

**Carbon Dioxide Capture for Storage  
in Deep Geologic Formations –  
Results from the CO<sub>2</sub>  
Capture Project**

**Geologic Storage of Carbon Dioxide  
with Monitoring and Verification**

*Volume 2*

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# **Carbon Dioxide Capture for Storage in Deep Geologic Formations – Results from the CO<sub>2</sub> Capture Project**

**Geologic Storage of Carbon Dioxide  
with Monitoring and Verification**

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***Volume 2***



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2005

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First edition 2005

#### Library of Congress Cataloging in Publication Data

A catalog record is available from the Library of Congress.

#### British Library Cataloguing in Publication Data

A catalogue record is available from the British Library.

ISBN: 0-08-044570-5 (2 volume set)

**Volume 1:** Chapters 8, 9, 13, 14, 16, 17, 18, 24 and 32 were written with support of the U.S. Department of Energy under Contract No. DE-FC26-01NT41145. The Government reserves for itself and others acting on its behalf a royalty-free, non-exclusive, irrevocable, worldwide license for Governmental purposes to publish, distribute, translate, duplicate, exhibit and perform these copyrighted papers. EU co-funded work appears in chapters 19, 20, 21, 22, 23, 33, 34, 35, 36 and 37. Norwegian Research Council (Klimatek) co-funded work appears in chapters 1, 5, 7, 10, 12, 15 and 32.

**Volume 2:** The Storage Preface, Storage Integrity Preface, Monitoring and Verification Preface, Risk Assessment Preface and Chapters 1, 4, 6, 8, 13, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33 were written with support of the U.S. Department of Energy under Contract No. DE-FC26-01NT41145. The Government reserves for itself and others acting on its behalf a royalty-free, non-exclusive, irrevocable, worldwide license for Governmental purposes to publish, distribute, translate, duplicate, exhibit and perform these copyrighted papers. Norwegian Research Council (Klimatek) co-funded work appears in chapters 9, 15 and 16.

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Printed in The Netherlands.

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## Chapter 24

# THE USE OF NOBLE GAS ISOTOPES FOR MONITORING LEAKAGE OF GEOLOGICALLY STORED CO<sub>2</sub>

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### ABSTRACT

One of the primary concerns in CO<sub>2</sub> storage is monitoring the storage site on a long-term basis for possible leakage of CO<sub>2</sub>. Concentrations of CO<sub>2</sub> vary widely in the Earth's crust, making detection of very small releases difficult. Small amounts of noble gas isotopes can be dissolved into the CO<sub>2</sub> being injected for storage and used as tracers to monitor CO<sub>2</sub> movement. Noble gases are chemically inert, environmentally safe, and are persistent and stable in the environment. The unique isotopic compositions that can be imparted to the CO<sub>2</sub> can be unambiguously identified during monitoring. Among the noble gases, xenon isotopes have commercial costs and availability suitable for use in large CO<sub>2</sub> storage operations. Required xenon volumes are low, simplifying handling and injection. Multiple batches of injected CO<sub>2</sub> at the same site could be imparted with different xenon isotopic compositions, making each of them identifiable with only a single xenon analysis. These characteristics are believed to make xenon a superior tracer to other options, SF<sub>6</sub> and <sup>14</sup>CO<sub>2</sub>. A case study in noble gas tracing at the Mabee Enhanced Oil Recovery field in West Texas indicates that unique noble gas isotopic compositions within a CO<sub>2</sub> injection stream can be detected and readily identified in outlying wells, and that noble gas behavior in a CO<sub>2</sub> storage setting will be systematic and predictable.

### INTRODUCTION

Noble gases (helium, neon, argon, krypton, xenon; Table 1) can be dissolved into CO<sub>2</sub> injected into geological formations for long-term storage and used as tracers when monitoring for CO<sub>2</sub> leakage or subsurface migration. Injected CO<sub>2</sub> is in a supercritical state and the noble gases will remain dissolved in that liquid. Using noble gases for subsurface tracing in this form is similar to using any common type of chemical tracer. However, leaking CO<sub>2</sub> will become a gas as it migrates to the Earth's surface. It is here that the noble gases become unique and highly valuable tracers. At the pressure and temperature conditions in which the supercritical CO<sub>2</sub> becomes a gas, the noble gases will also be released as gases. The noble gases will thereby track CO<sub>2</sub> gas migration toward the surface.

Noble gases become distinctive tracers when non-natural isotopic compositions are used. In the natural environment all of the noble gases have multiple isotopes, atoms of the same element with different numbers of neutrons. While the atomic ratios of the noble gas isotopes are generally very similar throughout the planet and atmosphere, commercial isotope separation makes available significant volumes of noble gases with certain isotopes enhanced over their natural abundances. Xenon, for example, occurs naturally in nine different isotopic states: <sup>124</sup>Xe, <sup>126</sup>Xe, <sup>128</sup>Xe, <sup>129</sup>Xe, <sup>130</sup>Xe, <sup>131</sup>Xe, <sup>132</sup>Xe, <sup>134</sup>Xe, and <sup>136</sup>Xe. The fractional abundance of each of these varies only slightly in nature; for instance, <sup>136</sup>Xe comprises about 8.9% of all natural xenon. However, pure xenon gas can be purchased that contains about 60% <sup>136</sup>Xe. Adding this to injected CO<sub>2</sub> would create a distinctive tracer with non-natural xenon isotopic ratios that later could be unambiguously identified when monitoring for leakage.

Since they are chemically inert and non-radioactive, noble gas tracers are persistent and stable in the environment. They are non-toxic and environmentally safe. After injecting CO<sub>2</sub> spiked with noble gas isotopes into a reservoir, the region surrounding and above the storage site could be monitored to detect

the distinctive noble gas isotopic signatures for decades to millennia. Because CO<sub>2</sub> will always be detected within the Earth's crust, the question for monitoring purposes will be whether its origin is natural or from injection. The isotopic signature of the noble gases measured with the CO<sub>2</sub> would indicate whether or not the gases originated within the storage site.

TABLE 1  
NOBLE GAS PROPERTIES AND CONCENTRATIONS RELEVANT TO THEIR USE IN CO<sub>2</sub> STORAGE

Noble gas	Atomic number	Atomic radius <sup>a</sup> (Å)	Natural stable isotopes	Atmospheric volume fraction of dry air <sup>a</sup>	Average seawater <sup>a</sup> (cm <sup>3</sup> STP/g)	Dakota aquifer <sup>b</sup> (cm <sup>3</sup> STP/g)	Dogger aquifer <sup>c</sup> (cm <sup>3</sup> STP/g)	Suggested primary tracer isotope (s)
He	2	1.8	2	$5.2 \times 10^{-6}$	$4.0 \times 10^{-8}$	$1.0 \times 10^{-5}$	$6.2 \times 10^{-4}$	<sup>3</sup> He
Ne	10	1.6	3	$1.8 \times 10^{-5}$	$1.7 \times 10^{-7}$	$2.0 \times 10^{-7}$	$3.2 \times 10^{-7}$	<sup>22</sup> Ne
Ar	18	1.9	3	$9.3 \times 10^{-3}$	$3.5 \times 10^{-4}$	$3.5 \times 10^{-4}$	$3.4 \times 10^{-4}$	<sup>36</sup> Ar
Kr	38	2.0	6	$1.1 \times 10^{-6}$	$8.5 \times 10^{-8}$	$8.2 \times 10^{-8}$	$8.3 \times 10^{-8}$	—
Xe	54	2.2	9	$8.7 \times 10^{-8}$	$1.1 \times 10^{-8}$	$1.1 \times 10^{-8}$	—	<sup>124,129,136</sup> Xe

The Dakota and Dogger aquifer concentrations given can be considered typical for deep continental groundwaters, although significant variations can occur.

<sup>a</sup> Source: Ref. [1].

<sup>b</sup> Source: Ref. [2]. Average of Group 3 waters, central Kansas.

<sup>c</sup> Sources: Ref. [3] for He, Ne, Ar and Ref. [4] for Kr. Values are averages of listed wells.

