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CARBON DIOXIDE CAPTURE USING A ZEOLITE MOLECULAR SIEVE SAMPLING SYSTEM FOR ISOTOPIC STUDIES (^{13}C AND ^{14}C) OF RESPIRATION

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ABSTRACT. A method for collecting an isotopically representative sample of CO_2 from an air stream using a zeolite molecular sieve is described. A robust sampling system was designed and developed for use in the field that includes reusable molecular sieve cartridges, a lightweight pump, and a portable infrared gas analyzer (IRGA). The system was tested using international isotopic standards (^{13}C and ^{14}C). Results showed that CO_2 could be trapped and recovered for both $\delta^{13}C$ and ^{14}C analysis by isotope ratio mass spectrometry (IRMS) and accelerator mass spectrometry (AMS), respectively, without any contamination, fractionation, or memory effect. The system was primarily designed for use in carbon isotope studies of ecosystem respiration, with potential for use in other applications that require CO_2 collection from air.

INTRODUCTION

The rapid increase in atmospheric CO_2 concentrations and concomitant rise in temperature observed in the last century have led to a need for a more accurate understanding of the link between the global carbon cycle and climate change (IPCC 2001). It is estimated that soils contain 1.6 Tt of carbon, a stock twice that found in the atmosphere and 3 times that of the terrestrial plant biomass (Schimel 1995). Both climate and land use are key regulators of ecosystem carbon stocks (Lindroth et al. 1998; Lloyd and Taylor 1994; Raich and Tufekcioglu 2000; Sanderman et al. 2003; Trumbore et al. 1996). Of particular importance in this respect is the balance between soil carbon sequestration and respiration that, if shifted, has the potential to contribute further to atmospheric CO_2 increases (Cox et al. 2000; Knorr et al. 2005; Mack et al. 2004).

Natural abundance carbon isotope tracers can be used as a means to better understand and predict how Earth's carbon reservoirs will respond to global change (climate, land use, pollution). Differences in the $\delta^{13}C$ signatures of C_3 and C_4 plants and derivative soil organic matter (SOM) have been used to examine rates of decomposition and turnover of SOM on time scales of 1 yr to hundreds of thousands of years (Balesdent and Mariotti 1996; Boutton 1996). Studies have also used radiocarbon analyses of bulk SOM to estimate rates of carbon cycling in a range of ecosystems (Harkness et al. 1986; Harrison 1996; Paul et al. 1997; Quideau et al. 2001; Richter et al. 1999). However, since SOM is composed of various pools of carbon cycling on different time scales (i.e. from hours to millennia), bulk measurements obscure the response of specific pools to both transient and long-term change. Furthermore, although measurements of ^{14}C in SOM have been used as a surrogate for soil respiration, Trumbore (2000) has suggested that this approach significantly underestimates CO_2 fluxes. Consequently, there is now considerable interest in the use of ecosystem and soil-respired CO_2 isotopic signatures to understand the role of environmental factors on the rate of organic matter decomposition and the magnitude and source of CO_2 fluxes.

Capture of CO_2 respired from soils for subsequent isotopic analysis has been achieved in the field using various methods, including cryogenic trapping, collection in evacuated flasks (e.g. Charman et al. 1999), and absorption in hydroxide solutions such as sodium hydroxide (e.g. Dörr and Münnich 1986). Each of these methods has its disadvantages, but common to all is the fact that they are impractical when used at remote locations in the field. For example, absorption of CO_2 in hydrox-

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ide solutions causes an isotopic fractionation effect (Keeling 1958), and the solutions are difficult to use in the field due to their caustic nature. Cryogenic trapping of CO_2 in the field using liquid nitrogen (b.p. –196 °C) is potentially hazardous and may result in the condensation of atmospheric O_2 (b.p. –183 °C). This may reduce the collection efficiency of CO_2 but more importantly could result in an explosive situation on recovery of CO_2 using a vacuum rig (Bauer 1992). A small number of studies have utilized zeolites (often referred to as molecular sieves) as an alternative method of CO_2 capture (Bauer et al. 1992; Bol and Harkness 1995; Gaudinski et al. 2000; Koarashi et al. 2002). The zeolite molecular sieve approach is easy to use and has none of the above disadvantages, thus making it ideal for field experiments and remote area research to determine the isotopic source of ecosystem and soil-respired CO_2. Furthermore, the molecular sieve material (synthetic faujasite) is reusable and can withstand temperatures of 500 °C almost indefinitely (Barrer 1959).

