The chemical history of $^{14}$C in deep oilfields

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Abstract

$^{14}$C is an overwhelming background in low-background underground experiments, to the point where the observation of the all-important (pp) neutrinos from the Sun can not be observed in carbon-containing experiments. This paper shows that $^{14}$C purity can be improved by four orders of magnitude by a careful selection of the gas field. Two large reduction factors are at work: the low chemical affinity of methane to single carbon, and the migration of natural gas away from nitrogen-bearing kerogen during as the oilfield matures.

Key words: solar, neutrino, detector
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1 Introduction.

All present solar neutrino and dark matter experiments, and most of the future or planned ones, use carbon-containing materials within the fiducial volume. In some cases, such as the current BOREXINO and KAMLAND detectors, the $^{14}$C beta decay (with an end point of 156 keV) background in hundreds of tons of organic scintillator is so overwhelming as to prevent observation of the all-important (pp) solar neutrino flux (with an end point of 217 keV).

In the case of the experiment we propose, the Solar Neutrino TPC, $^1$ methane is about 3% by volume and 12% by mass[1]. Because the TPC is directional, and because only a fraction of the fiducial mass is carbon, the TPC tolerance

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$^1$ TPC means Time Projection Chamber.
to $^{14}\text{C}$ impurities is at least three orders of magnitude above BOREXINO[2] and KAMLAND. Nonetheless a preliminary study indicates that $^{14}\text{C}$ might be a problem for the TPC[1], and that a $^{14}\text{C}$ reduction by a factor of ten or more would be desirable.

In view of these problems it is worth studying ways to reduce the content of $^{14}\text{C}$ of our experiments, which is defined as

$$r = \frac{^{14}\text{C}}{^{12}\text{C}}.$$

In the process we solve a puzzle related to low background physics. The BOREXINO Collaboration analyzed the $^{14}\text{C}$ content of methane before embarking in the construction of the large detector[3]. They found the limit $r < 10^{-18}$. However, once they built their first multi-ton prototype they found that, in their scintillator, $r = (1.94 \pm 0.09)10^{-18}$[2]. A recent measurement of another batch of scintillator, produced with petroleum from a different oilfield, gave another result, $r = 11 \times 10^{-18}$[4]. From the work described below, we conclude that the apparent discrepancy is most likely due to the fact that the former was methane, and the latter scintillator, and they have vastly different $^{14}\text{C}$ content.

Schoenert and Resconi[4] have provided a first understanding of the $r$ value in petroleum, and this work builds on their. They have identified the $^{14}\text{N}(\text{n},\text{p})^{14}\text{C}$ reaction as the main source of $^{14}\text{C}$, they have modeled the dependence of $r$ on the uranium content of the rock and the nitrogen content of the petroleum, and they have predicted a $r$ range of $10^{-16} - 10^{-20}$. Section 2 is mostly a description of their work.

In this paper the steps through which $^{14}\text{C}$ is originated and incorporated in molecules are retraced. All the carbon in use in our experiments was originally extracted from oilfields, and petroleum provided the industrial feedstock for the production of various plastics and scintillating liquids in use in low energy experiments. Our main result is that, if petroleum is carefully chosen, $r$ may go down to the $10^{-22}$ level, making (pp) solar neutrino experimentation at BOREXINO and KAMLAND a possibility. It is also all but certain that the Solar Neutrino TPC will have negligible $^{14}\text{C}$ backgrounds.

Section 2 summarizes the relevant information about geological strata, oilfield parameters, and underground nuclear interactions. Section 2 discusses also the first high precision $^{14}\text{C}$ measurement, by BOREXINO[2], and the likeliest possible explanation of the results. Section 3 briefly discusses isotopic separation, and provides experimental tables about the chemical reactivity of single carbon and hydrocarbons. Section 4 lists possible pitfalls, suggests a set of inexpensive measurements, and offers some criteria to select low $^{14}\text{C}$ hydrocarbons.
2 What we know.

2.1 Oilfields, gasfields and surrounding rock.

Oil and gas fields are found throughout the world in a wide variety of geological formations, over a range of depths from near the surface to 10000 meters. Much more rarely, hydrocarbons are encountered in metamorphic or igneous rocks. The most common types of sedimentary rocks hosting oil and gas pools are sandstone (predominantly SiO$_2$) and limestone (predominantly CaCO$_3$). Other lithologies such as shale (clay) are less common. Oil and natural gas are found in rock pores, whose typical size ranges from 0.1µm to 1mm. The petroleum content of the rock is typically 0.05-0.3 by volume.

