J. Rullkotter, Columbia University Press, New York, 2001; Mann and Stein, "Organic facies variations, source rock potential, and sea level changes in Cretaceous black shales of the Quebrada Ocal, Upper Magdalena Valley, Colombia," *AAPG, Bulletin* 81:556-576, 1997; Cruickshank and Rowland, "Mineral deposits at the Shelfbreak," *SEPM Special Publication* No. 33:429-436, 1983) obtained from outcrop on Venice Beach, Calif. (10%ONS). Rocks were analyzed for catalytic activity by a procedures described herein. The kinetic experiments with pure nickel to obtain nickel-equivalent curves ($\ln(k)$ vs T) are given in Mango (1996). Pure nickel powder was obtained from Sigma-Aldrich (sub-micron sized nickel powder, 99.999% Ni).

[0099] In a typical experiment, rock chips taken from the core were ground to a powder, sieved to 60 mesh, and placed in a reactor similar to that shown in FIG. 3 (rock sample=6.54 gm) in an atmosphere of argon. The hydrocarbon feed gas (3% Propane in hydrogen) was purified to remove oxygen by passing the gas through one or more oxygen scrubbers 302 (OR-10 Pd/Alumina oxygen removing purifiers, Johnson Matthey Gas Purification Technology). The Ultra-Pure hydrogen gas was also purified by passing it through an OR-100 Oxygen Removing Purifier fitted before the oxygen scrubber 302. The system was purged of residual air by a series of five pressure-vents. Referring to FIG. 3, reactor 301 was then heated to reaction temperature (250°

C.) under hydrogen flow and the 3-way valve 303 opened to FID detector 310. With liquid nitrogen in trap 309, hydrocarbon feed was then injected into the reactor by closing valve 308 and opening valve 305 (3% C₃/H₂ gas at 50 psi) for 1 minute. Valve 305 was then closed, valve 308 opened and valves 307 and 306 closed. After 30 minutes standing at 250° C., the reactor was opened to the FID detector 310 by opening valves 306 and 307. Thus, the catalytic methane generated in the reactor over 30 minutes was swept into the detector 310 with flowing hydrogen and the peak integrated ($A=1.02 \times 10^{+7}$ μV sec). From the calibration coefficient (using 3% propane in hydrogen to calibrate) 1.7×10^{-12} g methane/ μV sec, the yield was 1.73×10^{-5} g methane ($k=5.3 \times 10^{-6}$ g C/(g rock hr)).

[0100] Catalytic activity is expressed here as a ratio, the rate acceleration ratio α , defined as: $\alpha=(t_{\text{pure quartz}}/t_{\text{(rock)}})$, where t is the time required for 99% conversion of oil to gas at 200° C. Since pure quartz has no catalytic activity, $t_{\text{(pure quartz)}}$ represents thermal cracking calculated from Waples (Waples, D. W., "The kinetics of in-reservoir oil destruction and gas formation: constraints from experimental and empirical data, and from thermodynamics," *Org. Geochem.* 31:553-575, 2000). Because α spans 7 orders of magnitude for common rocks, catalytic activity is also expressed logarithmically in the acceleration index A : $A=\log(\alpha)$. Table 1 shows the acceleration indices for the 11 samples analyzed here including one containing 1% pure zero-valent nickel for comparison. FIG. 9 shows the data graphically, wherein rate acceleration index A ($\log(\alpha)$) for the 10 rock samples in Table 1 and the synthetic sample representing a sandstone associated with 10% outer-neritic Monterey shale (% ONS). Table 1 also lists rate constants for converting oil to gas at 200° C. in units g CH₄/(g rock hr) determined experimentally ($k(200^\circ \text{C.})$) was determined by nickel-equivalent curves). The rate acceleration ratio $\alpha=(t_{\text{pure quartz}}/t_{\text{(rock)}})$, where t is the time required for 99% oil conversion to gas at 200° C. Since pure quartz has no catalytic activity, $t_{\text{(pure quartz)}}=1.36$ Ma for oil thermally cracking to gas (Waples, 2000). For the present example, it was assumed that the rock had a 3% porosity filled with oil (0.013 g oil/g rock), thermally cracking to gas under first order kinetics and catalytically cracking to gas under zero-order kinetics. All of the rock samples designated D- are from Bastian Bay field except for D-48, a sidewall core sample from Lake Raccourci field. Samples designated SS are sandstone rocks with no visible signs of interbedded shale while SS/S rocks are sandstone rocks with interbedded shales clearly visible. Rock labeled (A) are adjacent SS and SS/S rocks as are the rocks labeled (B).