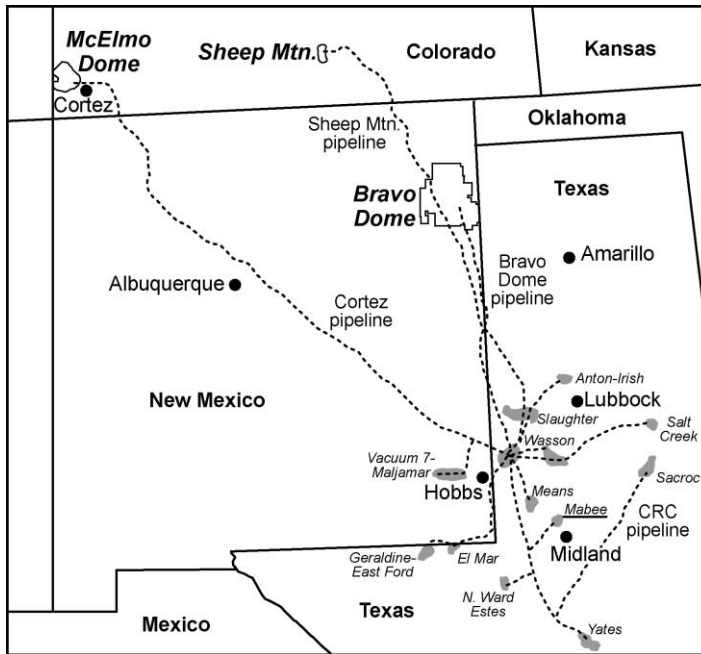
For the purposes of our initial calculations and assessments, we are assuming that the noble gas tracers move conservatively with the stored CO<sub>2</sub>. In reality, there will be partitioning of the noble gases between the phases present in the system (water, hydrocarbons, and a gas phase). Partitioning would not only affect noble gas tracers, but any potential tracer except for <sup>14</sup>CO<sub>2</sub> (<sup>14</sup>CO<sub>2</sub> is discussed below). Noble gas solubilities in waters and brines, and their temperature dependence, are fairly well known [1,5–9]. Data on noble gas solubilities in some hydrocarbons (hexane, decane, benzene) at 25 °C and 1 atm are available [10]. Kharaka and Specht [11] determined noble gas solubilities in two crude oils (API gravity 25 and 34) over the temperature range 25–100 °C. However, very little is known about the partitioning/solubility behavior of noble gases or other possible tracers in the *P–T–x* conditions of the CO<sub>2</sub> storage environment. Much more information will be needed before a complete assessment of noble gas or other tracers can be made. One of our recommendations provided at the end of this chapter is for research to obtain this information.

This chapter discusses a methodology for using noble gases in CO<sub>2</sub> storage. It covers injection methods, costs, detection and monitoring scenarios, and compares noble gases with other potential tracers (SF<sub>6</sub> and <sup>14</sup>CO<sub>2</sub>). We also present the results of a noble gas “tracer” study we performed in an enhanced oil recovery (EOR) field in the Permian Basin of West Texas.

## EXPERIMENTAL/STUDY METHODOLOGY

Noble gas tracing has been used successfully for large-volume groundwater tracing in several different locations [12]. The initial investigation, therefore, was to determine whether this technique was also suitable for CO<sub>2</sub> tracing. This involved an analysis of noble gas tracer costs, availability, detection limits, and a comparison with other potential tracers. It required an assessment of the amounts of tracer needed per mass of stored CO<sub>2</sub>, as well as an assessment of probable monitoring strategies. The amounts of any tracer required is a function of the type of system to be monitored; possibilities include groundwater, deep soil or formation gases, and ground surface emissions. An analysis of injection methods must also be made: is it feasible to label the entire CO<sub>2</sub> injection stream with noble gas tracers? If only portions of the injected stream can be labeled, monitoring will be compromised.

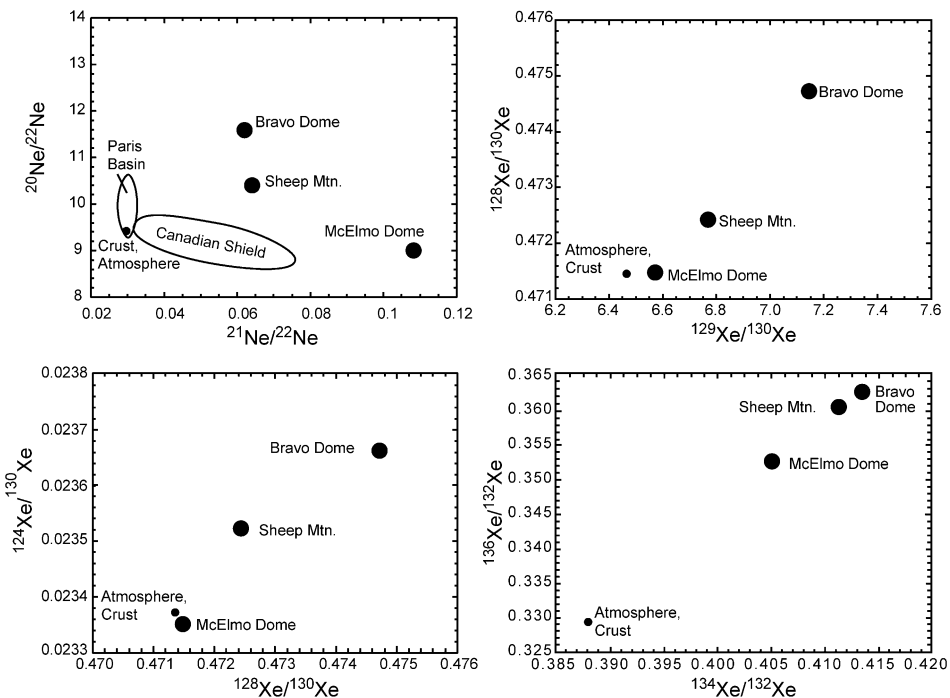
The investigation then turned to a “field demonstration” at an active EOR location. During the course of this study, no CO<sub>2</sub> storage operations were being conducted in which a noble gas tracer could be added and traced in the subsurface. The EOR setting was the closest available analogue. Fortuitously, the CO<sub>2</sub> being injected into the subsurface in the Permian Basin of West Texas contains noble gases that have very unique and recognizable isotopic characteristics [13]. The CO<sub>2</sub> originates from extensive CO<sub>2</sub> deposits (“domes”) in northern New Mexico and southern Colorado (Figure 1), and is piped to West Texas.



**Figure 1:** CO<sub>2</sub> distribution via pipelines (dotted lines) from the McElmo Dome, Sheep Mountain, and Bravo Dome CO<sub>2</sub> deposits to the Enhanced Oil Recovery fields in the Permian Basin. Only major or pipeline-termination EOR fields are shown, and many more exist. The Mabee EOR field is shown located just north of Midland, Texas.

Isotopic compositions of the noble gases in the dome CO<sub>2</sub> are unlike those of the noble gases naturally present within the Permian Basin, which will be typical crustal values (Figure 2). They are also distinct from atmospheric values. Large-scale CO<sub>2</sub> injection to enhance oil recovery has been going on since the 1970s. This permits an assessment of whether noble gas isotopic compositions would serve as a tracer of CO<sub>2</sub>. Rather than having to artificially add a noble gas tracer to a CO<sub>2</sub> stream and wait months to years for that CO<sub>2</sub> to migrate to a monitoring well or to the ground surface, the “experiment” had already begun many years ago.