Because petroleum originates from decayed biomass, it is supposed to contain far more nitrogen (via protein decomposition) than typical crustal rock. Nitrogen content of oil averages 2%, with variations depending on whether the organic matter was derived from plants, algae, or bacteria. The typical nitrogen content of crustal rock, in contrast, is a few tens of ppm.[5]

Oil and gas generally coexist with water, although occurrences in dry rock are recorded. Water occurs both as thin films adhering to grain surfaces and as discrete lenses within the hydrocarbon volume. Hydrogen sulfide (H$_2$S) is a common minor constituent of natural gas, as are carbon dioxide(CO$_2$) and nitrogen (N$_2$). In rare instances, these compounds can dominate the composition of natural gas.

Reservoirs occur at temperatures of 280 to 460K, a function of the reservoir depth and the local geothermal gradient. Reservoir pressures range up to $10^4$ atmospheres, corresponding to the weight of the overlying water column (hydrostatic pressure), the overlying rock column (lithostatic pressure) or intermediate values. Because Archimedes forces act on the petroleum, oil and gas tend to separate in depth within the same oilfield, although some gas typically dissolves in coexisting oil. Also, Archimedes forces may move petroleum laterally as it tries to move upward, with migrations of tens of kilometers possible.

The composition of most natural gas is dominated by methane, comprising more than 80% of the gas by volume. Some gases have been described with compositions highly depleted in methane and enriched in non-hydrocarbon gases such as nitrogen, helium, H$_2$S and CO$_2$. Oil has a very broad hydrocarbon spectrum.

In many cases considerable amounts of data exist about oil and gas fields, including well preserved samples of petroleum and host rock, and their chem-
physical composition, temperature, and pressure. Most oil and gas fields are also analyzed by lowering sensing tools on electric cable down boreholes (logging tools), in order to obtain information on the presence, type and concentration of hydrocarbons, the mineral composition of the rock, the amount of pore space and the presence of fractures.

2.2 Nuclear reactions in the rock and petroleum.

In the upper atmosphere, and all the way down to 50mwe below ground, the neutron flux (which, we will find later, ultimately controls the production of $^{14}$C) is essentially generated by downward cosmic rays[6]. At depths exceeding 300mwe however the cosmic flux has abated to negligible levels, and the reactions that ultimately produce $^{14}$C are dominated by nuclear reactions in the rock.

There are five reactions of interest which need to be considered[2], listed in Table 1. Their ordering represents the expected order of importance in typical crustal rock[2].

$\alpha$ particles in crustal rock are predominantly generated by the decays of $^{238}$U and $^{232}$Th, and their daughters. Neutrons are predominantly generated by ($\alpha$,n) reactions in other elements in the rock (such as Al, Mg, or Na). Because neutrons are ultimately generated by $\alpha$ particles, the neutron flux is ultimately controlled by Uranium and Thorium concentrations ($^{226}$Ra is a $^{238}$U daughter as well).

The range of neutrons, of course, far exceeds the size of the rock pores. The range of 1 MeV $\alpha$ particles is of order tens of $\mu$m. In all the reactions discussed above the $^{14}$C is imparted an energy of order 100 keV or larger, which results in a typical range of order one micron in rock, few $\mu$m in oil, and a fraction of a millimeter in gas, to be compared with pore sizes varying from 0.1$\mu$m to 1 mm.

Table 1
Reactions that produce $^{14}$C in an oilfield.

| Reaction     | $\sigma$ (millibarn) | Comment          |
|--------------|----------------------|------------------|
| $^{17}$O(n,$\alpha$) $^{14}$C | 235                 |                  |
| $^{14}$N(n,p) $^{14}$C      | 1830                |                  |
| $^{13}$C(n,$\gamma$) $^{14}$C | 1.4                 |                  |
| $^{11}$B($\alpha$,n) $^{14}$C | 20-200              | 2-5 MeV energy   |
| $^{226}$Ra$\rightarrow^{14}$C | -                   | Tripartition     |
Table 2
Average and range U, Th, B content in typical oilfield rock. The neutron flux $n$, last column, is defined in Sect. 2.3 and an order of magnitude estimate only is given.