Zeolites

Zeolites are 3-dimensional crystalline aluminosilicates of the alkali and alkaline earth elements (commonly sodium, potassium, and calcium) represented by the empirical molecular formula:

$$M_{2/n}O \cdot Al_2O_3 \cdot xSiO_2 \cdot yH_2O$$

where n is the valence of the cation and x and y are integers. Zeolites are used in the petrochemical and petroleum refining industries as ion exchangers, adsorbents, and selective catalysts (Yang 1997). The characteristics of zeolites (dehydrated zeolites in particular) that are of interest when partitioning an analyte gas from a mixture of gases, such as the separation of CO_2 from air, include uniform molecular pore size, polarity, reversible and selective adsorption (different cationic forms of zeolite can lead to significant differences in the adsorption of a given gas), and adsorption capacity. Firstly, the 3-dimensional framework of the crystalline aluminosilicate structure created via the sharing of adjacent oxygen atoms by SiO_4 and AlO_4 tetrahedra (Breck 1974) contains a network of uniform molecular-sized pores (3–8 Å; Flanigen 1991). This feature gives zeolites their molecular sieving property as the porous structure allows selective admittance of molecules with diameters less than that of the pore window size, while those that are larger are sterically or kinetically hindered. Secondly, the isomorphous substitution of aluminium for silicon in the crystalline lattice structure of a zeolite lends it an overall net negative charge. This negative charge is neutralized by an electrochemical equivalent of cations (Barrer 1978) such as sodium, barium, and potassium. Consequently, zeolites have a high affinity for polar molecules such as H_2O and CO_2. Competitive adsorption is typically of the order $H_2O>CO_2>N_2>O_2$ (Breck 1974) at ambient temperature and pressure. The affinity of polar molecules like CO_2 for substituted zeolites is due to an interaction between the molecule and the zeolite. In the case of CO_2, it is the interaction of its quadrupole moment with the electric field of the zeolite (Cui et al. 2003), resulting in high adsorption of monolayer coverage (Siriwardane et al. 2001). Furthermore, the isotherms applicable to many zeolites follow classification "I" of IUPAC (International Union of Pure and Applied Chemistry) grouping, also known as the Langmuir type adsorption isotherm (Ruthven 1984). A crucial property possessed by zeolites is reversible sorption. Desorption of a gaseous adsorbate from zeolite can be effectively controlled by the application of adequate temperature or pressure (BDH, no date), otherwise a hysteretic effect may occur. Finally, zeolites possess a high adsorption capacity at ambient temperature and pressure, even at low adsorbate concentrations (BDH, no date).

Zeolites in Isotope Studies of CO_2

Zeolites that have been used in the partitioning of the trace gas CO_2 from carrier gas streams include molecular sieve type 4A (Koarashi et al. 2002), a sodium aluminosilicate with an effective pore

diameter of 4.2 Å, and type 13X (Bauer et al. 1992; Bol and Harkness 1995; Gaudinski et al. 2000), another sodium aluminosilicate with an effective pore diameter of 7.8 Å (Flanigen 1991). Bauer et al. (1992) used standards of known isotopic composition to test molecular sieve type 13X incorporated within a vacuum rig. The use of a single ^{13}C standard, however, precluded the detection of any isotopic memory effect. Two standards were used for ^{14}C, but any tests for memory effect were not reported.

Bol and Harkness (1995) carried out a method validation of their sampling system (incorporating molecular sieve type 13X) using the ^{13}C signal of atmospheric CO_2. While accounting for possible isotope fractionation, this method was not designed to detect any memory effect or indeed any contamination via atmospheric CO_2 leaking into the sampling system. Gaudinski et al. (2000) made a study of the ^{14}C content of soil respiration using molecular sieve type 13X but do not report testing of their sampling system. In another soil respiration study, Koarashi et al. (2002) used molecular sieve type 4A; tests were made for quantitative recovery but not for isotope fractionation or memory effect.

In this paper, we describe the development of a sampling system intended for ecosystem respiration studies that utilizes molecular sieve type 13X. In addition, a rigorous analytical testing program was executed by repeated measurement of authenticated laboratory standards (both $^{13}CO_2$ and $^{14}CO_2$) to enable the detection of any atmospheric contamination, isotopic fractionation, or memory effect.

