THE USE OF ZEOLITE MOLECULAR SIEVES FOR TRAPPING LOW CONCENTRATIONS OF CO_2 FROM ENVIRONMENTAL ATMOSPHERES

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ABSTRACT. We describe a simple method for trapping low concentrations of CO_2 present in gas mixtures, such as air and soil respiration, using a zeolite molecular sieve (type 13×) for environmental carbon isotope studies. We employ reusable molecular-sieve cartridges and a lightweight battery-driven pumping system, developed to enable CO_2 collection in difficult and dangerous terrain or under extreme climatic conditions. The results of a small field experiment suggest that CO_2 could be quantitatively trapped on and recovered from the 13× molecular sieve, without any fractionation of the stable carbon isotope. The $\delta^{13}C$ of CO_2 was also independent of the amount of air $\leq$18 liters and rate at which it was collected, *i.e.* $\leq$1 liter of air/min.

INTRODUCTION

The Natural Environment Research Council (NERC) Radiocarbon Laboratory is involved in a field experimental study of the effects of global warming on the carbon turnover in upland soils, a part of the Terrestrial Initiative in Global Environmental Research (TIGER). One of our objectives is to compare the carbon isotope signature of carbon dioxide (CO_2) fluxes from artificially heated (3°C above ambient) and unheated British upland soils. The field work site of the study is on Great Dun Fell located at 845 m elevation in the Pennines in Cumbria. Great Dun Fell is a very cold, exposed, wet and windy site, with a slippery peaty terrain in hilly surroundings, and often shrouded by fog; not a terrain for carrying heavy equipment or dangerous chemicals.

Two well-established methods to collect CO_2 from gas mixtures are by 1) cryogenic trapping, or 2) static adsorption of CO_2 in sodium hydroxide (NaOH). The first method is especially problematic for environmental sampling in the field, as it requires a sizable amount of analytical equipment, in combination with the essential liquid nitrogen and dry-ice maker to be transported to the site. Collecting CO_2 using NaOH is logistically simpler, but the caustic character of NaOH does not make it easy to handle without adequate safety precautions. It was within this context that we focused on zeolite molecular sieves and their adsorption characteristics, *i.e.*, high capacity, selectivity and reversible adsorption with no hysteresis (see Breck 1974).

Thus we decided to design and test a CO_2 trapping system, based on lightweight, reusable molecular sieve cartridges, which could be used under extreme climatic conditions at poorly accessible or isolated sites, such as Great Dun Fell. The subsequent recovery of the CO_2 trapped on these molecular sieves in the laboratory should be quantitative, with no fractionation of ^{13}C and ^{14}C, and with enough CO_2 (2–5 mgC) being trapped and recovered for $^{14}CO_2$ analysis using accelerator mass spectrometry (AMS).

METHODS

Cartridge Preparation

The molecular sieve cartridges were prepared by filling quartz tubes with sieve material plugged in place with quartz wool. The molecular sieve was a synthetic sodium aluminosilicate (Type 13×, 1/16" pellets) purchased from BDH laboratory supplies (Merck Ltd). The sieve aperture is ≈10 Å, and the molecular diameters of N_2, O_2 and CO_2 (main gas constituents in air) are 2.98, 3.15 and 3.38 Å, respectively. For 13×, the Na^+ sieve is strongly polar, resulting in a preferential retention of CO_2 over

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other less polar gases in air, such as N_2 and O_2. No attempt was made to avoid H_2O vapor molecules adsorbed on the sieve, despite the fact that H_2O can prevent CO_2 being adsorbed on the 13x sieve or displace it once adsorbed. The laboratory vacuum rig for the activation and the recovery of CO_2 from the molecular sieve (Fig. 1) is a slightly modified version of a standard design used to collect CO_2 from sealed quartz tubes from the combustion of benzene samples.

Five quartz tubes were filled with 7–8 g of 13x molecular sieve. Each sieve was activated to eliminate any adsorbed H_2O, CO_2 and organic contaminants present, by evacuating the cartridge in a furnace (Carbolite MTF 10/15) to 0.1 torr at 500°C. When this vacuum was reached and held for *ca.* 5 min, the furnace was switched off, but pumping continued until the temperature fell below 250°C and the vacuum was <0.05 torr. The cartridge was then brought to atmospheric pressure by allowing nitrogen to be sucked into the quartz tube, and quickly removed from the furnace and allowed to cool to ambient temperature.