| Type of rock | U(ppm)   | Th(ppm)   | B(ppm)   | $n$ (n/grams/year) |
|--------------|----------|----------|----------|---------------------|
|              | Refs.[4,8,9] | Refs.[4,8,9] | Ref.[10] | Ref.[4]               |
| Sandstone    | 0.45 (0.2-0.6) | 1.7 (0.7-2.0) | 30 (5-70) | 1.                   |
| Limestone    | 2.2 (0.1-9.0)  | 1.7 (0.1-7.0) | 20 (2-95) | 1.                   |
| Shale        | 3.5       | 11       | 130 (25-800) | 1.                   |

2.3 The BOREXINO result and its interpretation.

BOREXINO\[2\] eventually measured $r$ in their scintillator to unprecedented accuracy and found it to be $(1.94\pm0.09)10^{-18}$. The original paper advances the hypothesis that the sample was contaminated by atmospheric carbon during production\[2\].

Schoenert and Resconi\[4\] first pointed out that the nitrogen content of oilfields is much higher than normal crustal rock (a nominal content of 5% is chosen in their analysis\[4\], a factor of 2.5 higher than that in Ref.\[7\]), and that as a result the reaction $^{14}\text{N}(n,p)^{14}\text{C}$ is the dominant one in oilfields. If that is the case, then $r$ in petroleum is regulated by three main factors:

- the neutron emission intensity
- the neutron absorption by nuclei other than $^{14}\text{N}$
- the $^{14}\text{N}$ concentration

The intensity is clearly regulated by the $^{238}\text{U}$ concentration in the rock. $^{232}\text{Th}$ is also a major contributor, however the concentration of these two isotopes tends to be correlated most everywhere in geological formations, so that only the $^{238}\text{U}$ concentration needs to be tracked. This concentration is defined as $U$. The dependence on $U$ is model independent, if $U = 0$ then $r$ will be extremely small. The $^{238}\text{U}$ content varies in a way familiar to low background physicists. Shale is known to have the highest uranium content of the three kind of strata considered here. Therefore obtaining petroleum from a limestone formation would contribute one order of magnitude.

The intensity is also regulated by the concentration of the various nuclei which ultimately generate the neutrons via $(\alpha,n)$, weighted by the relative cross section. This concentration is defined as $M$. This parameter regulates $r$ only under the hypothesis that the predominant reaction is initiated by a neutron. $M$ is made up of a long list of nuclides, which makes it a hard parameter to control. In view of our main problem, finding specifications for the oilfield
with low $^{14}$C , we have not sought a characterization of this parameter.

The neutron absorption will be dominated under most circumstances by the presence of boron concentrations (typically in the few tens ppm - few hundred ppm in crustal rock). This concentration is defined as $B$. Note that boron will lower $r$ only as long as the predominant reaction is initiated by a neutron. In the case where the predominant reaction is $^{11}$B($\alpha$,n) $^{14}$C , Boron will increase $r$. Boron content varies by more than two orders of magnitude in crustal rock (see Table 2).

Finally, the N concentration is defined as $N$, and regulates $r$ only if the reaction $^{14}$N(n,p) $^{14}$C is dominant. The nitrogen content of the rock may vary by a factor of a few, primarily depending on the shale content of the reservoir, since nitrogen content in rock is primarily associated with clay minerals.

We also identify $UM/B$ as $n$, the total neutron flux. $r$ is then roughly proportional to

$$r \propto \frac{UMN}{B} = nN.$$  

The formula above provides a starting point to try and reduce $r$ by selecting the appropriate oilfield as the feedstock source. Minimization of the ratio above will minimize the $^{14}$C/$^{12}$C ratio for petroleum in bulk.

3 The chemical history.

The previous Section described how to select the best possible OILFIELD. In this Section we describe how to select the best possible HYDROCARBON. It is also important to notice that this Section is totally unrelated to the previous one. Independent of the nuclear reaction that produces $^{14}$C , the nucleus starts its chemical history as a single carbon atom.

