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DEPARTMENT OF COMMERCE
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AIR SAMPLING PROCEDURES AND MEASUREMENTS OF THE AIR COMPOSITION OF THE SECOND BOAT PIT OF KHUFU'S PYRAMID

Pieter P. Tans[1], James W. Elkins[2] and Duane R. Kitzis[1]

ABSTRACT. A hole has been drilled in the roof of pharaoh Khufu's second boat pit with a drill and airlock system specially designed to exclude the exchange of outside air and the atmosphere inside the pit. Air samples have been obtained from three height levels inside the pit through an air probe inserted through the airlock. The air has been analyzed by gas chromatography for the chlorofluorocarbons F11, F12, carbon tetrachloride, and methyl chloroform, and for carbon dioxide, methane, carbon monoxide, nitrous oxide and hydrogen. The stability of the wet air samples in stainless steel and aluminum containers is unsatisfactory. The measurements of the air pressure in the pit during sampling as well as the composition of the air show that the boat chamber is not sealed. The present loss rate of the wood in the pit by decay is estimated to be between 200 g and 1000 g per year. We find evidence for substantial exchange of carbon between gaseous carbon dioxide and the limestone rock.

INTRODUCTION

There are two boat pits located just south of Khufu's pyramid on the Giza plateau (fig. 1). The first one was opened in 1954. It contained a remarkably well-preserved, 4600-year-old boat made of cedar wood. Apparently the pit had been so well sealed from the atmosphere that the wood had not suffered much decay. It has even been reported that the investigators could smell fresh cedar upon making the first opening in the ceiling. The second pit was never opened.

The sealed second pit gave us an opportunity to probe the environment inside the chamber, in an attempt to find out what environmental conditions may have contributed to that remarkable feat of conservation of the boat in the first pit. Secondly, if the second pit would be equally well sealed as the first pit apparently was, we may have an opportunity to sample "old" air. In that case there are two possibilities. If the second pit contains organic material, the composition of the air inside will have been modified by living organisms. Biogenic gases such as carbon dioxide, methane and nitrous oxide may have increased in the chamber, while oxygen may have decreased. A low oxygen concentration could have contributed toward preservation of the wood. On the other hand, the second pit could be found to contain only stone or metal objects. In that case, the concentrations of the major biogenic gases in the air inside may even be representative of the atmosphere well before the industrial revolution, when mankind started to change the atmospheric environment on a global scale. The three gases mentioned play an important role in the maintenance of the surface temperature of the earth, because they are strong absorbers of infrared radiation (the so called "greenhouse" effect).

Our industrialized society has introduced a number of gases into the atmosphere for the first time. Among those are the chlorofluorocarbons F12 and F11 (trade name "freons") that are used in packaging foam, as heat transfer medium in air conditioning systems, and as propellants

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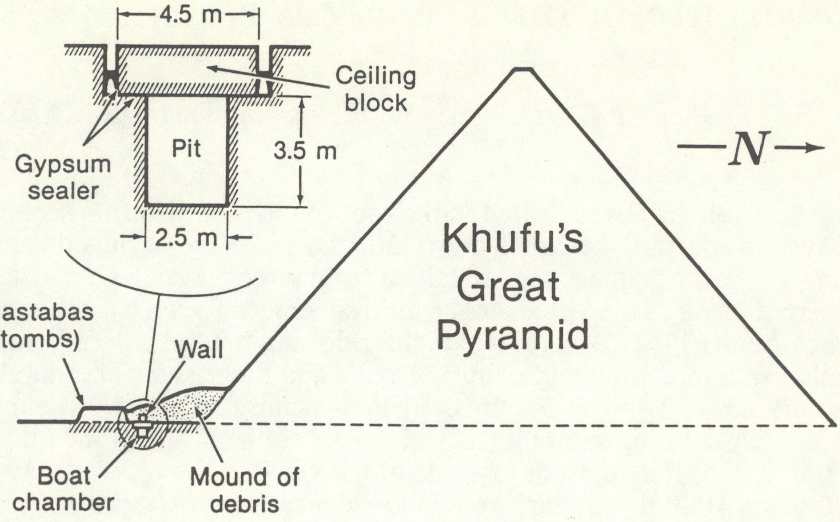

Figure 1.--Location of the boat pits with respect to Khufu's pyramid. They were discovered in 1954 when the mountain of rubble was cleared away.

in spray cans. As far as we know, there is no natural process that produces these gases. The freons are extremely stable and are presently increasing everywhere on earth in almost equal concentrations (at 4 to 5% yr^{-1}). Therefore, the presence of these freons in the air in the boat pit would be a very sensitive indicator of whether the pit is currently sealed with respect to the outside atmosphere.

The National Geographic Society, in collaboration with the Egyptian Antiquities Organization, organized an expedition to probe the environment of the second pit and to photograph its contents [El-Baz, 1988]. Drilling commenced on October 17, 1987. Breakthrough was achieved on October 19. The hole was re-sealed October 25.

TESTS OF THE AIRLOCK

The airlock system (fig. 2) to drill through the limestone and to extract air from the pit was designed by Robert G. Moores [1988]. Seals in vacuum systems are often made by rubber O-rings. There are a number of such O-rings in our airlock system. Many elastomers are very strong absorbers of the freons. If any O-ring has been exposed once to a high concentration of freons, it will thereafter remain a source of these gases in any situation where the freon concentration is low. Because we needed the ability to measure potentially very low freon concentrations in the boat chamber, we had to make sure that our airlock apparatus itself is not a source of freons. For this reason a lead gasket was chosen as the primary seal between the rock and the lower plate of the airlock assembly. In addition, the airlock was tested for freon contamination on three separate occasions.

The first test took place on June 19, 1987 in Baltimore, in the machine shop of Black and Decker. The airlock was mounted on a slab of concrete and a hole was drilled a few inches deep. After the upper plate of the airlock had been rotated by 90°, the drill was removed and replaced by the air probe, according to the procedure described by Moores [1988]. A gas sampling manifold and aluminum sample bottle were connected to the air probe and evacuated. A high pressure cylinder of freon-free nitrogen was connected to the airlock via a flexible stainless steel hose (for design of the airlock, see Moores, 1988). The airlock was pumped for 40 minutes. The pressure never fell below 1 torr, the upper limit of our vacuum gauge. We pressurized the airlock