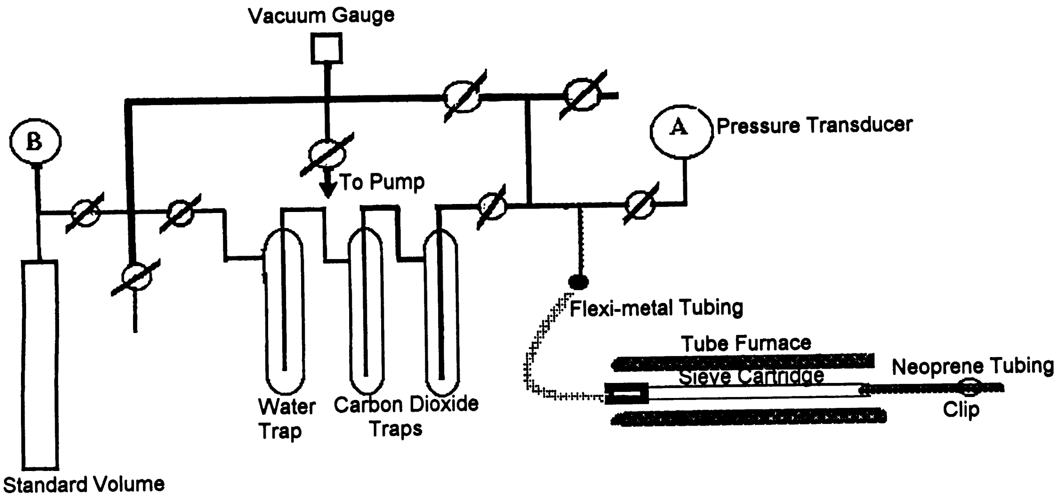

Fig. 1. Semi-micro vacuum rig used in the recovery of CO_2

CO_2 Collection

For the trapping of CO_2 from air, an activated sieve cartridge was connected to a small battery-powered pulse pump (Aerovironment Inc.) with a flow meter (Gilmont 65-MM) attached to the pump outlet. Pumping time was set on a timer, and the flow rate was adjusted using a tightening clamp until the required rate was achieved. When the desired pumping time had elapsed, the cartridge was disconnected and sealed.

The CO_2 was recovered from the molecular sieves by placing a cartridge in the furnace and connecting it to the vacuum rig (Fig. 1). The tube was then pumped at ambient temperature to <0.1 torr; once this vacuum was reached, the furnace was switched on, and pressure was monitored on transducer A, while heating the tube to 500°C. Once pressure had started to build, generally above 400°C, any gas not condensed in the liquid-nitrogen-cooled CO_2 traps (previously pumped <0.05 torr) was pumped away.

Pressure buildup in transducer A was checked every 5 min by isolating the traps from the furnace section. If any pressure had buildup, gas present was pumped through the liquid nitrogen traps to reduce the pressure in transducer A. This procedure was repeated until no pressure rise was observed. The furnace was then switched off and the cartridge was left to cool to <400°C and a vacuum <0.05 torr. The CO_2 was then cryogenically transferred to the calibrated volume, while being dried en route by a dry ice/industrial methylated spirit (IMS) trap and the pressure of CO_2 measured on transducer B. Finally, the CO_2 recovered from the molecular sieve was transferred into a mass spectrometry tube and the $\delta^{13}C_{PDB}$ values determined on a VG Optima isotope ratio mass spectrometer.

The trapping system was tested under field conditions. We sampled air in late winter 1994 on a small grass field located behind the NERC Radiocarbon Laboratory. The sample height was 10 cm above ground, and on most days, there was *ca.* 100% relative humidity (rain or snow).

The isotopic reliability of the 13× sieve was tested by comparing $\delta^{13}C_{PDB}$ values of CO_2 trapped by the throughput from 8 liters of air (collected at a rate of 400 ml air min^{-1}) with CO_2 collected by opening previously evacuated (>0.05 torr) 2-liter glass bottles. The $\delta^{13}C$ value and the amount of CO_2 recovered from the 13× sieve were measured at a flow rate of 600 ml air min^{-1} for three air volumes: 6, 12 and 18 liters, with the 12-liter volume being collected at three different flow rates: 200, 600 and 1000 ml air min^{-1}.

RESULTS AND DISCUSSION

A small difference was apparent in the mean $\delta^{13}C_{PDB}$ of CO_2 recovered from the 13× molecular sieve and that of the evacuated glass bottles (Table 1), but it was within the standard deviation (st. dev.) of the measurements from the two sample sets, indicating that no significant fractionation occurs during adsorption of CO_2 on the molecular sieve and its desorption and subsequent recovery.