We concentrate on methane (CH$_4$), the gas we chose as the quencher in the TPC[1]. There are several reasons to look at methane. It can be trivially separated from all other hydrocarbons by boiling off at 112K (ethane boiling point is at 184K), it can be easily stripped of extra hydrogen atoms by industrial methods, to manufacture a different hydrocarbon to be used as scintillator feedstock, and isotopically pure methane is commerically available. Its chemistry is different from that of other hydrocarbons, and it is the only hydrocarbon that can be extracted almost unmixed from a gas field.
3.1 *Isotopical separation.*

Commercial quantities of isotopically pure ($^{13}\text{C}/^{12}\text{C}$ ratio of $10^{-5}$ to $10^{-6}$, as opposed to the natural $^{13}\text{C}/^{12}\text{C}$ ratio of $10^{-2}$) methane are available, and are used to produce chemical diamond heat sinks with extreme heat conductivity. The typical cost is of order $10-50$ per gram for gram quantities (depending on purity), and while the cost would come down dramatically for mass production it is clear that the cost of kilotons of isotopically pure scintillator is prohibitive. It remains a viable possibility where kilograms of isotopically pure feedstock are needed.

The best current technology available for carbon isotopic enrichment makes use of carbon monoxide (CO)$^{[12]}$, where the heavier carbon nucleus changes the interatomic distance appreciably and makes separation easiest. If the ratio $^{13}\text{C}/^{12}\text{C}$ is decreased by a factor $K$ during enrichment, then $r$ is decreased by a factor $2K$. A plant that could produce large amounts of isotopically pure hydrocarbon is fairly complicated, and includes the transformation of CO into the desired feedstock, plus the disposal of large amounts of waste products.

3.2 *Single carbon chemistry.*

As stated above, no matter the nuclear reaction that produces the $^{14}\text{C}$, one always starts with a single carbon atom, with an energy of order 100 keV, eventually thermalizing in the medium and interacting to form a molecule.

A wealth of single carbon chemical data, interacting with dozens of hydrocarbons, were obtained in the 1960s and are reproduced here. Ref.$^{[13]}$, for example, cites over twenty works where the chemical history of radioactive single carbon in hydrocarbon mixtures was traced. Much of the data were obtained using $^{11}\text{C}$ isotopes, produced by irradiating the hydrocarbons with neutrons ($^{12}\text{C(n,2n)}^{11}\text{C}$). This has the advantage of including any “hot chemistry” effect in the measurements, as the $^{11}\text{C}$ isotope had to slow down and stop in the hydrocarbon medium, and in the process possibly interact with free radicals and/or excited molecules present in its wake. Indeed some of the data below suggest that “hot chemistry” is at work at the percent level. The chemistry of $^{11}\text{C}$ and $^{14}\text{C}$ are assumed to be the same for the precision of this work.

It is clear that methane is difficult to produce, starting from single carbon atoms in a hydrocarbon medium. Consider the following chain of reactions:

$$C + C_nH_m \rightarrow C_{n+1}H_m,$$
\[
\begin{align*}
&\leftrightarrow +H \rightarrow CH, \\
&\leftrightarrow +H \rightarrow CH_2, \\
&CH_2 + C_nH_m \rightarrow C_{n+1}H_{m+2}, \\
&\leftrightarrow +H \rightarrow CH_3, \\
&\leftrightarrow +H \rightarrow CH_4.
\end{align*}
\]

(1)

The formation of methane must proceed through four “hydrogen stripping” steps. If the hydrocarbon is pure methane, there are two branch-off points, the capture of single carbon to produce ethylene \((CH_4 + C \rightarrow C_2H_4)\), and the capture of the \(CH_2\) radical by methane to produce ethane \((CH_4 + CH_2 \rightarrow C_2H_6)\). In both cases the single carbon is sequestered in hydrocarbons that can be trivially separated by boil-off from methane.

The chemical cross section for “hydrogen stripping” tends to be small, compared with other processes. If \(H_2O\) or \(H_2S\) are present in quantity, though, they may act as donors of less strongly bound hydrogen atoms.

The single carbon, and the three intermediate radicals \(CH, CH_2, \) and \(CH_3\), are very reactive with lifetimes in a liquid hydrocarbon medium of order milliseconds. Over that time, they will collide hundreds of millions to billions of times with the surrounding molecules. Traces of compounds with high reactivity will drastically alter the outcome of an irradiation test.

In Table 3 the distribution of radioactive hydrocarbons is shown when methane, and methane mixed with other chemicals, are irradiated to produce \(^{11}\text{C}\). There are several points of interest here. First, pure methane reduces \(r\) by roughly a factor of 7. Second, the last four columns show that small amounts of other chemicals drastically alter the results. The reactivity of \(^{14}\text{C}\) with \(C_2H_4\) is about a million times higher than with methane. Third, the interaction with oxygen donors may produce sizeable amounts of \(^{14}\text{CO}\), which boils at a temperature lower than that of methane (82K as opposed to 111K). A double boiloff procedure is called for, where first natural gas is boiled off at 112K, leaving behind the higher hydrocarbons, and then CO is boiled off at approximately 105K, leaving the methane behind. We note that Table 5 below lists some gasfields with sizeable molecular oxygen content. It is not clear at this time if water can act as an oxygen donor.