EXPERIMENTAL

Sampling System Design

A closed-loop sampling system was designed (see Figures 1 and 2) for laboratory and field applications with elements similar to one described by Gaudinski et al. (2000). The sampling system incorporated the following components: a molecular sieve sampling cartridge (MSC), a CO_2 scrub, a bypass (to allow monitoring of CO_2 concentration before sampling), a water trap, a portable infrared gas analyzer (IRGA, PP Systems, UK), a sampling chamber, and a small battery-powered pump (AeroVironment Inc., USA).

The water trap, CO_2 scrubber, and sampling cartridges were made from quartz glass and based on an original design by Bol and Harkness (1995). Both ends of every cartridge were fitted with an autoshutoff Quick Coupling™ (Colder Products Company, USA) attached with short lengths of PVC tubing (Tygon, Fisher Scientific, UK). WeLoc® clips (Scandinavia Direct, UK) were placed across the PVC tubing between each end of the cartridge and the Quick Couplings to control gas flow into the MSC during operation. All junctions were made using T-connectors (Kartell Plastics UK Ltd., UK).

The CO_2 scrubber cartridge was filled with ~14 g of soda lime (BDH laboratory supplies, UK) and the water trap (similar quartz cartridge) filled with a desiccant, regular $CaSO_4$, Lab Grade –10+20 Mesh (Alfa Aesar, Germany). A similar but smaller-bodied quartz cartridge was filled with 3–4 g of molecular sieve type 13X (1/16″ pellets, BDH Laboratory supplies, UK). The contents of all 3 cartridges were held in place with quartz wool. During the initial development of the sampling system, molecular sieve types 4A and 5A were tested before settling on the use of molecular sieve type 13X, the performance of which we discuss herein.

The sampling chamber (~5 L) used for the test program was constructed from PVC pipe and sealed at both ends with nitrile rubber (LRC Products Ltd, UK). The chamber was connected to the CO_2 sampling system via 2 Quick Couplings and nylon tubing (see Figure 2). Gas flow pathways within the sampling system were manipulated using WeLoc clips.

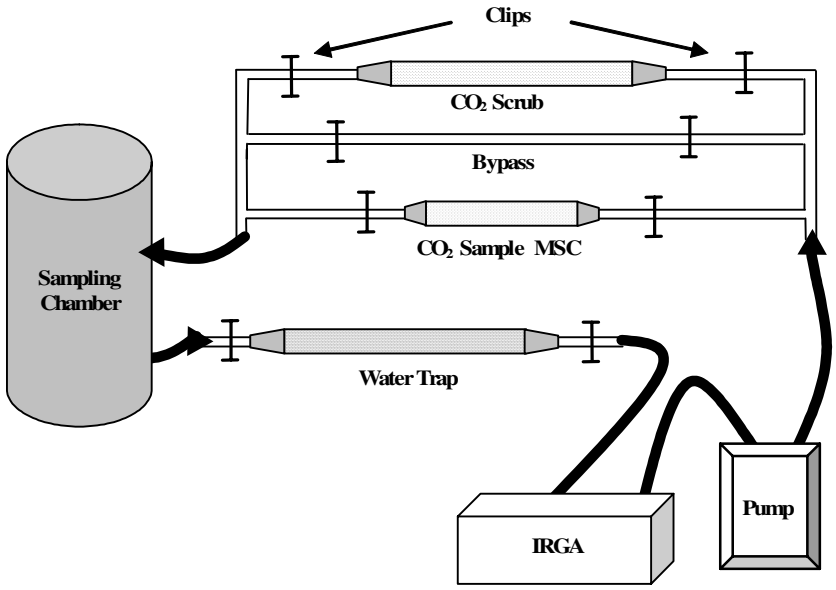

Figure 1 Schematic diagram of the molecular sieve sampling system. Gas flow pathways are manipulated by opening and closing the clips. Clips removed from the CO_2 scrub (soda lime) allow atmospheric CO_2 to be removed from within the sampling chamber. Removal of clips from the bypass allows CO_2 evolution inside the chamber to be monitored, thus ensuring that enough CO_2 has respired for ^{14}C analysis. Finally, clips are removed from the MSC to capture an isotopically representative sample of the CO_2 in the chamber. IRGA = infrared gas analyzer.