We were given access to the Mabee EOR field north of Midland, Texas by ChevronTexaco, its owners and operators (Figure 1). Samples were collected for noble gas analysis of the dome CO<sub>2</sub> prior to injection, and of gases being extracted in 13 outlying oil production wells within the Mabee field. The extracted gases from many wells covering large sections of the Mabee field is typically combined into a single return pipeline and added to incoming (new) dome CO<sub>2</sub> for reinjection. A sample of this “blend” CO<sub>2</sub> was also collected and analyzed for noble gas isotopic compositions. Thus we were able to simulate a field demonstration of noble gas isotopic tracing in which we could compare the isotopic compositions of injected noble gases and those of CO<sub>2</sub>-related gases outlying from the point of injection. This mimics a situation in which CO<sub>2</sub> would be injected for storage and then monitored through outlying wells in order to



**Figure 2:** Isotopic compositions of neon and xenon in CO<sub>2</sub> from the McElmo Dome, Sheep Mountain, and Bravo Dome CO<sub>2</sub> deposits. Atmospheric values given for comparison. Typical crustal values will be closer to atmospheric values than to CO<sub>2</sub> deposit values, as shown by the neon isotope fields from the Canadian Shield and Paris Basin. McElmo Dome, Sheep Mountain, and Bravo Dome data are from Caffee et al. [13]; Canadian Shield data from Bottomley et al. [14]; Paris Basin data from Castro et al. [3].

understand its subsurface distribution. It is important to note that the noble gas concentrations in the natural dome CO<sub>2</sub> are far less than those that could be imparted to CO<sub>2</sub> being injected for storage. In this respect, the Mabee analogue represents the most difficult monitoring situation we would expect to encounter.

Gas samples were collected in double-ended stainless steel high pressure bottles (<2000 psi) and shipped to Lawrence Livermore National Laboratory for noble gas isotopic analysis. Analytical methods were similar to those presented in Caffee et al. [13]. The noble gas lab consists of two VG5400 noble gas mass spectrometers. The first spectrometer is set up to analyze xenon isotope ratios with very high precision. Major isotope ratios ( $^{129}\text{Xe}$ ,  $^{131}\text{Xe}$ ,  $^{132}\text{Xe}$ ,  $^{134}\text{Xe}$  and  $^{136}\text{Xe}$ ) are reproducible in air and water standards at 0.05%. This instrument is also used for precise  $^3\text{He}/^4\text{He}$  measurements and the determination of tritium by the  $^3\text{He}$  in-growth method. The second spectrometer is dedicated to measuring large variations in noble gas isotope ratios and samples with high  $^3\text{He}/^4\text{He}$  and high tritium. This instrument also performs isotope dilution measurements of He, Ne, Ar, Kr and Xe abundances. Both spectrometer systems have automated, multi-port, sample processing systems able to handle gas and water samples.

## RESULTS AND DISCUSSION

### *Comparison of Tracers: Noble Gas Isotopes, SF<sub>6</sub>, and <sup>14</sup>CO<sub>2</sub>*

Theoretical aspects of the utility of potential tracers for CO<sub>2</sub> storage monitoring can be assessed on the basis of availability, costs, ease-of-use, detectability, and environmental safety. A generalized assessment of each



of these is impossible without making assumptions concerning the amounts of CO<sub>2</sub> to be stored, the rate at which it is put into storage, the purpose and location of the monitoring, and other specific aspects of the storage operation. For example, the cost of any tracer is likely to decrease with increasing amounts purchased. Likewise, detectability is a function of the purpose and location of the monitoring—monitoring for verification of subsurface location is different from ground surface monitoring for leakage.

For the purposes of an assessment of detectability, we considered the most difficult monitoring setting, ground surface emissions. For this we also considered a very conservative monitoring strategy in which the concentration of CO<sub>2</sub> in the soil gas, normally at about 1% in the environment, is raised an additional 1% (i.e. grows to 2% total). This is within the natural range of variations in soil gas CO<sub>2</sub>, such that CO<sub>2</sub> monitoring alone would not detect an abnormal variation. It is also far below the value at which vegetation stress would occur, giving an obvious signal of CO<sub>2</sub> leakage. For the assessment, we also assumed that all potential tracers move conservatively with the leaking CO<sub>2</sub>. The concentration of tracer required within the injected CO<sub>2</sub> will then be a function of the detection limits for the tracer and the level at which we desire to detect leaking CO<sub>2</sub>. For the assumption that we desire to detect a 1% CO<sub>2</sub> increase in soil gas, known natural background levels in the atmosphere (Table 1) and instrumental detection limits determined the amount of tracer required per unit mass of CO<sub>2</sub> (e.g. tracer/ton CO<sub>2</sub>). This then permitted the assessment of costs per unit mass CO<sub>2</sub> and potential availability. An assessment of the amounts of tracer required per year can be made by assuming an amount of CO<sub>2</sub> to be stored per year. For the purpose of discussion, we have used as an example the amount of CO<sub>2</sub> being injected at the Mabee EOR field. For the entire injection manifold, CO<sub>2</sub> storage would occur at the rate of  $3.8 \times 10^3$  metric tons/day, or about  $1.4 \times 10^6$  metric tons/year at full performance. Table 2 compares such criteria with respect to several noble gas tracers and two other potential tracers, SF<sub>6</sub> and <sup>14</sup>CO<sub>2</sub>.

TABLE 2  
COMPARISON OF TRACERS FOR MONITORING SHALLOW SOILS FOR LEAKING CO<sub>2</sub>

Tracer	Atmospheric concentration (cm <sup>3</sup> /cm <sup>3</sup> air)	Minimum detectable variation (%)	Required tracer concentration in stored CO <sub>2</sub> (cm <sup>3</sup> /cm <sup>3</sup> CO <sub>2</sub> , STP)	Required tracer per 10 <sup>-6</sup> m <sup>3</sup> CO <sub>2</sub> (L, STP)	Tracer cost (\$US/l)	Tracer cost/metric ton CO <sub>2</sub> (\$US)	Required tracer per year (L, STP)
<sup>3</sup> He	$7.2 \times 10^{-12}$	300	$2.17 \times 10^{-9}$	2.2	100	0.11	1532
<sup>22</sup> Ne	$1.7 \times 10^{-6}$	0.1	$1.68 \times 10^{-7}$	168	50	4.27	118629
<sup>36</sup> Ar	$3.2 \times 10^{-5}$	0.1	$3.16 \times 10^{-6}$	3161	1000	1610	2234515
<sup>124</sup> Xe	$8.7 \times 10^{-11}$	0.2	$1.75 \times 10^{-11}$	0.02	20000	0.18	12
<sup>129</sup> Xe	$2.5 \times 10^{-8}$	0.05	$1.25 \times 10^{-9}$	1.2	1000	0.64	883
<sup>136</sup> Xe	$8.7 \times 10^{-9}$	0.10	$8.70 \times 10^{-10}$	0.9	300	0.13	615
SF <sub>6</sub>	$1.0 \times 10^{-11}$	1000	$1.00 \times 10^{-8}$	10	1	0.005	7070
<sup>14</sup> CO <sub>2</sub>	$1.0 \times 10^{-14}$	300	$3.00 \times 10^{-12}$	0.003	5000	0.008	2

Minimum detectable variation values are based on observed natural atmospheric variations (“background”) and available analytical precision. They represent the minimum recognizable non-natural shift in isotopic ratios (or change in SF<sub>6</sub> concentration) that would provide a clear signal of the presence of the tracer in soil gas samples. Calculations assume soil gas is 1% natural CO<sub>2</sub> by volume. Calculated amounts of required tracer in the stored CO<sub>2</sub> are for detection of an additional 1% contribution from leaking CO<sub>2</sub> (i.e. total CO<sub>2</sub> = 2%). Minimum variation for <sup>14</sup>CO<sub>2</sub> (300%) is relative to ambient soil CO<sub>2</sub> (assumed 1%); with the additional 1% stored contribution it is equivalent to an isotopic shift of 150% (1.5 times modern atmospheric <sup>14</sup>C/<sup>12</sup>C). Tracer required per year is for the Mabee storage analogue discussed in the text (storage of  $1.937 \times 10^{-6}$  m<sup>3</sup> CO<sub>2</sub>/day (STP) for the entire injection manifold).