Table 4 shows the temperature and/or phase dependence of the chemical history of single carbon. While temperature and phase effects are clear, they only affect concentrations by factors of a few. Dose effects were clearly observed[18], and they are likely to be responsible for small discrepancies that can be found between different experiments. Ref.[18] lists a number of zero-irradiation percentages extrapolated from runs at different levels of irradiations. Irradiation dependence does not affect the precision of the conclusions below.
Table 3
Distribution of radioactive molecules when methane is irradiated. All values in percent. Ref.[14] had a typical sensitivity of 0.2% and errors of order 1%. Ref.[15] had a typical sensitivity of 2%.

| Contaminants | None (Ref. 14) | 0.12% O₂ (Ref. 14) | 2% O₂ (Ref. 15) | 2% C₂H₂ (Ref. 14) | 1.2% C₂H₄ (Ref. 14) |
|--------------|----------------|--------------------|-----------------|-------------------|---------------------|
| CO           | <0.2           | 20.4               | 26.8            | <0.2              | <0.2               |
| CH₄          | 13.9           | 1.5                | <0.15           | 1.9               | <0.2               |
| C₂H₂         | 17.7           | 30.0               | 32.3            | 32.8              | 25.2               |
| C₂H₄         | 12.4           | 28.0               | 30.5            | 29.5              | 23.5               |
| C₂H₆         | 23.9           | 3.1                | <0.5            | 6.0               | 3.4                |
| C₃H₈         | 11.1           | NA                 | <0.2            | <0.2              | 1.7                |
| Higher       | 20.9           | NA                 | 16              | 29.8              | 46.2               |

Generally, in Table 4, methane yields are of order 1-10% of the original sample, and they are smallest for smaller hydrocarbons, such as ethane, which is identified as the best ¹⁴C absorber amongst the alkanes. Heavier hydrocarbons seem to cluster around 5-7%. If all ¹⁴C is processed through interactions with C₂H₆, the ¹⁴C content of methane will be 2% of the original irradiation. Based on Table 3, we make the assumption that other hydrocarbons have much higher reactivity. Based on Table 5 below, we assume that other hydrocarbons in a gasfield are going to be primarily C₂H₆ and C₃H₈. Under these assumptions, and the measured branchings in Table 4, the ¹⁴C content of methane is reduced by a factor between 35 and 48 in a mixture with ethane and propane.

We conclude that in natural gas the isotopic distribution of methane is radically different from that of the other hydrocarbons present in the mix, which is one of the two main results of this work. The situation of oil is a lot more complicated. If there was no methane originally, then all the methane will contain ¹⁴C, as it is produced by the chemical reactions of Table 4. This is a problem that does not concern us. In our TPC, we plan to use boiled-off natural gas, and we expect it from the data above to be practically free of ¹⁴C.

4 Putting it all together.

Natural gas is formed by the maturation (chemical breakdown) of organic matter in shales and shaley limestones, followed by migration to and accumulation in reservoirs. In most cases, the concentration of nitrogen in the
natural gas is considerably lower than in the original organic matter due to chemical fractionation very early in the maturation process. Rarely, nitrogen is subsequently concentrated in natural gas by chemical reactions that destroy methane and other hydrocarbon gases. The large variance of nitrogen content (Table 5) reminds us that there are other sources of nitrogen underground, including atmospheric and non-biogenic sources, which may mix with natural gas.

We now rewrite the formula for $r$ as

$$ r \propto n(N + \epsilon_{rock})\epsilon_{CH4}. \quad (2) $$

$\epsilon_{rock}$ is the natural activity when no nitrogen is present (due to the other reactions in Table 1). The product $n\epsilon_{rock}$ is assumed to be $\sim 5 \times 10^{-21}[2]$. $\epsilon_{CH4}$ depends on the particular gas mixture, but under the hypothesis that ethane and propane dominate it is 0.02 to 0.03. When nitrogen is absent (e.g., the
Table 5
Gasfield location, depth, and chemical composition of the gas in southwestern US and northwestern Mexico. Data from Refs.[19] – [24].