Figure 2 The molecular sieve sampling system in field operation. The chamber is for demonstration purposes only.

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Molecular Sieve Cartridge Activation

To ensure that zeolite cartridges were free of contamination prior to sampling, MSCs were simultaneously heated to 500 °C using a tube furnace (Carbolite MTF 10/15, Carbolite, UK) and evacuated to 10^{-2} mbar (see Figure 3). A slush trap (consisting of dry ice and industrial methylated spirit) and a liquid nitrogen trap were used to aid desorption of any gases held on the zeolite. Each MSC was then allowed to cool to <30 °C and filled with high-purity N_2 gas to just above atmospheric pressure (~1100 mbar). We found that the new zeolite molecular sieve exhibited a small amount of hysteresis on first use (data not shown); therefore, fresh zeolite was first purged of all gases and then flushed with CO_2 in an air stream and repurged prior to sampling.

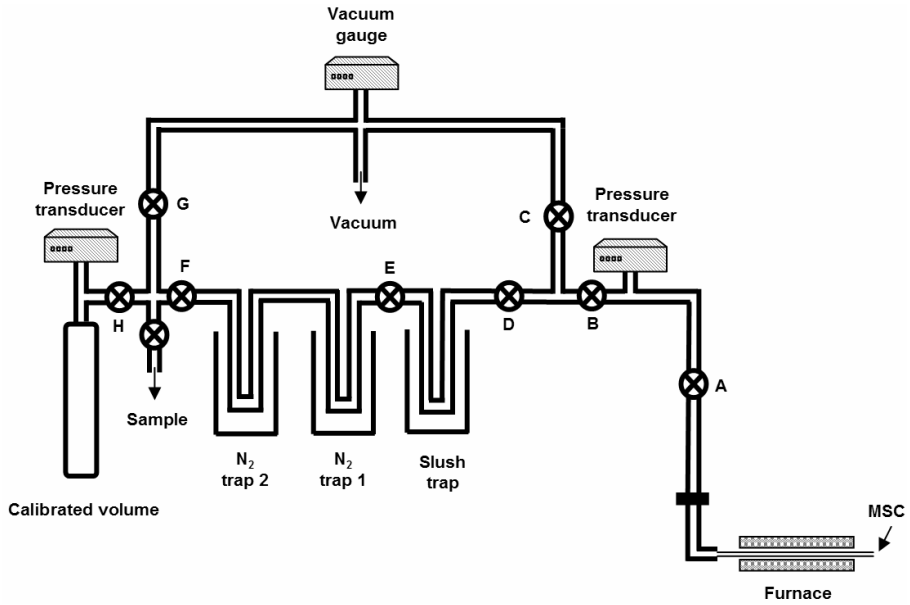

Figure 3 Schematic of the vacuum rig used in the desorption of CO_2 from the MSCs. Valves are labeled with capital letters.

CO_2 Sampling Procedure

A scored borosilicate glass tube containing a CO_2 standard was placed into the sampling chamber and positioned inside a cylindrical protrusion in one of the nitrile rubber seals. The sampling chamber atmosphere was then circulated by the pump (flow rate 500 mL min^{-1}) through the CO_2 scrubber cartridge and the CO_2 concentration monitored using the IRGA. The chamber was considered ready for testing when the CO_2 concentration had dropped below 10 ppm, whereupon the pathway through the CO_2 scrubber was closed and the pathway to the sample MSC was opened. This was considered acceptable for testing purposes because all standards were of a concentration greater than 1600 ppm CO_2 when released into the sampling chamber (i.e. the residual 10 ppm CO_2 accounted for <0.6% of the total).

The borosilicate glass tube containing a CO_2 standard was cracked within the sampling chamber, and the gas was pumped around the sampling system and through the MSC. The MSC was closed and sampling ceased when the sampling chamber CO_2 concentration had reduced to below 100 ppm.

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Molecular Sieve Cartridge Desorption Procedure

The MSC was attached to the vacuum rig with the WeLoc clip still in place and dead space air removed by opening valves A, B, and C (see Figure 3) until 10^{-2} mbar was attained, whereupon all valves were closed. The MSC was then detached from the vacuum rig and the WeLoc clip removed from the front end of the cartridge to allow passage into the tube furnace. After insertion into the furnace, the clip was replaced and the MSC reattached to the rig. The vacuum rig was then pumped down to 10^{-2} mbar. A slush trap and 2 liquid N_2 traps were activated by raising the Dewar flasks around the borosilicate glass traps of the rig and valves A, B, D, and E opened. The MSC was then opened to the traps and the furnace temperature raised to 500 °C.