TABLE 1

| Sample | Composition | Depth | k (200° C.) | $\alpha \times 10^{-3}$ |
|---------------|-------------|--------|-------------|-------------------------|
| D-45 | SS(A) | 13,507 | 2.49E-11 | 2.33 |
| D-49 | SS | 13,593 | 6.26E-11 | 5.85 |
| D-46 | SS/S(A) | 13,506 | 1.03E-10 | 9.66 |
| D-40 | SS(B) | 13,481 | 1.09E-10 | 10.2 |
| D-38 | SS/S | 13,445 | 1.52E-10 | 14.2 |
| D-42 | SS/S | 13,319 | 1.72E-10 | 16.1 |
| D-43 | SS/S | 13,319 | 1.78E-10 | 16.6 |
| D-44 | SS/S | 13,447 | 2.3E-10 | 21.5 |
| D-48 (Lake R) | SS/S | 16,128 | 3.3E-10 | 30.9 |
| D-41 | SS/S(A) | 13,481 | 6.0E-10 | 56.1 |
| 10% ONS | SS/S | — | 3.55E-7 | 332 |
| 1% Ni | — | — | 1.42E-3 | 1.33E+6 |

[0101] Rate constants were projected to subsurface temperatures assuming nickel-equivalence (i.e., Ni is dominant active metal in the rock). Oil conversion to gas was calculated from the geothermal gradient in Paine (1968) and the burial history curve of the Lower Miocene in South Padre Island (Huc and Hunt, "Generation and migration of hydrocarbons in offshore south Texas Gulf Coast sediments," *Geochimica Cosmochimica Acta*, 44:1081-1089, 1980). This gives an approximation of the critical depth, the depth at which the various reservoir rocks will convert 99% of their oil to gas. Because of the uncertainties in the assumptions, these depths are at best relative. While not intending to be bound by theory, there is probably substantial error in the estimated activities. This is because activity can only be lost in transportation and analysis, not gained. Thus, the indicated rates of conversion are probably below a rock's intrinsic rate of conversion—leading to an underestimation of activity. They are, nevertheless, qualitatively reliable. These rocks should be significantly catalytic at the basin depths indicated and rocks with interbedded shales should be significantly more active than those without shales.

[0102] The calculated depth for the most active natural rock (D-41, SS/S) was 8,300 ft and for the least active rock (D-45, SS), 10,700. A synthetic rock with 10% outer-neritic shale (10% ONS) would convert its oil to gas at about 7,000 ft, well above the critical depth of 10,000 ft. cited by Paine. Critical depths for all of the rocks analyzed in this study are shown in FIG. 10 along with an approximation of the critical depth for pure sandstone (pure quartz) which should retain oil to depths well below 20,000 ft. FIG. 10 also depicts hydrocarbon composition as a function of depth within the various reservoirs listed in Table 1. The line dividing oil and gas is the critical depth at which 99% of the oil within these rocks would convert to gas. A geothermal gradient was constructed from the data in Paine et al. (1968) and a time-temperature burial history was approximated from the South Padre Island burial curve in Huc and Hunt (1980). Each rock was assigned a nickel-equivalent Arrhenius equation ($\log(k)$ vs $1/T$) by fitting the measured rate constant for the rock to the Arrhenius equation for pure nickel (Mango, "Transition metal catalysis in the generation of natural gas," *Org. Geochem.* 24:977-984, 1996). Two assumptions were made to justify this: (1) k is directly proportional to metal concentration, and (2) Ni makes the major catalytic contribution to the rock's activity. The 99% conversion depth was obtained by integration over the time-temperature burial curve using nickel-equivalent rate constants. The data arbitrarily truncates at 22,000 ft.