Clearly the best tracer is <sup>14</sup>CO<sub>2</sub>. Its cost is low (\$0.008 per ton CO<sub>2</sub>) and only 2 L (STP) per year for the Mabee storage analogue would be required. Of all potential tracers, <sup>14</sup>CO<sub>2</sub> is the most likely to migrate conservatively with leaking CO<sub>2</sub>, since the leaking CO<sub>2</sub> will itself be partially <sup>14</sup>CO<sub>2</sub>. However, <sup>13</sup>C is

radioactive. Two liters (STP) of  $^{14}\text{C}\text{O}_2$  would contain about 5.6 Ci of activity. This is actually a small amount of radioactivity on the scale of  $\text{CO}_2$  storage. It would impart an activity to the stored  $\text{CO}_2$  equivalent to about half that attained in the  $\text{CO}_2$  in the northern hemisphere atmosphere in the mid-1960s from uncontained nuclear testing in the Pacific. For a leakage that raises soil gas  $\text{CO}_2$  concentrations by 1%, the increased radiation would be difficult or impossible to detect in the ambient air ( $\sim 80$  pCi per  $\text{m}^3$  air). Measurement would require accumulation of soil gas  $\text{CO}_2$ . Handling the  $^{14}\text{C}\text{O}_2$  2-L canisters during the injection process could be done safely with very simple protocols. The potential commercial availability of  $^{14}\text{C}$  is very high, since it is abundantly produced in power plant nuclear reactors. By scientific and technical standards,  $^{14}\text{C}\text{O}_2$  might be a desirable tracer and warrants further investigation. However, public perception is another matter. It is possible that public reaction to injection of radioactivity, no matter how small, would doom attempts to use  $^{14}\text{C}\text{O}_2$  as a  $\text{CO}_2$  tracer.

$\text{SF}_6$  is a well-understood synthetic tracer that is widely used in groundwater and other applications [15]. It is inexpensive and would be cost effective for  $\text{CO}_2$  storage monitoring (US\$1/L to \$0.005/ton  $\text{CO}_2$  stored). It has become increasingly prevalent in the atmosphere, and would therefore require fairly large amounts to be injected with the stored  $\text{CO}_2$  ( $\sim 7000$  L (STP) per year for the Mabee storage analogue). Atmospheric concentrations of  $\text{SF}_6$  are rapidly rising [16] and it is difficult to determine present injection requirement for detection in future decades or centuries (Table 2 lists a conservative estimate for long-term monitoring). Although  $\text{SF}_6$  is a relatively stable molecule, it can be expected to decompose over time in the subsurface. Its long-term, centuries to millennia, reliability as a  $\text{CO}_2$  tracer is unclear.

As Table 2 indicates, not all noble gases will be cost effective tracers of  $\text{CO}_2$ . The high atmospheric abundance of  $^{36}\text{Ar}$  necessitates a high concentration of  $^{36}\text{Ar}$  in the injected  $\text{CO}_2$ , resulting in a cost of nearly \$1600 (US) per metric ton  $\text{CO}_2$ . The required yearly volume for the Mabee analogue, over 2 million liters of  $^{36}\text{Ar}$ , is also prohibitive—for both availability and ease-of-use. A high atmospheric concentration also makes  $^{22}\text{Ne}$  an expensive choice for ground surface monitoring. However, the low commercial cost of neon (Table 2) and its high availability suggest that  $^{22}\text{Ne}$  could be considered in special circumstances. For example, it would be useful for subsurface tracing of supercritical  $\text{CO}_2$  where the natural background is insignificant, and therefore injected concentrations would be substantially lower. Although costs for  $^3\text{He}$  are low (\$0.11/ton  $\text{CO}_2$ ) and the necessary quantities required for the Mabee analogue are within obtainable amounts,  $^3\text{He}$  is very rare (only 0.00014% of natural helium is  $^3\text{He}$ ). For large-scale  $\text{CO}_2$  storage, availability would be problematic.

The three xenon isotopes listed in Table 2 appear to be efficient to use and inexpensive relative to  $\text{CO}_2$  storage costs. For the Mabee storage analogue, only 12 L of  $^{124}\text{Xe}$  (at STP) would be required per year, at a cost of \$0.18 per metric ton  $\text{CO}_2$ . This compares to current  $\text{CO}_2$  industrial separation costs in the range of \$50–\$100 per metric ton. The requirement for  $^{129}\text{Xe}$  is 883 L/year, equivalent to about four 55-gallon drums (at STP), and about 12% of the required volume of  $\text{SF}_6$ . The small volumes required greatly simplify injection logistics.

The fact that multiple xenon isotopes are available, inexpensive, simple to use, and highly detectable allows the possibility that there may be occasions where injecting batches of  $\text{CO}_2$  at the same location containing distinctly different xenon isotopic compositions (i.e. different proportions of  $^{124}\text{Xe}$ ,  $^{129}\text{Xe}$ , and  $^{136}\text{Xe}$ ). This would be useful in tracing subsurface migration of  $\text{CO}_2$  batches injected at different geographical locations within a field. It would also be useful for monitoring of locations where several different batches of  $\text{CO}_2$  were stored, perhaps by different corporations, in different geologic formations, or at different times. The unique isotopic signal would indicate which batch or batches were leaking to ground surface. Since the analysis would be only for xenon, only one measurement would be needed. Multiple tracers, or even multiple noble gases, would each require a separate analysis.

#### ***Availability of Noble Gas Tracers***

The commercial source for all of the noble gases is the Earth's atmosphere. Separation of noble gases from air, and from one another, can be accomplished by liquefaction/cryogenic methods. Separation of the individual noble gas isotopes is accomplished by gas centrifugation such as the technique that separates  $^{235}\text{UF}_6$  from  $^{238}\text{UF}_6$  for nuclear fuel (uranium enrichment). The commercial availability of xenon is currently adequate for the short term, and can be expected to increase in the future. Xenon is commonly used

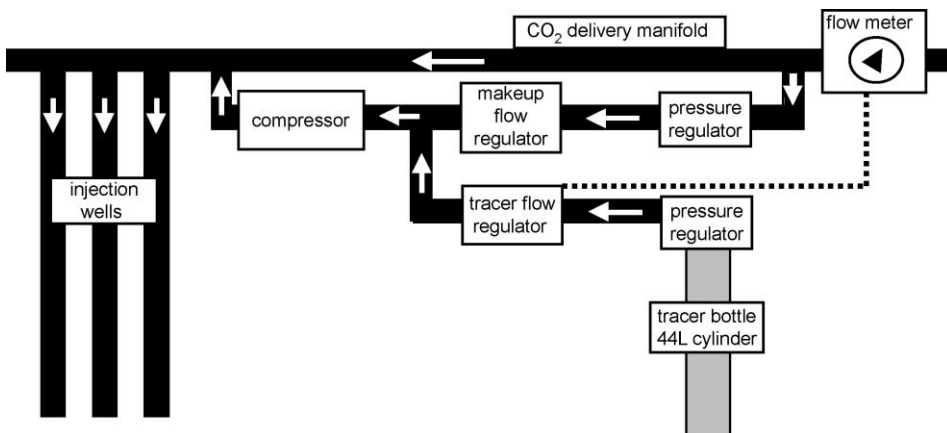
as an anesthetic and recently has begun to be used to enhance Magnetic Resonance Imaging (MRI) resolution. The MRI application uses exclusively  $^{129}\text{Xe}$ . A driving force for an increase in xenon availability is its use as a propellant in spacecraft ion engines, such as the NASA High Power Electric Propulsion (HiPEP) engine. A commercial demand for xenon for  $\text{CO}_2$  storage would result in a rapidly increased production.

A basic calculation indicates the total scope of potential xenon availability. The Earth's atmosphere contains an inventory of about  $7 \times 10^{13}$  L of  $^{124}\text{Xe}$  [1]. Total US required  $\text{CO}_2$  storage is expected to be about  $1 \times 10^9$  metric tons/year [17]. If injection for this storage amount were to occur for a century, a total of  $1 \times 10^{11}$  metric tons of  $\text{CO}_2$  would be stored (about  $5 \times 10^{13}$  m<sup>3</sup>  $\text{CO}_2$ , STP). The requirement for  $^{124}\text{Xe}$  tracer is 0.02 L per  $1 \times 10^6$  m<sup>3</sup>  $\text{CO}_2$ , STP (Table 2). The total 100 year requirement for  $^{124}\text{Xe}$  would therefore be about  $1 \times 10^6$  L, or about  $1.5 \times 10^{-6}\%$  of the atmospheric xenon. Clearly, the xenon inventory is sufficient.