CO_2 was collected at 500 °C under static vacuum for 20 min after which valves F and G were opened and any non-condensables pumped away until a vacuum of 10^{-2} mbar was achieved in the MSC. All valves were then closed and the second nitrogen trap was removed and replaced with the slush trap. The CO_2 was transferred to the calibrated volume and the pressure of the expanded gas was measured using a pressure transducer (BOC Edwards, UK), allowing the volume of CO_2 recovered to be calculated. CO_2 was subsequently aliquoted into mass spectrometry tubes and $\delta^{13}C$ ratios analyzed by isotope ratio mass spectrometry (IRMS; dual inlet, VG Optima, UK). Further sub-samples of CO_2 were flame-sealed in borosilicate glass tubes, one of which was prepared as a graphite target (Slota et al. 1987) for ^{14}C measurement by accelerator mass spectrometry (AMS), by the 5MV tandem accelerator at the Scottish Universities Environmental Research Centre (SUERC), East Kilbride, UK (Freeman et al. 2004; Xu et al. 2004).

EXPERIMENTAL DESIGN

A total of 8 CO_2 standards were used in tests (ranging from 8 to 11 mL), 4 for each of the 2 MSCs used. The range of standard volumes chosen ensured sufficient CO_2 for AMS ^{14}C analysis, duplicate IRMS analysis, and also for a sub-sample to be archived. The CO_2 standards were prepared from materials with a wide range of $\delta^{13}C$ and ^{14}C isotopic signatures: Carbonate, Sucrose, and Barley mash (see Table 1). The range of $\delta^{13}C$ values from +1.8 to –26.8‰ allowed for stringent testing of the sampling system since the test covers a much greater range of values than would likely be encountered in the field. This also enabled a sensitive test for memory effect by alternating capture of standards (i.e. the difference between the Barley mash standard and the Carbonate standard for $\delta^{13}C$ analysis is 28.6‰).

Table 1 $\delta^{13}C$ and ^{14}C consensus values for isotopic standards used in the analytical testing program of the molecular sieve sampling system.

Standard material	$\delta^{13}C_{VPDB}$ ‰ (±0.1)	^{14}C concentration (% Modern ±1 σ)
Carbonate	+1.8	Background
Barley mash	–26.8	116.35 ± 0.0084 (Gulliksen and Scott 1995)
ANU Sucrose	–10.5	150.61 ± 0.11 (Rozanski et al. 1992)

The standards had natural abundance ^{14}C values ranging from 150.6% Modern (Sucrose) to background (Carbonate). A Sucrose standard following a Carbonate standard affects a difference of ~150% Modern and again allowed for a sensitive test of memory effect. Each of the 2 sets of standards were captured and recovered from both of the MSCs (1 and 2) sequentially. Table 2 illustrates the running order of the 4 standards with the previous standard applied to the 2 MSCs also given. All

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values for ^{13}C are reported using the delta notation with $^{13}C/^{12}C$ variations relative to the international standard Vienna Pee Dee Belemnite (VPDB) as described by the following equation:

$$\delta^{13}C\,(‰) = \left[\frac{(^{13}C/^{12}C)_{Sample} - (^{13}C/^{12}C)_{VPDB}}{(^{13}C/^{12}C)_{VPDB}}\right] \times 1000$$

^{14}C data are reported as % Modern with samples being normalized to a $\delta^{13}C$ of –25‰ (Stuiver and Polach 1977).

Table 2 $\delta^{13}C$ and ^{14}C results for standard gases after adsorption and desorption from molecular sieve sampling cartridges 1 and 2 and subsequent recovery for analysis by IRMS and AMS. Numbers in brackets beside the run order identify which of the 2 MSCs were used. The $\delta^{13}C$ measurements are the mean of 2 replicate analyses.