[0103] The catalytic activities for relatively pure sandstone rocks (D-45, D-99, & D-40), although significantly lower than those associated with shales, were nevertheless surprisingly high, certainly high enough to impact the distribution of gas in these basins. Unlike outer-neritic shales which are enriched in metals through organic sedimentation, sandstone rocks enjoy no similar input. But sandstones do contain transition metals over a broad range of concentrations. Nickel, for example, varies from 5 to 230 ppm in the nine North American sandstones in FIG. 10. The Rhinestreet sandstone with 230 ppm Ni matches the most catalytic rock in nickel content, the outer-neritic Monterey shale with 250 ppm Ni. Metal concentrations, of course, do not necessarily equate with catalytic activity. Nickel is active only in its metallic form, all higher-valent nickel compounds are inactive. Because catalytic activity is pervasive across all

forms of sedimentary rocks analyzed herein, this suggests facile metal reduction in the subsurface. FIG. 11 depicts nickel concentrations in various sandstones from North America taken from Boggs (p. 165, 1995): (a) Shawangunk Formation (Silurian); (b) Millport Member of the Rhinestreet Formation (Devonian); (c) Oneota Formation (L. Ordovician); (d) Cloridorme Formation (Ordovician); (e) Austin Glen Member of the Normanskill Formation (M. Ordovician); (f) Renessalaer Member of the Nassau Formation (Late Proterozoic to Early Cambrian); (g) Renessalaer Member, additional analyses; (h) Rio Culebrinas Formation, Puerto Rico; (j) Turbidites from DSDP site 379A. Thus, the high metal content shown in FIG. 11 could very well signal significant activity in the subsurface. This would explain the unexpected activities measured here.

[0104] The results clearly support the hypothesis that outer-neritic shales impart sufficient catalytic activity to sandstone reservoir rocks to explain Paine's observation that these rocks contain predominantly gas at basin depths greater than 10,000 ft. The rocks from Bastian Bay and Raccourci fields are naturally catalytic and should convert oil to gas well below thermal cracking depths and certainly within the zones cited by Paine. All would accelerate rate of gas generation by factors ranging from 1,000 to well over 50,000. Similar catalytic activity can clearly be expected in the subsurface. Rocks are naturally catalytic and remain so over geologic time in subsurface environments. Potential poisons like water, sulfides, carbonates and so on are passive agents in the subsurface. If zero- or low-valent transition metals (LVTM) were poisoned by them, their activities would be irreversibly destroyed and remain so at the surface, which is clearly not the case. The conclusion that LVTM remain active in the subsurface is thus inescapable. This activity, however, does not guarantee paleocatalysis. Sustained catalysis requires a sustained supply of substrate, hydrocarbons and hydrogen—all of which are in abundant supply in petroliferous environments. Hydrogen concentrations are surprisingly high in gas habitats, on average 0.07% by volume of natural gas (Mango, "The origin of light hydrocarbons," *Geochim. Cosmochim. Acta* 64:1265-1277, 2000). This projects to a hydrogen partial pressure of 0.2 atm at 10,000 ft, certainly high enough to sustain the catalytic generation of gas.