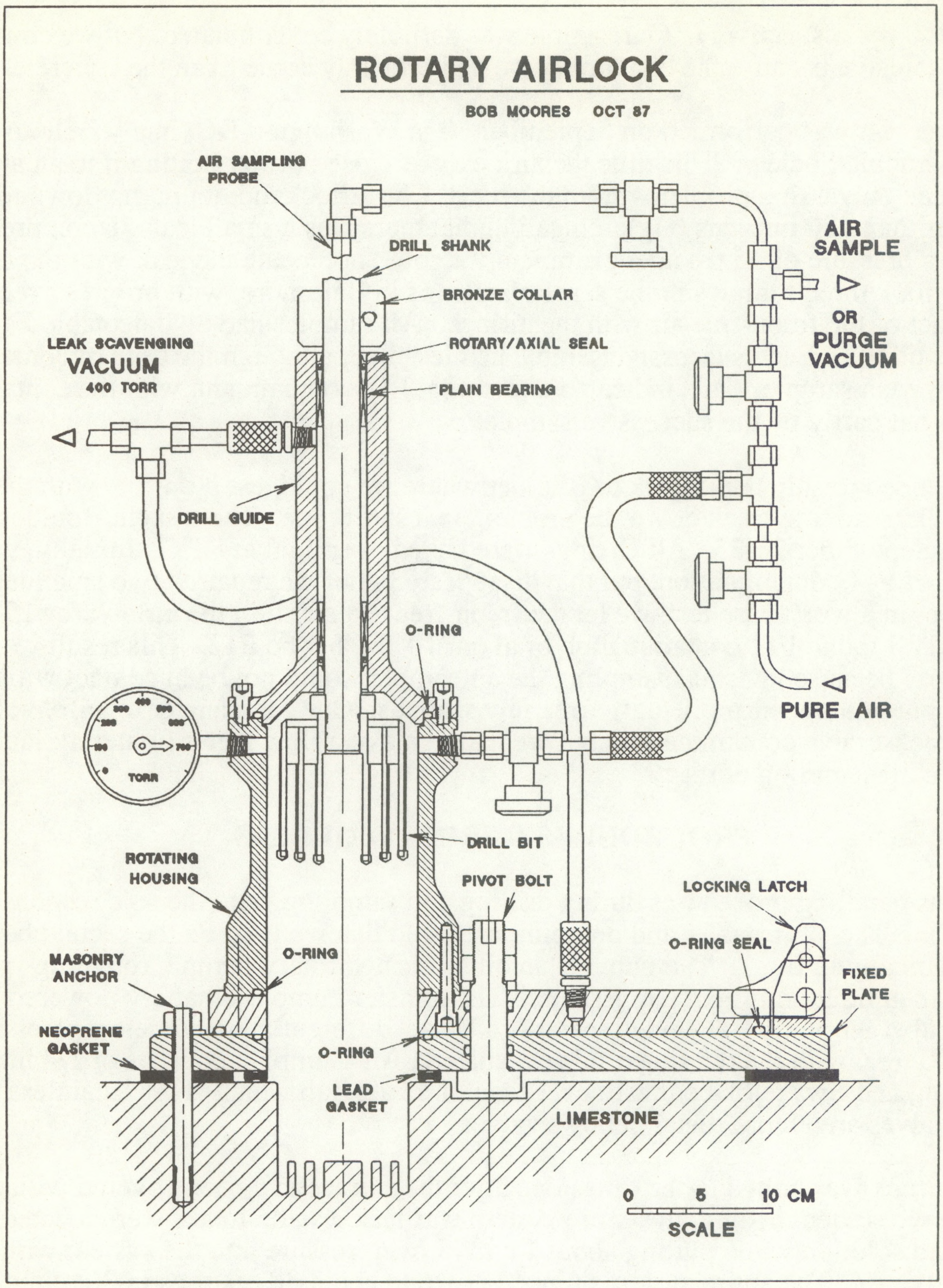

Figure 2.--Schematic of the airlock. The lower plate is bolted to the rock. The upper plate is rotated around the central pivot bolt. Lower-than-ambient pressure is maintained as an extra precaution by the "leak scavenging vacuum" in areas between multiple seals, also in the area between the lead and neoprene gasket (connection not shown). Drawing reproduced courtesy of Robert Moores.

to 15 psi above ambient pressure and could not detect any leaks with a soap solution. Therefore, we surmised that the concrete was outgassing at a high rate. We let freon-free nitrogen gas into the airlock at a pressure of 17 psi (absolute), and waited for 5 minutes before transferring that gas sample into the evacuated sample bottle. This sample contained 240 ppt (part per trillion) of F12 and 40 ppt of F11. The concentrations in "clean" air (e.g., at the South Pole) are currently about

400 ppt and 240 ppt respectively. Our sample was definitely contaminated, but we considered this test unconclusive because the contamination had probably come from the concrete.

Another test was performed on September 10 in Washington DC, in a warehouse of the National Geographic Society. This time the airlock was closed off by bolting it to an aluminum plate, to exclude outgassing problems from the rock. The airlock did not pump down to a pressure lower than 180 microns (Hg), indicating that there was a small leak. Upon pressurizing the airlock to a pressure of 15 psi above ambient we could not locate the leak with the soap solution. We took three samples in the same manner as in Baltimore, with progressively longer times of contact of the freon-free air with the airlock. All samples had no detectable F11, but large amounts of F12. Each successive sample had less F12, although the time of contact had increased with each sample. This indicated an internal F12 contaminant, with the contamination being flushed out partly by the successive samples.

We decided to ship the airlock to Boulder where we could test it on-line with the gas chromatograph in order to track down the problem in a short time. The tests in Boulder were performed on September 23-25. All O-rings were baked overnight at 80°C. Initially, we found a small amount of F11 contamination, but that disappeared after we repaired two small leaks in the airlock. When, in a worst case test, we let the freon-free test air sit in the airlock for 15 minutes to 1 hour, we still found F11 contamination of about 10 ppt, but no F12. This result we considered satisfactory because in actual sampling the air sample would not be in contact with the airlock itself, but with the airprobe only for a few seconds. Our gas transfer manifold did not produce any measurable contamination, but we had to move a flow meter (material: lucite) downstream of all sampling ports.

PROCEDURES DURING DRILLING

The gas handling procedures during drilling and sampling were the sole responsibility of one of us (PT). The gas transfer and pumping manifold that we used on the second boat pit is shown schematically in fig. 3. The pump is an oil lubricated rotary pump ("roughing" pump), with a cold trap at liquid nitrogen temperature. The transfer pump is a battery powered stainless steel KNF Neuberger pump. The manometer is a Heise differential manometer (precision 0.1 torr, span 1000 torr) with the reference side evacuated. All plumbing consists of 1/4 inch stainless steel tubing and Swagelok connections, except the cold trap which is 3/8" stainless steel tubing. The valves are Nupro metal bellows valves.

The airlock was bolted to the limestone after the surface had been covered with an epoxy layer. Before we started drilling, the entire system was leak tested. Leaks were located by applying a soap solution while putting about 1 atm of overpressure into the system with the clean air through valve #7. The entire system pumped down to about 30 microns in 30 minutes. The sample cylinders themselves (with valve #4 closed) pumped down to 1 micron, while the pressure did not go up measurably with the pump off for 5 minutes, indicating that there were no leaks and that the cylinders were dry. We started drilling on October 17, 1987. We had a total pressure of 25 psi (absolute) in the airlock. Immediately when we punctured the layer of epoxy, the pressure started to drop. Since no leaks could be found with the soap solution, we assumed that the rock was porous enough to absorb part of the overpressure. The first 1.2 m were drilled without the elaborate purging procedure with clean air.