| Location                   | Depth(ft) | CH₄% | C₂H₆% | C₃H₈% | N₂% | O₂% | H₂S% |
|----------------------------|-----------|------|-------|-------|-----|-----|------|
| Solano Co, CA              | 4700      | 96.9 | 1.9   | -     | 1.2 | -   | -    |
| Solano Co, CA              | 4500      | 94.6 | 2.7   | -     | 1.86| -   | -    |
| Contra Costa Co, CA        | 3500      | 89.523| 4.213| 2.04  | 1.85| 0.03| -    |
| Kern Co, CA                | 2160      | 99.77| 0.02  | -     | 0.16| -   | -    |
| San Joaquin Val, CA        | 4300      | 98   | 1.1   | -     | 0.6 | -   | -    |
| San Joaquin Val, CA        | 2500      | 94   | -     | -     | 4.65| -   | -    |
| San Joaquin Val, CA        | 8000      | 43.55| -     | -     | 55.76| - | -    |
| San Joaquin Val, CA        | 8500      | 81.1 | 8     | 4.56  | 0   | -   | -    |
| San Joaquin Val, CA        | 5500      | 99.33| 0.38  | 0.16  | -   | -   | -    |
| San Joaquin Val, CA        | 7500      | 92.3 | 4.2   | 2.27  | -   | -   | -    |
| Ventura Co, CA             | 4600      | 99.55| 0.15  | 0.11  | -   | -   | -    |
| Unita Basin, UT            | 5050      | 93.8 | 3.72  | 1.08  | 0.33| -   | -    |
| Unita Basin, UT            | 4600      | 98.58| 0.37  | 0.07  | -   | -   | -    |
| Unita Basin, UT            | 2875      | 9.3  | 5.91  | 2.01  | 0.42| -   | -    |
| Tampico Em., Mexico        | -         | 86.47| 4.95  | 3.49  | -   | -   | 1.79 |
| Tampico Em., Mexico        | -         | 70.92| 8.51  | 5.78  | -   | -   | 5.32 |
| Tampico Em., Mexico        | -         | 67.19| 11.48 | 8.67  | -   | -   | 2.77 |

8th row in Table 5),

\[ r \propto n_{\text{rock}} \epsilon_{CH4} \sim 1 - 2 \times 10^{-22}. \]  

This a level at which BOREXINO and KAMLAND may be able to work.

4.1 Possible pitfalls.

While it is clear that $^{14}$C does not end easily in methane, there are two possible ways for the isotope to later enter the methane component. They are discussed here.

- Bacterial activity. Vast amounts of bacteria live underground, and they
produce methane as a byproduct of their metabolic activity. If they are present in the gas field, they may reintroduce $^{14}$C in methane. Ref.[7] states that bacteria can exist in gas fields only if the temperature does not exceed 350K.

- Equilibrium reactions. For the selection method proposed here to work, $^{14}$C must stay in the hydrocarbon where it ended at the end of its chemical history for six half-lives or more (35000 years), much less than the average residence time of gas in a reservoir. If equilibrium reactions (e.g., $a + C_2H_4 \rightleftharpoons b + CH_4$, with $a$ and $b$ any other chemical) are significant, then $^{14}$C will have a way to redistribute itself uniformly across the hydrocarbon spectrum. These reactions do not happen at temperatures of a few hundred degrees Kelvin, witness the clear absence of alkenes in natural gas. The reactions do happen readily in the laboratory at room temperature in the presence of molecular hydrogen, which needs to be avoided at all costs.

4.2 A simple test.

Because chemical selection does not depend on the initial nuclear process, a simple and inexpensive apparatus could provide definitive proof of the arguments above. As long as the two pitfalls above are avoided, this test has no meaning for the TPC[1] - the $^{14}$C backgrounds from methane will be negligible no matter what. The test, however, would have ramifications for BOREXINO or KAMLAND, who may need three or four orders of magnitude suppression of $^{14}$C to be able to study ($pp$) neutrinos.

A pressure vessel would have to be filled by a mixture of materials that simulate an underground well (e.g., sand, salt water, oil or gas, and some nitrogen), and irradiated by a neutron source. The hydrocarbons can then be separated by boiloff and analyzed for $^{14}$C content. This test should be able to determine all the coefficients of Eq.(2), and it would also test the one assumption we made, that the single carbon reactivity in natural gas is dominated by non-methane compounds. We note that oil research companies, such as Schlumberger Doll, have such vessels readily available for use[25], so that only the liquids and gases, a boiloff apparatus, and a $^{14}$C counting device need to be provided.