Gas centrifuge technology required to separate the individual noble gas isotopes is abundant worldwide and currently underutilized. An example of the volumes of isotope separates that could be made available is the double-beta neutrino mass experiment being conducted as a US–European collaboration [18]. For the experiment, 10 metric tons ( $1.65 \times 10^6$  L, STP) of  $^{136}\text{Xe}$  is being used. This volume of  $^{136}\text{Xe}$  would be sufficient for  $\sim 2700$  years of  $\text{CO}_2$  injection at the Mabee storage analogue (Table 2). For the total US required  $\text{CO}_2$  storage of  $1 \times 10^9$  metric tons/year, this would be a 4-year supply. This would be sufficient time to “replenish” the supply using the currently available gas centrifuge technology.

#### *Addition of Noble Gases into the $\text{CO}_2$ Injection Stream*

The low annual volumes of xenon tracer required for  $\text{CO}_2$  storage monitoring simplify the methods required for injection. Figure 3 shows a generalized schematic of an injection system. To insure uniform solution of the xenon (or other noble gas) into the  $\text{CO}_2$  stream, a side-track make up flow is partitioned from the main  $\text{CO}_2$  delivery manifold by pressure regulation. Noble gas tracer is bled into this stream at a rate of perhaps a few cm<sup>3</sup> per minute (STP). A compressor in the side-track make up flow line insures solution of the tracer into the liquid  $\text{CO}_2$ . A tracer flow regulator coupled to the main  $\text{CO}_2$  manifold flow meter would insure constant concentration of the tracer in the injected  $\text{CO}_2$ .



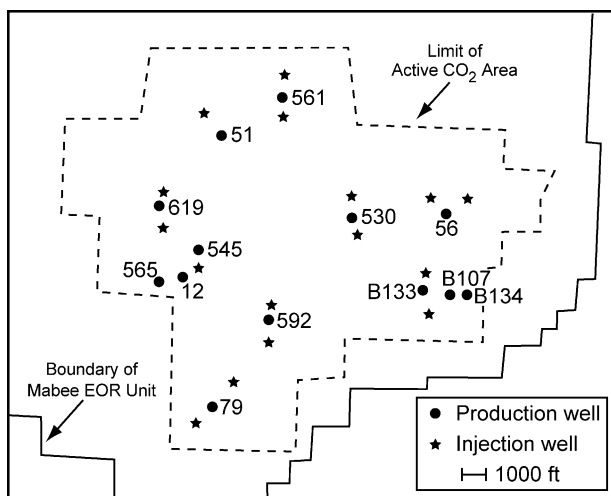
**Figure 3:** Conceptual schematic for the addition of noble gas tracers to  $\text{CO}_2$  during injection for long-term storage. The noble gases are mixed into a side-track make up  $\text{CO}_2$  flow and compressed for solution. A  $\text{CO}_2$  flow meter and the tracer flow regulator can be coupled (dotted line) to insure a constant concentration of noble gases in the injected  $\text{CO}_2$ . Tracer bottle cylinder size can be selected for optimal desired lifetime of injection (e.g. 1 year).

The size of the tracer bottle, depicted as a standard 44 L cylinder in Figure 3, could be chosen for ease of use and handling. If only 12 L of tracer are used per year, as in the Mabee storage analogue using  $^{124}\text{Xe}$ , one cylinder per year would be sufficient. However, in this case the tracer flow would be extremely small, about  $0.02 \text{ cm}^3/\text{min}$ . This suggests that it may be preferable for the tracer bottle to contain addition gas, probably  $\text{CO}_2$ , such that total flow would be more easily regulated.

**Field Demonstration: Noble Gas Tracing at the Mabee EOR Field, West Texas**

The fact that  $\text{CO}_2$  containing unusual noble gas isotopic compositions had been injected into Permian Basin oil fields for EOR since the 1970s permitted an analysis of the utility of using noble gases as  $\text{CO}_2$  storage tracers. A staged field demonstration, in which a noble gas tracer is artificially added to a  $\text{CO}_2$  stream, will be a valuable trial in the future. However, no new field  $\text{CO}_2$  demonstrations were being initiated during the time of our study, and unless an aggressive subsurface sampling strategy was to be employed, the demonstration could take months to years to complete. Ground surface monitoring in a field demonstration would only be useful if  $\text{CO}_2$  leakage to the surface were induced during the demonstration. Therefore, the use of the Permian Basin was advantageous to the assessment of noble gas behavior during injection of  $\text{CO}_2$ .

Figure 4 is a map of the Mabee EOR field in the Permian Basin. The locations of the 13 production wells at which gas samples were collected are shown, as are the locations of  $\text{CO}_2$  injection wells known to be operative during the sampling period. Because injection has been occurring at Mabee for many years, the entire subsurface has been affected by  $\text{CO}_2$  flooding. It is unclear whether the currently active injection had direct effect on the composition of the samples collected. However, the data clearly indicate that noble gas compositions in the collected gas are directly affected by compositions closely similar or identical to those in the  $\text{CO}_2$  being injected at the time of sampling.



**Figure 4:** Map of the southern portion of the Mabee EOR field. The sampled production wells are shown with adjacent sample numbers (see Tables 3 and 4). Injection wells are those known to be active during the sampling interval. The field contains many other production wells than those shown, occurring on approximate 1000 ft spacings.

Helium, neon, argon, and xenon concentration and isotopic data are presented in Tables 3 and 4, and shown in Figures 5 and 6. Sample “KMCO2” is  $\text{CO}_2$  directly from the supply pipeline feeding the Mabee field (Figure 1). Sample “Blend  $\text{CO}_2$ ” is a composite gas collected from a  $\text{CO}_2$ -return pipeline that mixes produced gases from many production wells in the field, including some of those sampled individually by us. The produced  $\text{CO}_2$  from this pipeline is mixed with the incoming KMCO2 pipeline

TABLE 3  
CONCENTRATIONS AND ISOTOPIC COMPOSITIONS OF HELIUM, NEON, AND ARGON IN GASES FROM THE MABEE EOR FIELD

Sample	<sup>4</sup> He (ppmv)	<sup>3</sup> He (ppmv)	<sup>3</sup> He/ <sup>4</sup> He ( ÷ <sup>3</sup> He/ <sup>4</sup> He air)	<sup>20</sup> Ne (ppmv)	<sup>21</sup> Ne/ <sup>20</sup> Ne	<sup>22</sup> Ne/ <sup>20</sup> Ne	<sup>36</sup> Ar (ppmv)	<sup>40</sup> Ar/ <sup>36</sup> Ar	Excess <sup>21</sup> Ne (ppmv)	Excess <sup>40</sup> Ar (ppmv)
KM CO2	1086	2.42 × 10 <sup>-4</sup>	0.161	0.0055	0.00996	0.1086	0.0185	12432	3.82 × 10 <sup>-5</sup>	225
Blend CO2	703	2.39 × 10 <sup>-4</sup>	0.246	0.0138	0.00504	0.1040	0.0556	3255	2.83 × 10 <sup>-5</sup>	165
Mabee 545	826	3.61 × 10 <sup>-4</sup>	0.316	0.0211	0.00449	0.1035	0.1018	1984	3.16 × 10 <sup>-5</sup>	172
Mabee 12	838	3.14 × 10 <sup>-4</sup>	0.217	0.0148	0.00480	0.1036	0.0614	3114	2.66 × 10 <sup>-5</sup>	173
Mabee 565	550	3.25 × 10 <sup>-4</sup>	0.427	0.0177	0.00398	0.1026	0.0797	1757	1.76 × 10 <sup>-5</sup>	116
Mabee 619	881	3.20 × 10 <sup>-4</sup>	0.262	0.0193	0.00480	0.1046	0.0705	2979	3.50 × 10 <sup>-5</sup>	189
Mabee 561	821	2.92 × 10 <sup>-4</sup>	0.257	0.0130	0.00509	0.1043	0.0558	3333	2.73 × 10 <sup>-5</sup>	169
Mabee B133	–	–	–	0.0182	0.00432	0.1033	0.0705	2636	2.42 × 10 <sup>-5</sup>	165
Mabee 79	708	3.24 × 10 <sup>-4</sup>	0.331	0.0179	0.00422	0.1032	0.0759	2148	2.20 × 10 <sup>-5</sup>	141
Mabee 51	691	3.42 × 10 <sup>-4</sup>	0.358	0.0205	0.00397	0.1028	0.0878	1879	2.01 × 10 <sup>-5</sup>	139
Mabee 530	693	2.87 × 10 <sup>-4</sup>	0.300	0.0143	0.00458	0.1041	0.0578	2751	2.28 × 10 <sup>-5</sup>	142
Mabee 56	449	2.68 × 10 <sup>-4</sup>	0.431	0.0204	0.00387	0.1026	0.0759	1792	1.79 × 10 <sup>-5</sup>	114
Mabee 592	773	3.68 × 10 <sup>-4</sup>	0.344	0.0194	0.00426	0.1032	0.0962	1850	2.46 × 10 <sup>-5</sup>	150
Mabee 107	799	3.55 × 10 <sup>-4</sup>	0.321	0.0154	0.00455	0.1037	0.0642	2633	2.40 × 10 <sup>-5</sup>	150
Mabee B134	508	2.91 × 10 <sup>-6</sup>	0.414	0.0133	0.00400	0.1031	0.0543	2247	1.35 × 10 <sup>-5</sup>	106
Air	5.22	7.22 × 10 <sup>-4</sup>	1.000	16.45	0.00299	0.1020	31.6	295.5	0	0