From thereon each drilling cycle consisted of: drilling through about one inch of rock, lifting of the drill and removal of drill head, cleaning of the drill and removal of debris from the bottom of the hole with an industrial vacuum cleaner, re-assembly of the drill head, lowering of the drill, and purging the hole with clean air. As a precaution against chalk dust getting into the gas transfer system, we always gave a little blast of clean air through valve #8 before we started

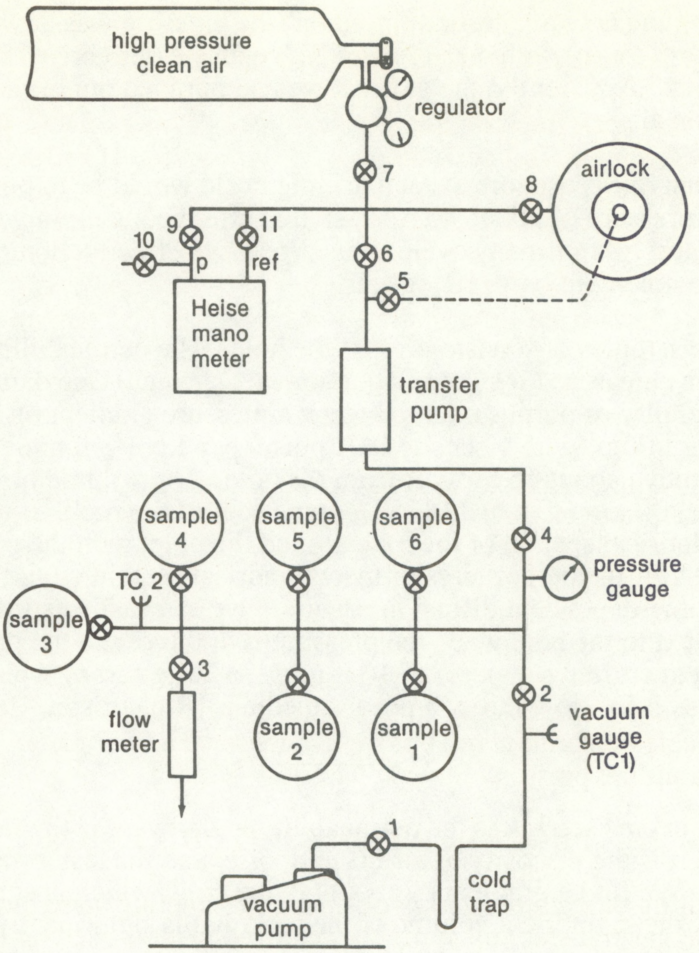

Figure 3.--Schematic view of the sampling setup. The crossed circles are valves.

pumping, to clean the dust from the port and the valve. Purging was accomplished by pumping the airlock for 2 minutes through valves #8, 6, 4 and 2, with #7 and 5 closed. Then #6 was closed and clean air admitted through valve #7.

The clean air had earlier been pumped into a Luxfer aluminum high-pressure cylinder at Niwot Ridge, at an altitude of approximately 3.5 km in the Rocky Mountains. The following traps had been used to remove the indicated trace gases: cold trap at -80°C (water vapor), aquasorb (water vapor), ascarite (carbon dioxide), molecular sieve 13X (nitrous oxide, freons) and ambersorb (heavier halocarbons). Methane is still present at ambient concentrations in the Niwot tank, as is probably carbon monoxide.

When we started the purging procedure the hole was very hard to pump down. After 20 minutes the manometer still registered 265 torr. A little later the cold trap froze up. From the pumping speed at 1 atm and the gradual pressure decrease, we estimate that about 100 liter STP (0°C and 1 atm) of air had been pumped at that point. When saturated with water vapor at 25°C, that amount of air should hold a little over 2 g of water, enough to freeze up the trap with ice. It also indicates that there is a substantial amount of water in the limestone. Because of the large amount of water vapor and the high flow through the pump we decided not to cool the trap any more. We tested the airlock again with overpressure and the soap solution. No leaks were found. Upon pumping the hole again for 10 minutes, the pressure was down to 320 torr. We then filled it to 760 torr (1 atm) with clean Niwot Ridge air. After about 15 seconds the pressure had dropped to 640 torr. Apparently, the gas that we had pumped out of the rock was being replaced with the clean air.

We decided that our procedure at each drilling cycle would be to pump for 2 minutes and then fill the hole to a pressure of about 900 torr, so that after about a minute the pressure would be back to about 760 torr. After many cycles, this procedure effectively replaces the air in the limestone close to the hole with Niwot Ridge air.

We took three samples of limestone from the hole. The permeability is 7 millidarcy and the porosity is 29% , as measured by Core Laboratories, Denver. (One darcy [unit = cm^2] is defined as the permeability of porous material when a pressure gradient of 1 atm cm^{-1} causes a flow of 1 cm^3 sec^{-1} of a fluid (with viscosity 0.01 poise) per 1 cm^2 of rock area.) During each pumping cycle we remove about 15 L of air from the hole. The volume of the hole is about 8 L and the final pressure 400 torr, so that 11 L STP comes out of the rock. If the 11 L is removed uniformly from a cylindrical section of the rock around the hole, with the porosity 29% and the residual pressure 400 torr, the outer radius of that cylindrical section would be about 14 cm. Without solving the time-dependent diffusion equation, we can easily estimate the air pressure gradient in the rock next to the hole when the pressure is 400 torr and the pump is removing a volume (not STP, but at current pressure) of 10 L min^{-1}, a large part of which is coming out of the rock. The expression for flow through porous media is [Richardson, 1961] :

$$Q = \frac{k\,2\pi\, rL}{\eta}\,\frac{dp}{dr}$$

Q is the volume flow in cm^3 sec^{-1}, k is the permeability in darcys, r is the radius of the hole in cm, and L the length, η is the viscosity of air in centipoise, and the last term is the pressure gradient in atm cm^{-1}. We find a gradient of about 60 torr cm^{-1}, which is entirely consistent with the earlier estimate of the cylindrical volume of the rock that is significantly depleted of air.

As the hole became deeper, the residual pressure after 2 minutes of pumping went up gradually from 360 torr at a depth of 4 ft, to 430 torr shortly before breakthrough. The pressure behavior was anomalous during the last cycle before we broke through, when after 2 minutes of pumping the pressure went down to 310 torr, significantly lower than during the previous step. Were we close to a layer that was less permeable? Immediately upon breakthrough, we pumped the hole for 1 1/2 minutes, enough to replace the Niwot Ridge air in the hole with pit air. The pressure in the pit was the same as the outside pressure to within the precision of the manometer, 0.1 torr. Since we had seen a diurnal variation of the barometric pressure of a few torr during the previous days, that observation signaled that there was a chance of only about one in twenty that this pit could be well sealed. In a sealed chamber, the pressure would not follow outside pressure variations. During the following days the inside and outside pressure was always the same, even after taking out a few hundred liters of air for sampling, which should have dropped the inside pressure by more than 1 torr. Thus, it became quite clear that the boat chamber was not sealed.

SAMPLING PROCEDURES

The drill was pulled up and into the airlock housing that was rotated 90° to seal off the hole. The sleeve and housing holding the drill was replaced with the sleeve holding the air probe. The top of the air probe, a hollow stainless steel tube of 1/2" outside diameter, was connected to 1/4" copper tubing with a Swagelok fitting. We connected the copper tubing to valve #5 (fig. 3). The airprobe was pumped and leak tested, filled with 1 atm of Niwot Ridge air and rotated over the hole. The air probe was then lowered into the hole and samples were taken from three levels inside the chamber.