[0105] All deltaic rocks analyzed here exhibit surprisingly high levels of catalytic activity, accelerating rates of gas generation by factors from 1,000 to well over 50,000. These activities are, moreover, low estimates of natural activities. Activity can only be lost in transportation from the subsurface and analysis, not gained. The rocks are probably more active than the analyses of the present invention might suggest. This could explain the most striking features to Bastian Bay hydrocarbons, the fact that they are essentially without oil (>95% gas and condensates). Because condensates represent the final stages of oil's conversion to gas, Bastian Bay hydrocarbons are approaching terminal maturity, maturity not easily explained by thermal evolution alone. Most Bastian Bay production is below 15,000 ft, at temperatures below 160° C. (Paine et al., 1968). Oil should remain stable at these temperatures for at least 100 Ma (Waples, 2000), and should thus be thermally stable indefinitely in Miocene reservoirs. In-reservoir thermal cracking simply cannot explain the extensive amounts of gas and condensates in the Bastian Bay field. The measured activities of Bastian Bay reservoir rocks place the oil floor

somewhere below 8,000 ft for the more active rocks, and below 11,000 ft. for the less active. This will explain most of the light hydrocarbons in the basin. If catalytic gas generated in migration is included, as oil converts to gas while passing through conduit rocks of high activity, the nearly complete disappearance of oil becomes understandable. Bastian Bay reservoir rocks are naturally catalytic and their measured activities reasonably explain the composition of hydrocarbons in Bastian Bay. Rocks with interbedded shales are on average five times more active than pure sandstone rocks and this explains Paine's general observation for all fields in the basin that reservoirs associated with outer-neritic shales have a high probability for gas at depths below 10,000 ft.

[0106] Thus, in light of the foregoing, the present invention provides extremely sensitive assays for determining the catalytic activity of rock samples based upon any ZVTM-induced (and possibly LVTM-induced) catalytic decomposition of hydrocarbon material to generate methane (e.g., in parts-per-billion quantities). Such catalytically-generated methane is unequivocal evidence of zero-valent metals dispersed on the rock's surface. Such catalytically-generated methane, if present, is indicative of the intrinsic catalytic activity of the rock sample, and via projection, the source reservoir. Furthermore, when such assays are coupled with well logging, they provide a well log that includes catalytic activity that is useful in correlating stratigraphic units across a basin and in predicting hydrocarbon composition (% gas) within different strata at various depths throughout a basin.

[0107] All patents and publications referenced herein are hereby incorporated by reference. It will be understood that certain of the above-described structures, functions, and operations of the above-described embodiments are not necessary to practice the present invention and are included in the description simply for completeness of an exemplary embodiment or embodiments. In addition, it will be understood that specific structures, functions, and operations set forth in the above-described referenced patents and publications can be practiced in conjunction with the present invention, but they are not essential to its practice. It is therefore to be understood that the invention may be practiced otherwise than as specifically described without actually departing from the spirit and scope of the present invention as defined by the appended claims.

What is claimed is:

1. A well logging method comprising:

- a) obtaining sedimentary rock samples during the course of well logging, wherein said sedimentary rock sample potentially comprises zero-valent transition metal; and
- b) analyzing said sedimentary rock samples by a method comprising:
 - i) a sample preparation step for exposing fresh surface of a quantity of the sedimentary rock sample;
 - ii) a reaction step for exposing the sedimentary rock sample to hydrogen gas and a hydrocarbon material in an exposure environment under assay exposure conditions, the hydrocarbon material comprising hydrocarbon species having two or more carbons and wherein said exposure leads to the catalytic generation of methane gas if zero-valent transition metal is present within the sedimentary rock sample; and

- iii) an analysis step for ascertaining the presence of methane catalytically-generated by zero-valent transition metal potentially present in said rock sample and, if present, for ascribing an intrinsic catalytic activity to said sedimentary rock,

wherein said analyzing yields a well log with intrinsic catalytic rock activity as a function of well depth.

2. The well logging method of claim 1, wherein the sample preparation step of said analyzing involves a grinding process for exposing fresh surface of a quantity of sedimentary rock sample.

3. The well logging method of claim 1, wherein the sample preparation step of said analyzing is carried out under inert conditions.

4. The well logging method of claim 1, wherein the exposure environment of the reaction step of said analyzing is carried out under conditions selected from the group consisting of static, flow, and combinations thereof.