“Excess <sup>21</sup>Ne” and “Excess <sup>40</sup>Ar” refer to excess abundances of <sup>21</sup>Ne and <sup>40</sup>Ar, relative to <sup>20</sup>Ne and <sup>36</sup>Ar, compared to atmospheric values; the excess abundances are due to subsurface contributions.

TABLE 4  
CONCENTRATIONS AND ISOTOPIC COMPOSITIONS OF XENON IN GASES FROM THE MABEE EOR FIELD

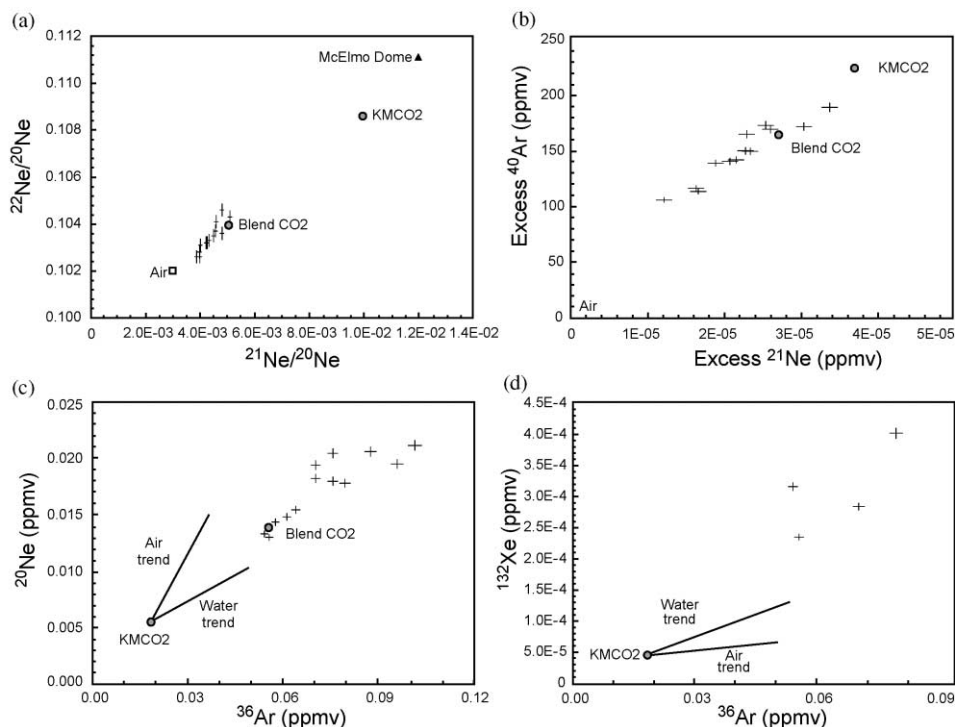
Sample	$^{132}\text{Xe}$ (ppmv)	$^{124}\text{Xe}/^{132}\text{Xe}$	$^{126}\text{Xe}/^{132}\text{Xe}$	$^{128}\text{Xe}/^{132}\text{Xe}$	$^{129}\text{Xe}/^{132}\text{Xe}$	$^{130}\text{Xe}/^{132}\text{Xe}$	$^{131}\text{Xe}/^{132}\text{Xe}$	$^{134}\text{Xe}/^{132}\text{Xe}$	$^{136}\text{Xe}/^{132}\text{Xe}$
KMCO2	$4.52 \times 10^{-5}$	0.00358 0.00009	0.00345 0.00009	0.07094 0.00007	0.97643 0.00049	0.14976 0.00015	0.77812 0.00039	0.40606 0.00020	0.35329 0.00018
Mabee 561	$2.35 \times 10^{-4}$	0.00351 0.00009	0.00333 0.00008	0.07127 0.00007	0.98316 0.00049	0.15102 0.00015	0.78747 0.00039	0.39057 0.00020	0.33316 0.00017
Mabee 565	$4.02 \times 10^{-4}$	0.00358 0.00009	0.00336 0.00008	0.07145 0.00007	0.98214 0.00049	0.15139 0.00015	0.78834 0.00039	0.38956 0.00019	0.33132 0.00017
Mabee 619	$2.84 \times 10^{-4}$	0.00367 0.00009	0.00350 0.00009	0.07132 0.00007	0.98009 0.00049	0.15076 0.00015	0.78724 0.00039	0.39109 0.00020	0.33361 0.00017
Mabee B134	$3.16 \times 10^{-4}$	0.00358 0.00009	0.00336 0.00008	0.07133 0.00007	0.98294 0.00049	0.15115 0.00015	0.78855 0.00039	0.38969 0.00019	0.33142 0.00017
Air	$2.34 \times 10^{-2}$	0.00354 0.00001	0.00330 0.00002	0.07136 0.00009	0.9832 0.0012	0.1514 0.00012	0.7890 0.0011	0.3879 0.0006	0.03294 0.0004
$^{238}\text{U}$ sf							0.1549 0.0059	1.458 0.033	1.761 0.031
McElmo Dome		0.00348 0.00002	0.00323 0.00001	0.07017 0.00007	0.97745 0.0049	0.14883 0.00010	0.77892 0.00039	0.40514 0.00020	0.35276 0.00018

The values for " $^{238}\text{U}$  sf" refer to isotopic ratios derived during the spontaneous fission of uranium.

CO<sub>2</sub> for reinjection. Thus Blend CO<sub>2</sub> can be considered an overall average of the CO<sub>2</sub> from the Mabee active CO<sub>2</sub> area.

The incoming pipeline CO<sub>2</sub> (KMCO<sub>2</sub>) is isotopically similar to CO<sub>2</sub> from the McElmo Dome. Although there are opportunities for mixing of the CO<sub>2</sub> from the various CO<sub>2</sub> deposits during transport to West Texas, it appears that the injected Mabee CO<sub>2</sub> is mostly from the McElmo Dome. It had been thought by the operators of the Mabee field that the CO<sub>2</sub> originated from the Bravo Dome, and we had begun this study anticipating Bravo isotopic compositions.