We had decided to collect whole air samples, without drying of the air stream, in order not to compromise a precise measurement of the freons (and possibly heavier halocarbons). In addition we would then have the ability to analyze the water vapor in the samples. This collection method increases the possibility of interaction of some of the gaseous components with the walls of the containers because of the presence of water. Therefore, we employed two different kinds of sample containers for the collection of the air samples. One kind consisted of 8.4-L stainless-steel spheres that had been passivated internally with a proprietary "Summa" (Scientific Instrumentation Specialists, Moscow, Idaho) treatment. The others were 3.4-L aluminum tanks (Luxfer) the inside of which had first been caustic etched and acid washed, then treated with a proprietary passivation treatment "Aculife" (Scott Specialty Gases, Plumsteadville, PA). On the outside the aluminum cylinders were not unlike air tanks for divers. Our experience with air sampling has been that it is nearly impossible to find a sample container that does not interact with at least some of the gaseous constituents of the sample. In general, different containers will interact with different gaseous molecular species.

The following procedure was followed for each air sample. Air was drawn through the sampling manifold by the transfer pump through valves #5 and #4, with #6 and #2 closed. Before the air was admitted into one of the sample cylinders, three flushing cycles are executed. A cycle consists of closing valve #4, opening #2 and pumping down to 100 microns, followed by closing #2, opening #4 and when the pressure in the manifold is over 1 atm, also opening #3 to allow flushing of the manifold for 1 minute at the rate of 4 L/minute. When the sample is taken, valve #3 is closed and the cylinder valve is opened slowly so that the pressure in the manifold remains above 1 atm. Each air sample is pumped up to a total pressure of 2 atm (absolute).

During the flushing, one of us (P.T.) took a sniff of the air coming out of the chamber. He did not smell cedar; he could not smell anything at all except, maybe, a slight hint of staleness. Several other people confirmed this impression during other flushing cycles.

Three samples were taken initially in immediate succession. The first one with the air probe at a depth of 145 cm (57") below the ceiling of the chamber, into a stainless sphere. The next one at a depth of 81 cm (37"), into a Luxfer aluminum cylinder and the last one at 18 cm (7") below the ceiling, into a stainless sphere. We took samples from three levels because of the possibility that the air inside the chamber might not be completely mixed when there is continuous production or consumption of gases in the wood.

Next, samples were taken for Dr. Essam Hussein Ghanem of the Botany and Microbiology Department of Alazhar University in Cairo and for Ashraf Mahrous of the National Center for Radiation Research and Technology, also in Cairo. When the last piece of limestone fell into the pit, some dust would have been stirred up, and micro-organisms might be present in the air. Samples were taken from three levels for each of these two organizations. The air was taken from valve #3, after removal of the flowmeter, and it was flowed through saline nutrient solutions, and through particle filters for pollen analysis. Also in this case we flushed the lines first for 1 minute at a flow of 4 L min^{-1} in the case of the saline solutions, and for 4 minutes at a flow rate of 1 L min^{-1} in the case of the particle filters, before the samples were taken.

If the concentration of some gases would turn out to be depth dependent, we had destroyed part of that stratification by the turbulence created by the falling of the last piece of limestone when the drill broke through. The stratification would have been partly restored by diffusion during the long time delay between breakthrough and sampling (9 hours). If we take for the molecular diffusion constant a value of 0.2 cm^2 sec^{-1}, the characteristic displacement of a molecule by diffusion is about 1 m in that time span. However, we decided to provide a crude measurement of the amount of disturbance in case there would be real stratification. We pulled up the air probe, rotated the airlock, took a stone that would fit through the hole, cleaned it with

100% alcohol and put it into the airlock. Then we filled the airlock with clean air and rotated it so that the stone fell to the bottom. After 1 1/2 hours we took three more samples in small (0.5-L, passivated) stainless steel cans according to the same procedure that we followed earlier. This would allow us to see the difference between concentrations before and after the stone fell. We had brought a total of six of those small cans for samples of the outside air at the pyramids, but decided to use three for this experiment.

During the flushing before each of the last three samples, we had removed the flow meter and the flushed air went through a Nuclepore particle filter capturing particles larger than 0.1 microns. The chance that we will find any particles of biological origin on these filters is very small, however. Small particles falling through still air quickly reach a constant terminal velocity or Stokes velocity, in which the gravitational and the drag forces are equal and opposite. If we assume that biological particles have the density of water then the Stokes velocity is 3 mm sec^{-1} for round particles of 10 micron diameter and a hundred times smaller for particles of 1 micron diameter. If a particle falls 1 m in the 2 hours between the dropping of the stone and the collection of the filter sample, its Stokes velocity will have to be 0.14 mm sec^{-1}, which corresponds to a particle diameter of roughly 2 microns. Therefore, we cannot expect to find biological particles larger than about 2 microns. The same argument applies to the air samples that had been flushed a few hours earlier through the saline solutions and the pollen filters. The size limit is about 1 micron in that case, because of the longer waiting time between the falling of the limestone and the sampling. At this point we did not know how high above the wood our air intake was at its lowest position (145 cm below the ceiling). Later we estimated, after the pictures had been taken, that it was still 70-80 cm. We do not know to what height dust is carried when the air is stirred by a falling stone, but 1 m is not likely to be an gross underestimate.

Initially we had kept open the possibility to take three more samples from a second location if we would decide to drill another hole. On October 22 it was decided that a second hole was not necessary and we took three more samples in the same place, after 2 1/2 days of surveying the chamber with video and still cameras. Samples were again taken from three depth levels following the procedure outlined above. Microbiological samples from these depths were also taken for Samira Mansour and Magdi Bahgat of the Botany Department of Suez Canal University. The flushing procedures were the same as for the other biological samples. Then a final particle sample was taken by pumping 200 L of air through a Nuclepore 0.1 micron particle filter.

From Luxfer cylinder X134481, air was flushed into reagent tubes with nutrient gels for Mohamed Ewiess Mahmoud Ahmed of Cairo University, Botany department.

On October 25, the hole was sealed while a temperature and humidity probe (Vaisala HM31) remained inside. The temperature inside the pit was 27.5°C (accuracy 0.3°C) and the relative humidity 84% (accuracy 2%).

Three outside air samples have been taken at different times according to the following procedure. On top of the 4 ft high wall, upwind of the activities at the drilling site, a 5-ft high stainless steel intake tube was connected to a KNF Neuberger gas transfer pump, and from there the air was led through copper tubing into a 0.5 L passivated (medical grade, electropolished) stainless steel cylinder. The cylinder had two valves and the air was flushed through the cylinder for 7 minutes at the rate of 4 L min^{-1}, after which the last valve on the cylinder was closed. The transfer pump then pressurized the cylinder to 2 atm (absolute) and the other valve was closed. All connections were Swagelok. The samples were taken on October 19 at 2:15 pm (cylinder 4103-87), October 20 at 0:05 am (4101-87) and on October 24 at 10:00 am (4102-87), local time.

RESULTS

1. Deductions from the pressure measurements

The pressure measurements during the sampling and the photographic surveying (water stains along the ceiling) have already shown that the chamber is not sealed at present. We can get some idea of the size of the air leak for two limiting cases. When air was pumped through the Nuclepore filter at the rate of 4 L min^{-1}, the leak was large enough to sustain that rate of flow without generating a pressure differential between outside and inside of more than 0.1 torr. The inflow of new air is probably not due to outgassing of the limestone, because in that case one would expect some time delay, with the minute pressure differentials that were observed. The most likely cause is a direct leak to the outside.