5. The well logging method of claim 1, wherein the assay exposure conditions of said analyzing method comprise a temperature of between about 200° C. and about 450° C., and a hydrogen partial pressure of between about 0.1 torr and about 500 torr.

6. The well logging method of claim 1, wherein the reaction step of said analyzing method comprises a duration of between about 1 minute and about 30 days.

7. The well logging method of claim 1, wherein the hydrocarbon material used in the reaction step of said analyzing method comprises hydrocarbon species having 2-25 carbon atoms.

8. The well logging method of claim 1, wherein said analyzing method further comprises a separation step for separating any catalytically-generated methane from any other hydrocarbon species potentially present after the reaction step, wherein said separating is done by a method selected from the group consisting of condensing the other hydrocarbon species on a cold trap, chromatographic means, and combinations thereof.

9. The well logging method of claim 1, wherein the analysis step of said analyzing method involves detecting the presence of catalytically-generated methane using a detection device selected from the group consisting of a flame ionization detector, a mass-selective detector, a spectroscopic detector, an electron capture detector, a thermal conductivity detector, a residual gas analyzer, and combinations thereof.

10. The well logging method of claim 1, wherein ascribing an intrinsic catalytic activity to said sedimentary rock in the analysis step of said analyzing method further comprises determining a rate constant, k , associated with a given set of reaction conditions and a reaction duration, as utilized in the reaction step.

11. A well logging method comprising:

- a) obtaining sedimentary rock samples potentially comprising a quantity of at least one zero-valent transition metal during the course of well logging; and
- b) analyzing said sedimentary rock samples by a method comprising the steps of:
 - i) processing the sedimentary rock sample to provide freshly exposed surface;
 - ii) exposing the sedimentary rock sample to hydrogen gas and a quantity of hydrocarbon material in an

exposure environment under a set of assay exposure conditions, the hydrocarbon material comprising hydrocarbon species having at least two carbons, such that methane is catalytically generated if zero-valent transition metal is present within the sedimentary rock sample; and

- iii) analyzing the exposure environment for any catalytically-generated methane, generated as a result of said exposing, in order to ascertain the presence of zero-valent transition metal within said sedimentary rock sample and, if present, ascribing an intrinsic catalytic activity to the sedimentary rock for the set of assay exposure conditions,

wherein said analyzing yields a well log with intrinsic catalytic rock activity as a function of well depth.

12. The well logging method of claim 11, wherein the processing step involves a grinding process for exposing fresh surface of the sedimentary rock sample.

13. The well logging method of claim 11, wherein the processing step is carried out under inert conditions.

14. The well logging method of claim 11, wherein the exposure environment is selected from the group consisting of a static system, a flow system, and combinations thereof.

15. The well logging method of claim 11, wherein the assay exposure conditions comprise a temperature of between about 200° C. and about 350° C., and a hydrogen partial pressure of between about 0.1 torr and about 500 torr.

16. The well logging method of claim 11, wherein the step of exposing comprises a duration of between about 1 minute and 30 days.

17. The well logging method of claim 11, wherein the hydrocarbon material used in the exposing step comprises hydrocarbon species having 2-25 carbon atoms.

18. The well logging method of claim 11, further comprising a step of separating any catalytically-generated methane from any other hydrocarbon species potentially present after the exposing step, wherein the separating is done by a method selected from the group consisting of condensing the other hydrocarbon species on a cold trap, a chromatographic means, and combinations thereof.

19. The well logging method of claim 11, wherein the step of analyzing involves detecting the presence of catalytically-generated methane using a detection device selected from the group consisting of a flame ionization detector, a mass-selective detector, a spectroscopic detector, an electron capture detector, a thermal conductivity detector, a residual gas analyzer, and combinations thereof.

20. The well logging method of claim 11, wherein ascribing an intrinsic catalytic activity to said sedimentary rock in the step of analyzing further comprises determining a rate constant, k , associated with a given set of reaction conditions and a reaction duration, as utilized in the reaction step.

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