5 Outlook.

In this work we have advanced the work of Schoenert and Resconi in three important ways. First, we have identified that there is a chemical selection at work that depletes the $^{14}$C content of methane (that is, we have introduced
$\epsilon_{CH_4}$ in Eq. (2)). Therefore, we have also identified the best petroleum as gas. Second, we note that nitrogen becomes more easily separated from gas than from oil, as shown in Table 5 (we minimize $N$ in Eq. (2)). Third, because hydrogen stripping is identified as the primary chemical reaction for $^{14}$C to enter methane, we can better specify (or test in the future, Sect. 4.2) the properties of a gas field that is depleted in $^{14}$C.

Several things need to be stressed before giving the specifications for the perfect gasfield. The result of Eq. (3) is to be understood as an order of magnitude estimate. Variations in the $M$ and $B$ parameters may be at that level, and may not generally be known. We also note that the $U$ parameter is generally not known for many oilfields, whereas the gas composition is generally well known (Table 5). There are practical advantages in picking a gas field based on easily measurable quantities (just the gas composition).

We stress once again that isotopic purification by chemical means works regardless of the nuclear source of $^{14}$C. Purification by nitrogen content will work if nitrogen is the primary source of $^{14}$C.

5.1 The perfect gasfield.

It is clear from the discussion that only a gasfield should be considered, if large reductions in $^{14}$C are sought. Here we list the properties of the gas field. The first three are meant to minimize the values of Eq.(2), whereas the last four are meant to avoid $^{14}$C migrating back into the petroleum, avoid hydrogen donors, atmospheric contamination, and carbon monoxide. The first two conditions were given first by Schoenert and Resconi[4].

Low nitrogen content. Gaseous nitrogen content is readily measured and can be very low. Besides the gas fraction that is nitrogen, some attention is to be given to the potentially nitrogen-rich shales that often form the seal rock above a reservoir. For the TPC purposes, a nitrogen content not exceeding 10% (most gasfields) is adequate. For BOREXINO or KAMLAND, the nitrogen content should be below or of order 1%. Two orders of magnitude $^{14}$C reduction are available by simply requiring low nitrogen.

Proven low uranium content. This is the cut that will reduce the number of candidate gasfields. Only the U/Th content of a number of them is known. Note that this condition is not necessary for the TPC, gas analysis alone should provide sufficiently pure methane.

Methane/ethane/propane dominated mixture. The vast majority of gasfields satisfy this requirement, so it is hardly worth mentioning. This data is easiest to obtain. Almost two orders of magnitude decrease in $r$ are available
here (Tables 3 and 4). Under all circumstances the reduction should be at least one order of magnitude (Table 3).

**Minimum water.** It is not clear that the chemical and nuclear properties of water will ultimately contribute an increase in $r$. On the positive side, underground water can be extremely saline, chlorine is a strong neutron absorber (similar to Boron, once their concentrations are taken into account) and water is an oxygen donor, which helps sequester $^{14}\text{C}$ (Table 4). On the negative side, water may or may not be an hydrogen donor, water of meteoric origin may be present in the gasfield and carry atmospheric $\text{CO}_2$, which has $r = 10^{-12}$. A further layer of complexity is introduced by having water in film or lens form. This is one of the major reasons to go through the testing procedure described in Section 4.2. The biological reason for avoiding water is that if there is no water, there can not be any bacterial activity.

**No bacterial activity.** This specification can be enforced by requiring the reservoir temperature to be at least 350K.

**No $\text{H}_2\text{S}$.** The most loosely bound hydrogen underground belongs to $\text{H}_2\text{S}$, and so it needs to be avoided. We note that this parameter is also easily measured, and that $\text{H}_2\text{S}$ can be absorbed by the rock if iron is present.

**Double boiloff.** All other chemical species that may carry $^{14}\text{C}$ boil at temperatures well above methane, except $\text{CO}$. A second boiloff should be performed to vent any possible CO traces before use.

**Other considerations.** It is possible that oxygen donors, such as oxygen and carbon dioxide, will help suppress $^{14}\text{C}$ (Tables 3 and 5). On the other hand, it is possible that these compounds be of atmospheric origin. Unless the reservoir is deep enough to exclude atmospheric contamination, it is best to require low levels of any non-hydrocarbon gas. The effect of these compounds can be tested using the setup of Sect. 4.2.

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