We can make an estimate for the size (diameter) of the hole required if we assume that it consists of a long tube of 2 m length. In the opposite limiting case we assume the leak to consist of many interconnected pores and microcracks in the gypsum plaster that the builders of the chamber had poured between the ceiling blocks in an apparent attempt to create a tight seal. In that case we can give an estimate for the permeability of the plaster.

The material flux (Q) in a long (length L) tube (diameter d) under laminar flow conditions is given by Poiseuille's law:

$$Q = \frac{\pi d^4}{128 L} \frac{P \Delta P}{\eta}$$

For Q we have the pumping speed of 4 atm L min^{-1}, while the pressure p is 1 atm and the pressure differential Δ p across the tube is at most 0.1 torr (1/7600 of 1 atm). The viscosity (η) of air is 0.00017 poise or g cm^{-1} sec^{-1}. From this it follows that the tube diameter has to be 9 mm or more. Quite a macroscopic dimension!

The other extreme hypothetical case is where we have to deal only with the permeability of the plaster. The volume flux through porous media is again given by

$$Q = \frac{k A}{\eta} \frac{dp}{dL}$$

The flux Q is 4 L min^{-1}, the pressure differential is again 0.1 torr. k is the permeability parameter of the gypsum. We assume that the gypsum fills vertical cracks between the limestone ceiling blocks of 3 mm width and the same for the crack along the bottom, where the blocks rest on a wide ledge. For the average block thickness we take 160 cm and for the width of the ledge 100 cm. There are close to 40 blocks. It follows that k would have to be 200 darcy, a value characteristic of very loose sand with a porosity close to 50% [Richardson, 1961]. The gypsum is obviously less permeable than that. We probably have a situation of many macroscopic small cracks in the gypsum and between the gypsum and the limestone, and possibly some large cracks as well.

Having seen the pressure behavior of the pit, it will be easy to estimate the amount of air exchange with the outside via the following mechanism. The atmospheric pressure is continually varying by a small amount. Each time the pressure goes up, air is being pushed into the chamber, and vice versa when the atmospheric pressure drops. This process is slow enough that the air that has been pushed in will mix thoroughly by molecular diffusion (see earlier estimate) with the rest of the air in the chamber before a pressure drop starts pulling air out of the chamber again. This same process also assures intimate contact of the air with the wood in the chamber and the walls. They are all breathing.

All we need is a detailed atmospheric pressure record from Cairo. This record has been promised to us by the Egyptian Antiquities Organization, but we have not received it. To obtain an estimate of what the pressure variations might be in Cairo, we have looked at the atmospheric pressure records at the GMCC site in Samoa (14°S, 171°W), a southern hemisphere site at sea level. On average, a fraction of 0.5% per day would be pumped in and out of an underground chamber in Samoa. The same mechanism would pump 0.25% per day in Washington DC and 0.35% per day in Key West [Humphreys, 1940].

2. Movement of gases through the limestone

In the estimates of the previous section, we have treated the limestone itself as impermeable. That is obviously not the case. Core Laboratories described the limestone as chalk. Chalk is a soft, fine grained, fossiliferous form of calcium carbonate. The grains are so small that it appears amorphous, but it is actually crystalline with a very high internal surface area. There will be both bulk flow in the presence of pressure gradients through the pores of the chalk and gaseous diffusion through the air in the interconnected pores in the absence of any pressure gradients.

Mass flow directly through the limestone cannot sustain our observed flow rate of 4 L min^{-1} at a pressure differential of 0.1 torr. From the measured permeability and the spatial dimensions we calculate 15 $\text{cm}^3\ \text{sec}^{-1}$, which is only 0.4% of the observed flow.

Gaseous diffusion through the pores could make a substantial contribution to the air exchange between the pit and the outside. The diffusion coefficient is substantially smaller than in free air, not only because the pores take up only a part of the bulk volume, but also because the most direct pathways are often blocked (sometimes called the tortuosity factor). The situation is not unlike that in soils, or in some coal deposits. The diffusivity through the gas of the pores in the chalk could be lower than the diffusivity in free air by a factor of 10 to 50 [Carman, 1956].

The exchange time of the pit air with the outside air via gaseous diffusion is estimated by

$$t = \frac{x\,V}{D\,A}$$

The volume (V) of the pit is 260 m^3, and x is the thickness of the ceiling stones (160 cm). For the area (A) through which the diffusion takes place we will take the area of the ceiling, about 75 m^2, (although the effective area should be a bit larger), and for the diffusivity we might try values between 0.015 and 0.003 $\text{cm}^2\ \text{sec}^{-1}$, because the free air diffusivity of CO_2 is 0.14 $\text{cm}^2\ \text{sec}^{-1}$. (We found a measured value for gas diffusivity through gypsum plaster: 0.002 $\text{cm}^2\ \text{sec}^{-1}$ [Bakker and Hidding, 1969].) The values of 0.015 and 0.003 yield exchange times of 45 and 220 days respectively. It would appear that diffusion through the limestone itself is an important contributor to the total gas exchange.

3. Mixing of gas in the boat pit

Molecular diffusion provides a mechanism for mixing of the gases in the pit, but is it the only mechanism? Temperature gradients inside the pit may cause thermal convection. The diurnal temperature variation does not penetrate deeply enough into the rock. The thermal conductivity of chalk is $2{*}10^{-3}$ cal $\text{cm}^{-2}\ \text{sec}^{-1}/\text{C}\ \text{cm}^{-1}$, the density is 2 g cm^{-3}, while the specific heat is 0.20 cal $\text{g}^{-1}\text{C}^{-1}$. This results in an attenuation depth of the diurnal temperature cycle in the rock of 12 cm. The thickness of the roof of the pit is 160 cm. The lack of a diurnal temperature variation is confirmed by the temperature measurements (precision 0.1°C) inside the pit.

The seasonal temperature cycle has an attenation depth of 220 cm, and the phase velocity of this yearly temperature wave is 14 m yr^{-1}. The amplitude of the annual temperature cycle in Cairo is 7°C. In uniform rock strata of the kind at the Giza plateau the amplitude at 160 cm (top of the pit) will be about 3.4°C, and at 500 cm (bottom of the pit) 0.7°C. The situation is more complicated in the vicinity of the cavity formed by the boat chamber, but for order-of-magnitude estimates we will neglect that, as well as the fact that there are temperature phase differences between the top and the bottom of the pit. Therefore, we will assume that during the fall season there exists a temperature gradient along the side walls of the pit where the bottom is warmer than the top by 2.5°C.

If the wall is either warmer or colder than the air itself, free convection will occur. In the first case a layer of air close to the wall will warm up due to heat conduction and will start to rise because of thermal expansion. Viscous forces will limit the speed of rise. These processes can be described by dimensionless numbers, the Prandtl number and the Grashof number [Jakob, 1949; Eckert and Drake, 1959]. In our case the flow remains laminar and we estimate that the typical horizontal heat transfer from the walls is $2\text{-}4*10^{-5}$ cal cm^{-2} sec^{-1}. This is of sufficient magnitude to dominate the heat budget and the circulation of the air inside. The heat input from the side walls also translates into a vertical transport of heat because of the air circulation. This vertical heat transport is of the same magnitude as the vertical transport through solid rock at a depth of 160 cm, while it is stronger than the heat transport through the rock at 500 cm. It follows that the temperature distribution in the rock adjacent to the pit is influenced by the "thermal short circuit" formed by the circulating air, and vertical temperature gradients and heat inputs will be less than the estimates above.