Run order	Standard material	Publication code	$\delta^{13}C_{VPDB}$ (±0.1‰)	^{14}C concentration (% Modern ±1 σ)
Previous	Sucrose	—	—	—
1 (1)	Carbonate	SUERC-4181	+1.7	1.23 ± 0.02
2 (1)	Sucrose	SUERC-4182	–10.7	150.59 ± 0.44
3 (1)	Barley mash	SUERC-4183	–26.9	116.91 ± 0.36
4 (1)	Barley mash	SUERC-4187	–26.8	116.37 ± 0.27
Previous	Carbonate	—	—	—
1 (2)	Sucrose	SUERC-4188	–10.6	150.06 ± 0.41
2 (2)	Carbonate	SUERC-4189	+1.7	1.28 ± 0.02
3 (2)	Barley mash	SUERC-4191	–26.7	114.78 ± 0.28
4 (2)	Barley mash	SUERC-4192	–26.8	115.94 ± 0.36

RESULTS

During initial development of the molecular sieve sampling system, testing was undertaken at each stage using CO_2 standards of known volume and $\delta^{13}C$. These results are not presented but led to modifications to the design of the MSCs and the MSC activation and desorption procedures, which are described in the Discussion.

The results of the $\delta^{13}C$ and ^{14}C analysis of standards used to test the final design of the MSCs and procedures are displayed in Table 2. The table shows that all $\delta^{13}C$ results were within 2 σ of the consensus values of the standards. The ^{14}C concentrations of the 2 Carbonate standards (SUERC-4181 and -4189) were higher than the usual levels obtained at the laboratory for background standards (i.e. for blanks combusted in sealed quartz tubes or processed by acid hydrolysis) but were identical at 2 σ. The remaining standards were therefore background-corrected using the mean ^{14}C concentration of these 2 carbonates (1.25% Modern). With one exception, all results for the ^{14}C standards were within 2 σ of the consensus value.

DISCUSSION

Several studies have reported the use of a zeolite molecular sieve to capture CO_2 from air streams for isotope measurement (see Introduction). Of these, few present the results of tests used to verify their sampling methods. Through the development of our sampling system we made a number of changes to the original MSC design and operating procedures. Only when these changes were made did the

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sampling system deliver quantitative trapping and recovery of CO_2 with preservation of isotopic integrity.

During the initial developmental stages of the sampling system, molecular sieve types 4A (pore window size 4.2 Å) and 5A (pore window size 4.9 Å; Dyer 1988) were tested for CO_2 capture before we settled on the use of molecular sieve type 13X (pore window size 7.8 Å). The kinetic diameter of CO_2 is 3.3 Å (Breck 1974), calculated from the minimum equilibrium dimension of 3.7 Å (as opposed to the Lennard-Jones approach), and so types 4A and 5A were deemed to have pore windows large enough to imbibe the CO_2 molecule. However, improved yields of CO_2 and $\delta^{13}C$ values that were much closer to the consensus values of the standards were obtained on initial testing of zeolite molecular sieve type 13X. Consequently, further testing of types 4A and 5A was abandoned.

Molecular sieve type 3A (effective pore diameter of 3 Å) was originally employed as a desiccant but was found to adsorb a small amount of CO_2 despite the fact that the kinetic diameter of this molecule is larger than the effective pore window size of the zeolite. This anomaly is due to 2 phenomena: 1) the oxygen framework of a zeolite is capable of being polarized (i.e. distorted); 2) both the zeolitic framework and the adsorbate molecule are continually vibrating under the influence of temperature, the net effect of which creates changes of ~0.4 Å in the size of the pore window (Dyer 1988). The combined effect of these processes is the adsorption of molecules of apparently larger diameter than that of the pore windows (measured crystallographically).

An important modification to the MSCs was to reduce the length of the section of quartz glass cartridge containing the zeolite molecular sieve material. Originally, this part of the MSC was the same length as the tube furnace used for desorption of CO_2 as based on the design of Bol and Harkness (1995). From their tests, Bol and Harkness (1995) reported mean recovery rates of only 88% of CO_2 (although they had other evidence suggesting greater recovery rates). However, with incomplete recovery of the sample, the risk of isotopic fractionation and memory effect remains. In the center of a tube furnace, there is a zone of uniform temperature (Carbolite, no date) that extends only to about 2.5 times the diameter of the tube measured from the outside of the furnace. Any area outside this central zone is likely to be at a lower temperature due to heat loss at the ends of the furnace. Only when the length of the main body of the MSC was reduced so that all the molecular sieve material was within the zone of uniform temperature did sample recoveries consistently reach ~100% and isotope results agree with consensus values. Prior to this modification, it is possible that some CO_2 that had been desorbed at 500 °C from within the zone of temperature uniformity was readsorbed onto cooler zeolite outside the zone. This was confirmed by moving the tube furnace backwards and forwards around the ends of the MSC while the MSC was attached to the vacuum rig during discharge. This movement resulted in an increase in pressure registered by the vacuum gauge.