Relative to KMCO<sub>2</sub>, the Mabee production samples have all acquired a noble gas isotopic component similar to that in the Earth's atmosphere ("Air"; Figure 5a). The origin of this component could be either native to the oil producing geologic formations (and therefore present prior to any oil production), water that is injected in large amounts alternating with CO<sub>2</sub> injection (a process called "wagging", or "WAG", water-alternating-gas/CO<sub>2</sub>), or from atmospheric contamination during sampling. The latter can be seen not to be the case by the <sup>20</sup>Ne–<sup>36</sup>Ar trend shown in Figure 5c. Mixing KMCO<sub>2</sub> directly with atmosphere ("Air") during sampling would produce a trend toward higher <sup>20</sup>Ne relative to <sup>36</sup>Ar. Instead, the samples follow a trend similar to that involving mixing of KMCO<sub>2</sub> with water. The difference between the two trends is derived from the variable solubility of neon and argon in water, which results in a different Ne/Ar ratio in



**Figure 5:** Isotopic compositions and concentrations for neon, argon, and <sup>132</sup>Xe from gases sampled at the Mabee EOR field. Data from production wells are shown as small crosses indicating analytical precision. Sample KMCO<sub>2</sub> is taken directly from the CO<sub>2</sub> supply pipeline at the Mabee field prior to injection. Blend CO<sub>2</sub> is taken from the return pipeline, and represents an overall mixing of gases captured at active wellheads throughout the active CO<sub>2</sub> area (see Figure 4). The significance of the water and air trends is discussed in the text.

water than in air. This might indicate that noble gases dissolved in the WAG water have a strong effect on the isotopic compositions of the produced gases.

The water trends on Figure 5 depict trajectories for KMCO<sub>2</sub> mixing with water in equilibrium with the atmosphere. Figure 5b indicates that there must be a component present in addition to, or perhaps other than, a component that would be provided by atmosphere-equilibrated water. The <sup>40</sup>Ar and <sup>21</sup>Ne depicted in Figure 5b represent the excess amounts of these isotopes, relative to <sup>36</sup>Ar and <sup>20</sup>Ne, beyond those present in the atmosphere (i.e. by definition air contains no excess <sup>40</sup>Ar or <sup>21</sup>Ne). The excess amounts are from subsurface production of <sup>40</sup>Ar and <sup>21</sup>Ne, through radioactive decay of <sup>40</sup>K and the nucleogenic reaction <sup>18</sup>O( $\alpha,n$ )<sup>21</sup>Ne. If the KMCO<sub>2</sub> component mixed only with air, or with water in equilibrium with air, the Mabee samples should trend toward zero <sup>40</sup>Ar and <sup>21</sup>Ne (the origin), which they do not. They trend toward a position with elevated Excess <sup>40</sup>Ar relative to Excess <sup>21</sup>Ne. Thus the component mixing with KMCO<sub>2</sub> must originate within the subsurface.

Xenon isotopic systematics also show the presence of a subsurface component in addition to KMCO<sub>2</sub> (Table 4). The production well gases appear to be enriched in <sup>134</sup>Xe relative to <sup>136</sup>Xe in a manner consistent with the presence of xenon from spontaneous fission of uranium in the subsurface (Figure 6). Spontaneous fission would also increase <sup>132</sup>Xe concentrations, and Figure 5d shows <sup>132</sup>Xe enhanced relative to both water and air trends originating at the KMCO<sub>2</sub> composition.

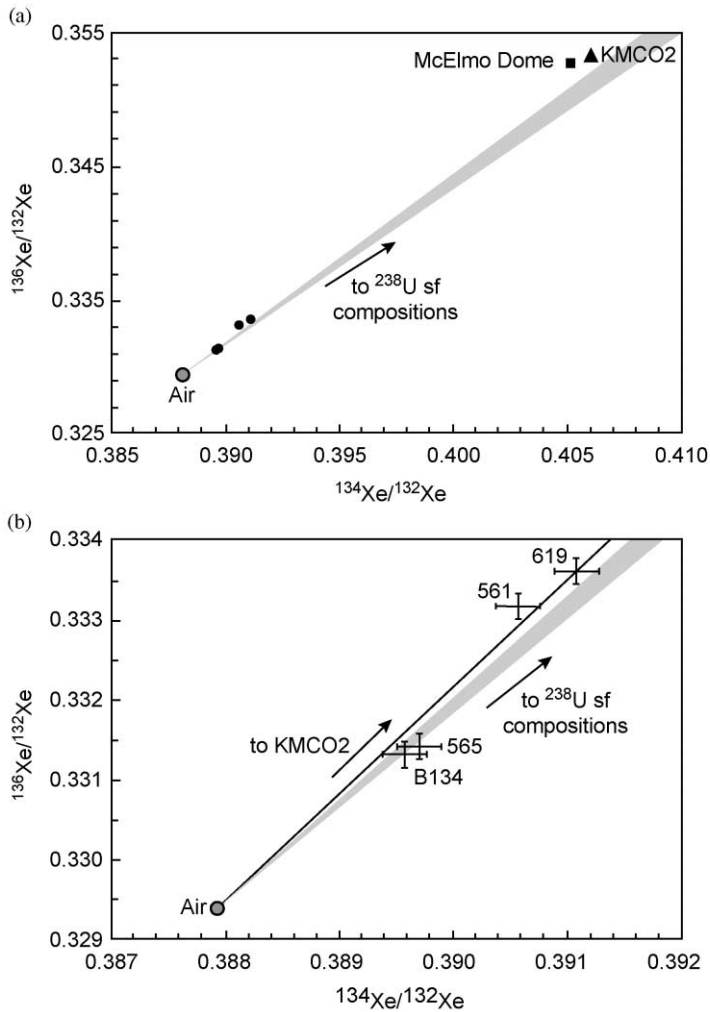
We were not able to collect samples of the WAG water and do not know if it contained the subsurface component indicated in Figures 5 and 6. If it did, the WAG water must be fairly old and derived from a deep groundwater aquifer. Instead, however, we tend to believe the subsurface component originated within the oil producing reservoir itself. The distributions of the isotopic compositions shown in Figures 5 and 6 could be derived from a simple two-component mixture of KMCO<sub>2</sub> and a native subsurface component with air-like neon isotopic ratios, slightly enhanced <sup>20</sup>Ne over <sup>36</sup>Ar, and enhanced <sup>132</sup>Xe, <sup>134</sup>Xe relative to <sup>136</sup>Xe, and Excess <sup>40</sup>Ar.

How does all of this relate to noble gas tracers in CO<sub>2</sub> storage? The Mabee field “demonstration” resulted in several important observations. First, and most important, the noble gas tracer (KMCO<sub>2</sub>) is not completely “lost” in the subsurface. What was injected can be detected. The production well data require the presence of the KMCO<sub>2</sub> component. Tracer tests, particularly those in the deep subsurface, are known to be problematic in that the tracer apparently can be fractionated away from the traced fluid and lost to the surroundings. This did not occur, as indicated by the KMCO<sub>2</sub> component present in all samples. Second, even though a subsurface component and possibly a WAG water component, is detected in the produced gases, the KMCO<sub>2</sub> component is always clearly identifiable. If today the injected CO<sub>2</sub> migrates away from the Mabee active CO<sub>2</sub> injection area (Figure 4) and is collected from external wells, the KMCO<sub>2</sub> noble gas fingerprint will be clearly identifiable. Third, the McElmo Dome CO<sub>2</sub> sampled as KMCO<sub>2</sub> has a <sup>124</sup>Xe concentration of about  $1.62 \times 10^{-7}$  ppmv (Table 4). The required concentration for ground surface monitoring (Table 2) is about two orders of magnitude higher than this. Therefore, the tracer amount calculated for surface monitoring will clearly be sufficient for subsurface monitoring. This is especially true if the subsurface component originates in the WAG water, since CO<sub>2</sub> stored without WAG water would not be affected. This was an important check of the verity of the calculations presented in Table 2. Fourth, the isotopic compositions observed in the Mabee sample suite were very systematic. The data generally formed linear trends (Figure 5) with deviations explainable by known subsurface components (e.g. uranium spontaneous fission). Alternatively, had the data set been chaotic and unexplainable, it would have raised serious questions about the behavior and thus utility of noble gases in a CO<sub>2</sub> storage setting. Finally, the Mabee test demonstrated the analytical ability to detect in a CO<sub>2</sub> storage setting, even very subtle variations in isotopic compositions. Compositions imparted by xenon isotopic tracers would not be nearly so subtle. Thus the Mabee test demonstrated that the noble gas tracer technique can be a robust and reliable tracer method in CO<sub>2</sub> injection setting.