Another way in which thermal convection could be produced is by the heat produced by the decay of the wood. Assuming that the caloric content of the wood is close to 4 kcal g^{-1}, the decay (200 g of wood per year, see section 5b) produces heat at the rate of 0.025 cal sec^{-1}, or $3.4*10^{-8}$ cal cm^{-2} sec^{-1}. This amount of heat input is insignificant compared to that which derives from the seasonal temperature gradient in the rock.

4. The trace gas composition of the air on the Giza plateau

The composition of the outside air is very variable (table 1) and the trace gas concentrations are higher than the background concentrations that we measure over the oceans [Schnell and Rosson, 1988]. The variations of the trace gas concentrations in the outside air on the Giza plateau are strongly correlated, as is to be expected. Sample 4101-87 shows the highest levels of all trace species measured. Generally, the three samples that we took are representative of moderately polluted urban air.

5. The trace gas composition of the air in the boat pit

a. *Halocarbons*

The concentration of F12 is 512 ppt, and F11 is 299 ppt inside the chamber (table 2). The F12 and F11 values are based on the R. Rasmussen (Oregon Graduate Center) 1985 corrected scale. These concentrations are uniform with height (see fig. 5) and are in the middle of the values measured in the outside air. The ratio of F12 to F11 is systematically a little higher for the air samples inside than outside. The results for methyl chloroform and carbon tetrachloride display much more variability than the freons, and they tend to be somewhat higher for the samples inside than outside. These results confirm that the chamber contains essentially modern urban air. The samples that we took inside the chamber on October 22 show a slightly higher F12 concentration, especially at the lowest level. This is probably due to a slight contamination

Table 1.--Trace gas concentrations of the outside air in Giza. A comparison is given with measurements at Mauna Loa Observatory (Hawaii), with uncertainty estimates in parentheses.

Sample and date collected (M/D/Yr)	Date Measured	CO_2 ppm	CH_4 ppb	N_2O ppb	CO ppb	H_2 ppb	F12 ppt	F11 ppt	Ratio F12/F11	CH_3CCl_3 ppt	CCl_4 ppt
4103-87	10/29/87	-	-	-	-	-	444	275	1.6	-	-
10/19/87	11/12/87	356	-	-	-	-	-	-	-	-	-
	12/03/87	-	-	-	-	-	469	273	1.7	167	111
4101-87	10/29/87	-	-	-	-	-	544	396	1.4	-	-
10/19/87	11/12/87	381	-	-	-	-	-	-	-	-	-
	12/01/87	-	2094	-	586	689	-	-	-	-	-
	12/04/87	-	-	317	-	-	544	364	1.5	178	124
	01/07/88	-	2096	-	649	699	-	-	-	-	-
	01/27/88	384	-	-	-	-	-	-	-	-	-
4102-87	10/29/87	-	-	-	-	-	437	258	1.7	-	-
10/24/87	11/12/87	352	-	-	-	-	-	-	-	-	-
	12/01/87	-	1785	-	177	477	-	-	-	-	-
	12/03/87	-	-	311	-	-	418	268	1.6	156	104
	01/07/88	-	1785	-	196	490	-	-	-	-	-
	01/29/88	348	-	-	-	-	-	-	-	-	-
Mauna Loa	October	346	1680	307	85	520	434	250	1.7	150	110
(20°N)	1987	(0.3)	(5)	(2)	(5)	(60)	(6)	(4)		(13)	(7)

produced by the plastics of the photography equipment. We estimate (molecular diffusion) that a volume of a few m^3 around the location of the cameras could have been affected on that date. The thermally induced circulation in the chamber has not equalized the concentrations at the lowest level and two higher levels. At the time of writing of this report, the contamination introduced by the cameras will probably have been diluted to below our detection limits.

b. *Carbon dioxide*

The air inside the pit has a concentration of CO_2 about 390 ppm (part per million) higher than the outside air (Table 2, fig. 5). One of the samples has also been run on a Fourier transform infrared spectrometer. The CO_2 spectrum is shown in fig. 4. We calculate from this spectrum and the known band strengths a concentration of 745 ppm, confirming the values obtained by gas chromatography. There must be an internal source of carbon dioxide. It is probably produced by the decay of the wood of the boat.

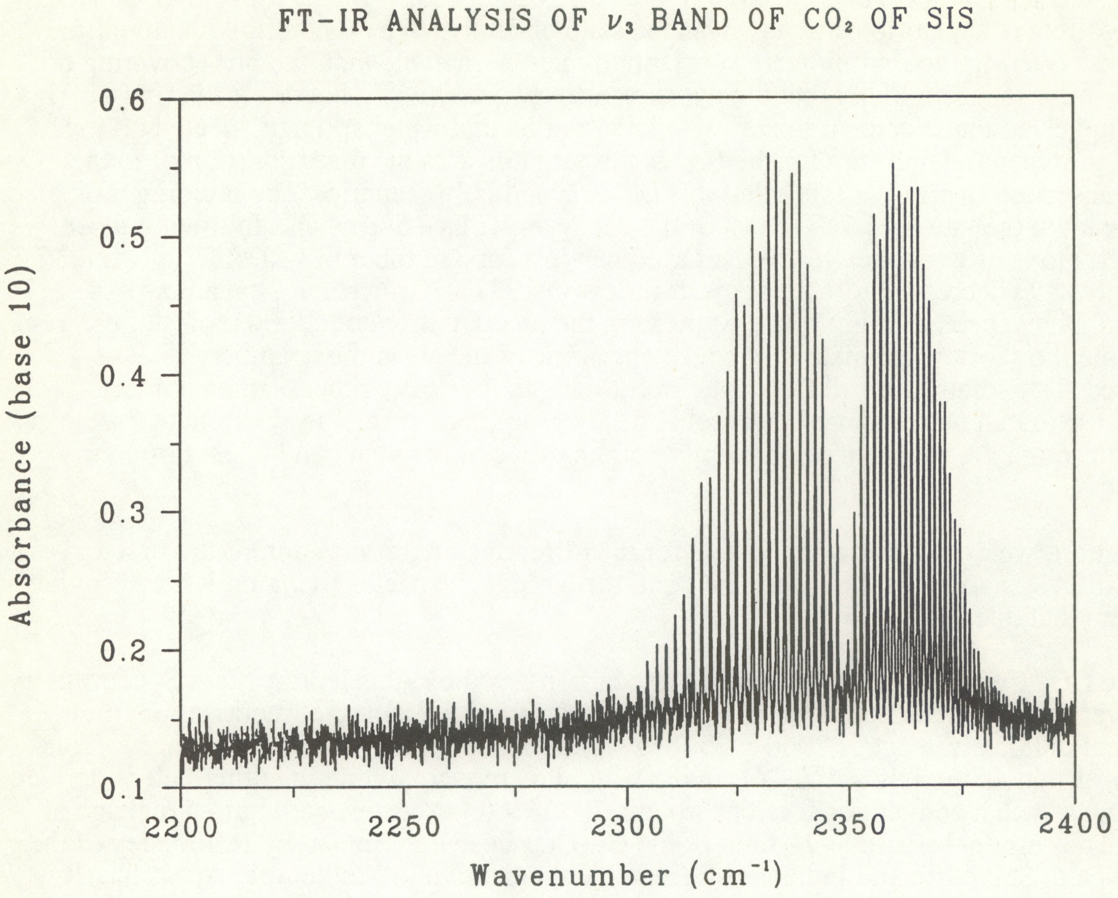

Figure 4. Fourier transform infrared spectrum of sample SIS-1 in the vicinity of the CO_2 absorption band. 10 cm pathlength, 500 mm Hg pressure, measured CO_2 concentration is 745 ppm.