In the procedure of Bol and Harkness (1995), MSCs were prepared by heating to 500 °C and evacuating to a best vacuum of 0.05 to 0.1 torr. We reduced this pressure to 10^{-2} mbar (0.0075 torr) for both activation and sample desorption. In this study, a higher vacuum ensured a sample recovery of >97% and an isotope signature consistent with the consensus value. The lower recoveries (~88%) observed by Bol and Harkness are therefore most likely due to incomplete desorption of CO_2 from the zeolite molecular sieve.

Another modification was the type of clips used to seal either end of the MSCs before and after sampling and to manipulate gas flows around the sampling system. The original design by Bol and Harkness (1995) utilized stainless steel Hoffman clips. These clips are relatively heavy, unwieldy to use, and require care to ensure that the tubing is sealed (plates of the Hoffman clip have to be paral-

lel). These were replaced with WeLoc clips, which are lighter; much easier to use, particularly in the field; and hold the required vacuum (10^{-2} mbar).

After all modifications were made, the sampling system was tested. Results are presented in Table 2. Since all ^{13}C results and all but one of the ^{14}C results of the standards recovered using the system fell within 2 σ of the consensus values, the results demonstrate that this sampling system collects isotopically representative samples of CO_2 from air streams.

The ^{14}C concentration of the Carbonate background standard was observed to be higher than the usual laboratory background (blank). This was not surprising given the greater number of potentially contaminating steps involved in the capture and desorption of the Carbonate standard (e.g. large surface areas of the molecular sieve material and the sampling system). It is possible that further modifications to the system could be made to provide a lower background value. However, current background levels are not considered to pose a particular limitation. First, the ^{14}C concentrations in the 2 background standards were statistically identical, suggesting a constant contribution that can be used to background-correct the other results. Secondly, the system is intended for the measurement of the ^{14}C concentration of ecosystem respiration, which is likely to be Modern (Gaudinski et al. 2000) and therefore little affected by variations in background.

We attribute a 1-σ error of ±0.1‰ to the IRMS measurement of $\delta^{13}C$. The $\delta^{13}C$ results were all within 2 σ of the consensus values, showing that the sampling system enabled capture, recovery, and analysis of a CO_2 sample without isotopic fractionation. For ^{14}C, there may be a suggestion of a memory effect in the results presented in Table 2 with, for example, the ^{14}C result for SUERC-4191 falling to the side of the previous standard applied to the MSC. However, there are also instances in the results that would not indicate any memory effect, e.g. the result for SUERC-4182 (150.59% Modern) is almost exactly the same as the consensus value (150.61% Modern), yet the previous standard on the MSC was a background standard (SUERC-4181).

The single result that fell outside the consensus value (SUERC-4191) could possibly be explained by a small amount of air contamination, assuming air would have a contemporary ^{14}C concentration of about 107% Modern (Levin and Kromer 2004). However, there are many examples in Table 2 that strongly suggest that they have not been contaminated with air. In the example of SUERC-4191, it is likely that the contamination would also have reflected a detectable shift in the $\delta^{13}C$ result due to the amount of air required (which was not the case). Consequently, since the results from the measurement of both ^{13}C and ^{14}C concentration, for a range of different standards, fell within 2-σ error of the consensus value (with the exception of one ^{14}C result), we believe that this molecular sieve sampling system provides a reliable method to collect isotopically representative samples of CO_2 from air streams.

CONCLUSIONS

A sampling system has been developed and tested for the collection of CO_2 from air, which is easy to use, safe, portable, and suitable for use in the laboratory or at remote locations. Results from the measurement of standards collected using the system show that it can be used reliably to capture representative samples of CO_2 for isotopic studies. Although primarily designed for use in carbon isotope studies of soil and plant respiration, the system could be used for other applications that require CO_2 collection from air.

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