TABLE 1. $\delta^{13}C_{PDB}$ values of CO_2 trapped from 8 liters of air on 5 13× molecular sieves when compared to CO_2 collected by opening in 5 evacuated 2-liter glass bottles

	13× molecular sieve	Glass bottle
	−9.7	−9.4
	−9.5	−9.3
	−9.5	−9.3
	−9.2	−9.3
	−9.1	−9.9
Mean	−9.5	−9.4
Standard deviation	0.2	0.3

The other results of the stable isotope measurements suggest that the $\delta^{13}C_{PDB}$ of the CO_2 recovered from the 13× sieve was not significantly affected by the pumping rate at the selected air volume (Table 2), nor by the amount of air sampled (Table 3). In this instance, the variation in $\delta^{13}C$ values among replicate 13× sieves are smaller with larger volumes of air sampled.

The isotopic results of this part of the experiment, *i.e.*, CO_2 trapped on a molecular sieve from a stream of gas are within ± 0.2‰, similar to observations by Bauer, Williams and Druffel (1992). The main difference is that, in the latter study the gas stream consisted of CO_2 added to clean N_2 and O_2, with no H_2O present. In our experiment, water was present in the atmosphere (100% relative humidity) and is likely to have been adsorbed on the sieve while air was pumped through it. The fact that the isotopic signature was not significantly affected indicates that the 13× sieve may be used in the field to collect CO_2 from gaseous mixtures even if it rains or snows.

TABLE 2. The $\delta^{13}C_{PDB}$ values of CO_2 recovered from 5 replicate 13× molecular sieves when 12 liters of air were sampled at 3 different pumping rates

	Pumping rate		
	200 ml air min^{-1}	600 ml air min^{-1}	1000 ml air min^{-1}
	-9.6	-8.6	-9.1
	-8.6	-8.8	-8.6
	-8.8	-8.2	-9.0
	-8.7	-8.6	-9.3
	-8.8	-8.6	-8.7
Mean	-8.9	-8.6	-8.9
Standard deviation	0.4	0.2	0.3

TABLE 3. The $\delta^{13}C$ values of CO_2 recovered from 5 replicate 13× molecular sieves when 3 different air volumes were sampled at the rate of 600 ml air min^{-1}

	Volume collected		
	6 liters of air	12 liters of air	18 liters of air
	-10.2	-8.6	-8.5
	-8.0	-8.8	-8.5
	-8.6	-8.2	-8.5
	-8.4	-8.6	-8.5
	-8.5	-8.6	-8.4
Mean	-8.7 (-8.4*)	-8.6	-8.5
Standard deviation	0.8 (0.3*)	0.2	0.1

*If sieve no. 1 is excluded

We did not measure the actual atmospheric CO_2 concentration during our experiment. The CO_2 content of the atmosphere has no fixed value as it follows diurnal and seasonal patterns (Freyer 1979). If we therefore try to calculate the maximum amount of CO_2 that could be trapped on the sieve (air volume sampled × its CO_2 content), we need to estimate the atmospheric CO_2 concentration at the time of sampling. If we set the ambient CO_2 concentration of 350 ppm, then the average recovery rate of the 30 molecular sieves used in this experiment was 88% (st. dev. 11%). But if the actual CO_2 concentration was higher than 350 ppm then recovery rate decreases linearly at the rate of 10% for every 50 ppm increase in atmospheric CO_2 concentration. An ambient value of 350 ppm CO_2 could be a rather conservative estimate as sampling took place near the surface of the grassland and soil respired CO_2 could have contributed to higher CO_2 concentration in the air that was sampled.

The fact that the $\delta^{13}C$ values of most samples were within the standard error of each other suggest that the *true* recovering rates must have been relatively high (thus also suggesting that the pCO_2 during the experiment might not have been very much above 350 ppm), as isotopic fractionation is likely to become more pronounced when recovery rates are low. The potential for highly efficient trapping and recovery of CO_2 from environmental atmospheres on the molecular sieve is supported by evidence from two additional experiments. These are: 1) twice 12 liters (at 200 ml min^{-1} for 60 min) of a control gas from a cylinder (with 500 ppm CO_2) was trapped on a molecular sieve and on both occasions recoveries were >95%; and 2) in a field experiment in which atmospheric CO_2 was monitored with a mobile lab using a gas chromatograph (GC), ambient values dropped from 340–360 ppm to below 10 ppm after inserting the molecular sieve in the system to strip the CO_2 from the air. This implies that >97% of the CO_2 was stripped from the air.

CONCLUSION

The findings of the field experiments indicate that low concentrations of CO_2 present in some gas mixtures can be trapped on and recovered from zeolite 13× molecular sieves, without any isotopic fractionation of the stable carbon isotopes.

The designed field equipment is easy to carry, simple to use and reliable even in adverse weather. Together with the quality of observed data, these characteristics indicate a great potential of this system in future environmental CO_2 flux studies for which sampling is required in difficult and dangerous terrain or poor weather.

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