It is easy to estimate the rate of this decay if we consider the limestone itself to be impermeable. It equals the excess concentration times the volume of the chamber (260 m^3) times the exchange rate with outside air. Taking the Samoa number for the air exchange rate, we find that 7 moles of carbon per year are transformed into carbon dioxide, which corresponds to 84 g of carbon. Carbon constitutes about half the weight of (oven-dry) wood, so that about 170 g of wood is decaying per year. This is a very slow rate of decay compared to the initial weight of the ship. From the size of the boat from the first pit we surmise that the initial dry weight of the wood may have been somewhere between 20,000 and 40,000 kg. Multiplying 170 g yr^{-1} by 4600 yr we obtain 800 kg. In other words, if the present loss rate is characteristic for the entire time of burial of the boat, it would still have to be in mint condition. It is also possible that the initial loss rate was much higher, and that now only a fraction of the original weight is left. The photographs of the boat may shed some light on this issue. However, the above estimate of 170 g yr^{-1} is a lower limit, because we also have to take into account gaseous diffusion through the limestone itself. If we assume the lower value for the diffusion constant, 0.003 cm^2 sec^{-1}, the total loss of wood is 350 g yr^{-1}. Assuming the high value for the diffusion constant, 0.015 cm^2 sec^{-1}, the loss of wood would be 900 g yr^{-1}.

Photographs indicate that the condition of the second boat is much worse that the first. Several big timbers appear to be in an advanced state of decay. We do not think that the limestone blocks covering the first pit were substantially less permeable than the ones covering the second. Nor does it seem likely that the gypsum sealer worked much better for the first pit. It has been suggested that a cement mixer, with its vibration and water spillage, located on top of the second pit when the museum for the first boat was built, was the main contributor to the decay of the second boat. We think that this is a very unlikely scenario. The building took place during 4 years in the late sixties. If most of the decay took place during and following those years, several tons of wood per year must have been lost for a number of years. Why would the rate of decay have decreased to 1 kg per year or less in 1987? Furthermore, the amount of oxygen could have been rate-limiting. At present, the pit contains about 2000 moles of oxygen. If we assume the shortest estimate of the residence time of the air in the chamber, 45 days (Results, sec. 2), and also that all the oxygen is utilized in the decay process, then at most 400 kg of wood per year can be consumed by aerobic decay processes. If the lower estimate for the gas diffusivity through the rock is true, then only 150 kg of wood per year can be lost through aerobic decay.

In short, we do not know the reason for the difference in preservation of the first and second boat. An analysis of the wood itself and the biological species living on it may provide an answer to that question.

The CO_2 from tank SIS-1 has been radiocarbon dated by Accelerator Mass Spectrometry at the University of Arizona in Tucson, AZ. When corrected for isotopic fractionation, the conventional radiocarbon age is 2080 ± 85 (one sigma) B. P. (Donahue, pers. commun). This date confirms that about half of the CO_2 in the boat pit is modern, while the other half is derived from an object with a conventional radiocarbon age of 4100 yr (corresponding to a real age of 4600 yr). The carbon-13/carbon-12 ratio of the CO_2 has been determined by R. Francey of the Commonwealth Scientific and Industrial Research Organization in Melbourne, Australia. It is -12.5 permil PDB, which falls between the value for air and wood, although it is somewhat on the heavy side (towards air). We do not know the isotopic ratio in the wood itself.

The radiocarbon age of 2080 yr is surprisingly old. If we assume that the CO_2 in the pit is a mixture of 350 parts modern CO_2 with excess C-14 of 17% (due to the atmospheric testing of nuclear bombs) and 400 parts old CO_2 with a radiocarbon age of 4100 yr, the resulting apparent age should have been 1160 yr. That would suggest an admixture of about 100 ppm of CO_2 with no C-14. the carbon component of the limestone rock is C-14 free. Carbon dioxide exchanges carbon with limestone in the presence of liquid water [Mook, 1980]. The suggestion of carbon exchange with the limestone is enhanced by the high value of the C13/C12 ratio. The carbon-13 value of most wood falls between -21 and -28 per mil PDB. If the CO_2 in the pit consisted only of an air component (-8 per mil) and a component from the decay of wood, the resulting C-13 value should have been between -14.9 and -18.7 per mil. A component of 100 ppm that has exchanged with the limestone (0 per mil) would raise the expected C-13 values to between -12.1 and -14.9 per mil.

The exchange between gaseous CO_2 and the limestone may have wider geochemical implications. While the total amount of CO_2 in the atmosphere is not affected, its isotopic composition may be influenced significantly by the exchange. Especially temporal global changes in C-14 and C-13 may be dampened by the interaction with a large limestone reservoir. If this process is significant on a global scale, we will have to re-think the interpretation of C-14 and C-13 variations in terms of the global carbon budget.

There is a gradient of 13 ppm between the highest and the lowest sample we took on October 22. We think that it is due to mixing of Niwot Ridge air (with zero CO_2) into the pit close to the hole during the days of the photographic survey.

c. *Methane*

The methane concentration is 1761 ppb (table 2, fig. 5), which is roughly 80 ppb (see Table 1) higher than in background air at this latitude and time of the year. The higher concentration is consistent with the location at the edge of a large urban area, but is rather low compared to what has been measured in other urban locations [Blake et al., 1984]. The relatively low methane concentrations indicate that there are no termites in the wood. Termites would have produced large quantities of methane. That would suggest fungi as the agents responsible for the decay. However, we cannot fully exclude the possibility that CH_4 is both produced and consumed (see H_2 and CO) in the chamber, but we consider such a scenario unlikely for two reasons. There is only a small chance that the measured concentrations would happen to be close to the concentrations in the outside air and also the extreme uniformity of the measured concentrations suggest that any ongoing production or consumption processes must be weak.

d. *Hydrogen and carbon monoxide*

The hydrogen concentration in the pit is below our detection limit of about 50 ppb. Because the concentration in the outside air is in the neighborhood of 500 ppb, that means that hydrogen in the pit is vigorously consumed. The lifetime of hydrogen in the chamber has to be at least 10 times (500ppb/50ppb) shorter than the residence time of the air (see Results, section 2). The lifetime is therefore between 4 and 10 days or shorter. The carbon monoxide concentrations in our samples (table 2, fig. 5) are all well below the background concentrations of the northern hemisphere, which is of the order of 150 ppb. The sample values vary, which is due to the instability of this trace gas in our cylinders. The concentration of CO is almost stable in the large stainless steel containers. If we only take account of the results for those containers, the CO concentration in the pit would be between 20 and 30 ppb, which is far below the ambient concentration in the outside air. Consequently, the lifetime of CO in the pit is similarly short, on the order of 1 week. There are species of bacteria that consume H_2 and CO. They could be present in the boat pit, or even in the limestone rock (so called "endolithic microorganisms"). However, in the latter case it would be doubtful that they could be as effective in lowering H_2 and CO as they are observed to be, because diffusion through the bulk of the rock constitutes only part of the gas exchange.

e. *Nitrous oxide*

The concentrations of this gas are elevated by only about 20 ppb above background levels. Nitrogen makes up 0.1% to 0.3% of wood, so that the maximum N_2O concentration excess to be expected would be 0.001 to 0.003 times the CO_2 excess, if all the nitrogen would be converted to nitrous oxide during the decay. The observed N_2O excess is much smaller. The N_2O values are based on Standard Reference Materials (SRM's) from the National Bureau of Standards. A Porapak Q column in a backflush mode on an electron capture gas chromatograph was used to separate the N_2O in the air independently of the CO_2 concentration of the tomb. The N_2O concentration profile in fig. 5 shows a gradient with concentrations 10 ppb higher at 145 cm than at 15 cm. The gradient seems to suggest a N_2O source near the bottom, possibly from the boat or groundwater (which can contain very high N_2O, >100 ppm) or a soil-like covering consisting of wood debris and microorganisms.