### **Monitoring for Noble Gas Isotopes**

Strategies for noble gas monitoring at CO<sub>2</sub> storage sites will depend heavily on site-specific geological and hydrological characteristics, and on risk assessment parameters such as leak location probabilities





**Figure 6:** Isotopic compositions for xenon from gases sampled at the Mabee EOR field. Sample KMCO2 is taken directly from the CO<sub>2</sub> supply pipeline at the Mabee field prior to injection, and can be seen to have the approximate xenon isotopic composition of the McElmo Dome. Gray shaded field from Air to  $^{238}\text{U}$  spontaneous fission (sf) values represents potential compositions derived by subsurface addition of fission-derived  $^{136}\text{Xe}$  and  $^{134}\text{Xe}$  to air. Bottom diagram is a close up showing analytical precision of the Mabee samples, and their relation to the spontaneous fission field and KMCO2-Air mixing line.

(e.g. borehole leakage) and degree of early warning required. A significant amount of work is yet required concerning both of these topics before definitive monitoring strategies can be developed.

In general, monitoring could be of two types. Noble gases and CO<sub>2</sub> escaping from deep formations may dissolve into waters and brines of overlying hydrostratigraphic units. In such cases, monitoring deep groundwaters for the distinctive noble gas isotopic tracer may be preferable. A considerable amount of work

has been done concerning natural noble gas signatures in both deep and shallow groundwater [2,4,19–23]. As indicated in Table 1, noble gas concentration in continental aquifers are typically about two orders of magnitude lower per gram water (i.e.  $1 \text{ cm}^3$ ), than atmospheric concentrations per  $\text{cm}^3$  air. For a given gas flux derived from stored  $\text{CO}_2$ , noble gas tracers could be easier to detect in these aquifers than in soil gases, provided that the noble gas flux dissolves into the aquifer water. Sampling would also be somewhat more certain for aquifers than for soil gases. As soil gas is collected, air from above ground surface may be pulled into the sampler; such atmospheric “contamination” is much easier to avoid in ground water sampling. The desirability of deep aquifer monitoring is dependant on the expected behavior of leaking  $\text{CO}_2$  and noble gases in the strata overlying the storage formation. Much more work, including expansion of numerical models of  $\text{CO}_2$  and noble gas migration, is required.

Ultimately, even though aquifers may be monitored, ground surface monitoring will be desirable. Table 2 was constructed on this premise. Any of the various methodologies available for collection of soil gases could be employed. The amount of gas required for analysis by noble gas mass spectrometry is very small, and the problem will not be in the volume of gas to be collected, but in insuring that the gas collected is representative of the soil gas being emitted. However, multi-liter sampling and repetitive sampling will likely be sufficient.

A study was conducted at our laboratory several years ago that would appear significant for soil gas monitoring for  $\text{CO}_2$  leakage [24]. In the study,  $\text{SF}_6$  and  $^3\text{He}$  tracers were released together by a chemical detonation at about 350 m depth. The ground surface was monitored at several locations above the release, including along an adjacent geologic fault.  $\text{SF}_6$  was detected in the fault zone 50 days after detonation (nothing was ever detected outside the fault zone). The  $^3\text{He}$  was not detected for an additional 325 days. It had been expected, following conventional wisdom, that  $^3\text{He}$  would be detected first. The small atomic size of helium would cause it to be less impeded in its migration than the larger  $\text{SF}_6$ . Numerical modeling using the NUFT unsaturated transport code was successful in reproducing the tracer breakthrough sequence and timing. The helium apparently had access to micropathways that exclude  $\text{SF}_6$  due to its size. The  $\text{SF}_6$  migration path had less tortuosity and was more directly upward within the fault zone. This study raises the possibility that a xenon isotopic tracer (atomic radius 2.2 Å; Table 1) could migrate to ground surface faster than leaking  $\text{CO}_2$  (1.4 Å C–O linear bond distance). If so, it could provide an early-warning system for leaking  $\text{CO}_2$ .

An additional monitoring consideration is that geologic  $\text{CO}_2$  storage may be sited in oceanic shelf/basin regions such as the North Atlantic oil fields (e.g. Sleipner). Monitoring in these locations would involve direct monitoring of seawater. This is perhaps the easiest scenario for noble gas tracer detection due to the low noble gas concentrations in seawater (Table 1). Oceans have a very significant capacity for buffering  $\text{CO}_2$  concentration. Initial releases of leaking  $\text{CO}_2$  would not be detectable by direct  $\text{CO}_2$  monitoring nor by monitoring biological effects associated with increased aqueous  $\text{HCO}_3^-$ . Noble gas isotopic compositions within bottom waters could be significantly altered by noble gas emissions from leaking  $\text{CO}_2$  storage sites. However, assessment of oceanic monitoring will require an examination of the effects of ocean bottom currents, ocean sediment pore water behavior, and pore water diffusion, among other processes.

## CONCLUSIONS

Noble gas isotopes, particularly xenon isotopes, may provide a mechanism for leakage monitoring and subsurface tracing of stored  $\text{CO}_2$ . They are chemically inert, environmentally safe, persistent, and stable in all environments. While  $^3\text{He}$  and  $^{36}\text{Ar}$  may be suitable only for special uses due to availability and high costs,  $^{124}\text{Xe}$ ,  $^{129}\text{Xe}$ , and  $^{136}\text{Xe}$  are inexpensive and readily available. Only small volumes of these xenon isotopes would be needed (<900 L per year for the Mabee storage analogue), simplifying handling and injection. The Mabee field test conducted as part of this study demonstrated that unique noble gas isotopic compositions injected with  $\text{CO}_2$  can be readily detected in production wells. Even though other isotopic components are present in the subsurface, the unique isotopic fingerprint can always be identified. The noble gases behave in a systematic and predictable manner in the  $\text{CO}_2$  injection setting, indicating that the noble gas tracing technique would be a robust and reliable method. Many aspects of potential monitoring methods must yet be formulated, but monitoring in deep aquifers, ocean waters, and the ground surface, for which the calculations presented here are intended, all appear achievable.

## RECOMMENDATIONS

Very important questions remain concerning both the partitioning behavior of tracers in the CO<sub>2</sub> storage environment and the techniques for the monitoring process itself. The lack of data on partitioning was discussed above. Monitoring strategies that need to be addressed include deep versus shallow (Earth surface) monitoring, the value of focusing monitoring along geologic structures, and the possibility that some tracers may serve as an early warning of CO<sub>2</sub> migration to the surface. These issues lead to the following recommendations for future work:

1. Laboratory-scale studies should be conducted to document partition coefficients and solubilities of noble gases and other tracers for the phases, and the  $P$ - $T$  conditions, to be encountered in the CO<sub>2</sub> storage environment.
2. Based on this partitioning and solubility data, numerical modeling should be conducted to simulate the behavior within the storage reservoir and overlying strata of noble gases and other tracers dissolved in injected CO<sub>2</sub>. This will provide a mechanism for assessing a variety of monitoring strategies.
3. Field tests should be conducted examining the upward migration of CO<sub>2</sub> and large- and small-atomic radii noble gases for the purpose of assessing the possibility that certain tracers may be capable of providing an early warning of CO<sub>2</sub> migration to the surface. These tests could be conducted at shallow depths (perhaps < 300 m).
4. A field demonstration at a potential storage site is needed in which only CO<sub>2</sub> and noble gas tracers are injected (no EOR, no WAG water), and for which leakage is induced and aggressive monitoring is conducted. It is only in this more realistic setting that a true evaluation can be made of the potential for noble gas tracing of CO<sub>2</sub>.

## NOMENCLATURE

EOR enhance oil recovery  
 ppmv parts per million by volume  
 STP standard temperature and pressure (= 25 °C and 1 atm)  
 WAG water-alternating-gas (CO<sub>2</sub>)

## ACKNOWLEDGEMENTS

We would like to thank Jeff Woliver and Craig Goodyear of ChevronTexaco Corporation in Midland, Texas for giving us access to the Mabee EOR field, for providing us with information concerning the production and injection wells, and for helping with field logistics for sampling. We also thank two anonymous reviewers for their helpful comments which improved the content and presentation of this chapter. This work was performed under the auspices of the US Department of Energy by the Lawrence Livermore National Laboratory under contract W-7405-Eng-48.

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