Assuming the slowest possible gas mixing in the chamber, namely molecular diffusion only, this gradient would imply a source of N_2O of $3.2 * 10^{-10}$ moles/sec. If we also assume the

Table 2.--Trace gas concentrations inside the boat chamber

Sample and height of collection	Date Measured	CO_2 ppm	CH_4 ppb	N_2O ppb	CO ppb	H_2 ppb	F12 ppt	F11 ppt	Ratio F12/F11	CH_3CCl_3 ppt	CCl_4 ppt
Small canisters, collected 10/20/87											
4200-87	10/29/87	-	-	-	-	-	511	300	1.7	-	-
57"	11/12/87	750	-	-	-	-	-	-	-	-	-
(145 cm)	12/01/87	-	1765	-	106	<50	-	-	-	-	-
	12/04/87	-	-	337	-	-	517	302	1.7	230	118
	01/07/88	-	1763	-	185	<50	-	-	-	-	-
	01/29/88	753	-	-	-	-	-	-	-	-	-
4202-87	10/29/87	-	-	-	-	-	508	296	1.7	-	-
32"	11/12/87	749	-	-	-	-	-	-	-	-	-
(81 cm)	12/03/87	-	-	328	-	-	515	292	1.8	180	116
4201-87	10/29/87	-	-	-	-	-	513	301	1.7	-	-
7"	11/12/87	746	-	-	-	-	-	-	-	-	-
(18cm)	11/24/87	-	1763	-	62	<50	-	-	-	-	-
	12/04/87	--	-	329	-	-	514	293	1.8	187	147
Large containers, collected 10/19/87											
SIS-1	11/13/87	749	-	-	-	-	-	-	-	-	-
57"	11/23/87	-	-	-	-	-	510	297	1.7		-
(145 cm)	12/01/87	-	1761	-	27	<50	-	-	-	-	-
	12/03/87	-	-	326	-	-	507	301	1.7	-	-
	12/16/87	-	-	330	-	-	507	285	1.8	268	167
X134486	11/13/87	720	-	-	-	-	-	-	-	-	-
(Luxfer)	11/23/87	-	-	-	-	-	514	306	1.7	--	-
32"	12/01/87	-	2890	-	102	26400	-	-	-	-	-
(81 cm)	12/04/87	-	-	579	-	-	516	259	2.0	183	178
SIS-3	11/13/87	750	-	-	-	-	-	-	-	-	-
7"	11/23/87	-	-	-	-	-	515	301	1.7	-	-
(18 cm)	12/01/87	-	1762	-	24	<50	-	-	-	-	-
	12/04/87	-	-	316	-	-	506	294	1.7	161	133
	01/07/88	-	1765	-	31	<50	-	-	-	-	-
	01/28/88	755	-	-	-	-	-	-	-	-	-
Large containers, collected 10/22/87											
X134481	11/13/87	727	-	-	-	-	-	-	-	-	-
(Luxfer)	11/23/87	-	-	-	-	-	584	297	2.0	--	-
46"	12/01/87	-	2085	-	75	26800	-	-	-	-	-
(117 cm)	12/04/87	-	-	432	-	-	574	277	2.1	302	139
	01/07/88	-	2288	-	106	41000	-	-	-	-	-
	01/28/88	721	-	-	-	-	-	-	-	-	-

Table 2.--Trace gas concentrations inside the boat chamber-continued

Sample and height of collection	Date Measured	CO_2 ppm	CH_4 ppb	N_2O ppb	CO ppb	H_2 ppb	F12 ppt	F11 ppt	Ratio F/12/F11	CH_3CCl_3 ppt	CCl_4 ppt
SIS-2	11/13/87	742	-	-	-	-	-	-	-	-	-
26"	11/23/87	-	-	-	-	-	528	299	1.8	-	-
(66 cm)	12/01/87	-	1760	-	20	<50	-	-	-	-	-
	12/04/87	-	-	319	-	-	523	291	1.8	245	124
	01/07/88	-	1761	-	28	<50	-	-	-	-	-
	01/28/88	746	-	-	-		-	-	-	-	-
X134504	11/13/87	714	-	-	-	-	-	-	-	-	-
(Luxfer)	11/23/87	-	-	-	-	-	532	300	1.8		
6"	12/01/87	-	2688	-	80	27600	-	-	-	-	-
(15 cm)	12/04/87	-	-	582	-	-	529	275	1.9	-	-
	01/07/88	-	3196	-	105	42800	-	-	-	-	-
	01/29/88	694	-	-	-	-	-	-	-	-	-

shortest residence time of the air in the chamber (45 days) then the average concentration inside should be 125 ppb higher than outside, which we do not observe. The observed concentration gradient could be an artifact caused by drift in the containers.

STABILITY OF THE SAMPLES IN THE CONTAINERS

The stability of many of the trace gases in the stainless steel and aluminum cylinders is disappointing. Our experience with dry gases in these containers has generally been good, but apparently the presence of (condensed) liquid water on the walls of the containers is detrimental to the preservation of the samples. The outside air samples were also not dried during their collection, but the storage does not seem to have affected them. There was not enough moisture in the air to cause condensation inside the cylinders. Most of the samples have been measured on two occasions (tables 1 and 2), more than a month apart, in order to check for the effect of storage time on the concentrations.

We will discuss the wet cylinders only. The stability plots showing the concentration of the trace gases during time in storage are shown in fig. 6. Solid lines indicate the results with the least drift, "X" marks the best guess on the true concentration, and dashed lines indicate unstable results. F12 was stable within our experimental precision in both aluminum and stainless steel cylinders. The higher F12 (dashed lines) values were probably due to contamination of the tomb by outgassing of the elastomers from the camera during the last day of activities at the site. CO went up slightly in the large stainless cans, but substantially, between 20 and 80 ppb, in the small stainless and aluminum cylinders. Hydrogen is undetectable in the stainless containers, but in the aluminum cylinders its concentration equals tens of ppm and is increasing. We do not think that wall reactions with the stainless steel caused the hydrogen to be below our detection limits, because similar cylinders with samples from over the Pacific Ocean, that also had condensed liquid water in them, showed no anomalies in the hydrogen concentration. Nitrous oxide has increased substantially in the wet Luxfer cylinders. The CH_4 values increased in the wet alumi-

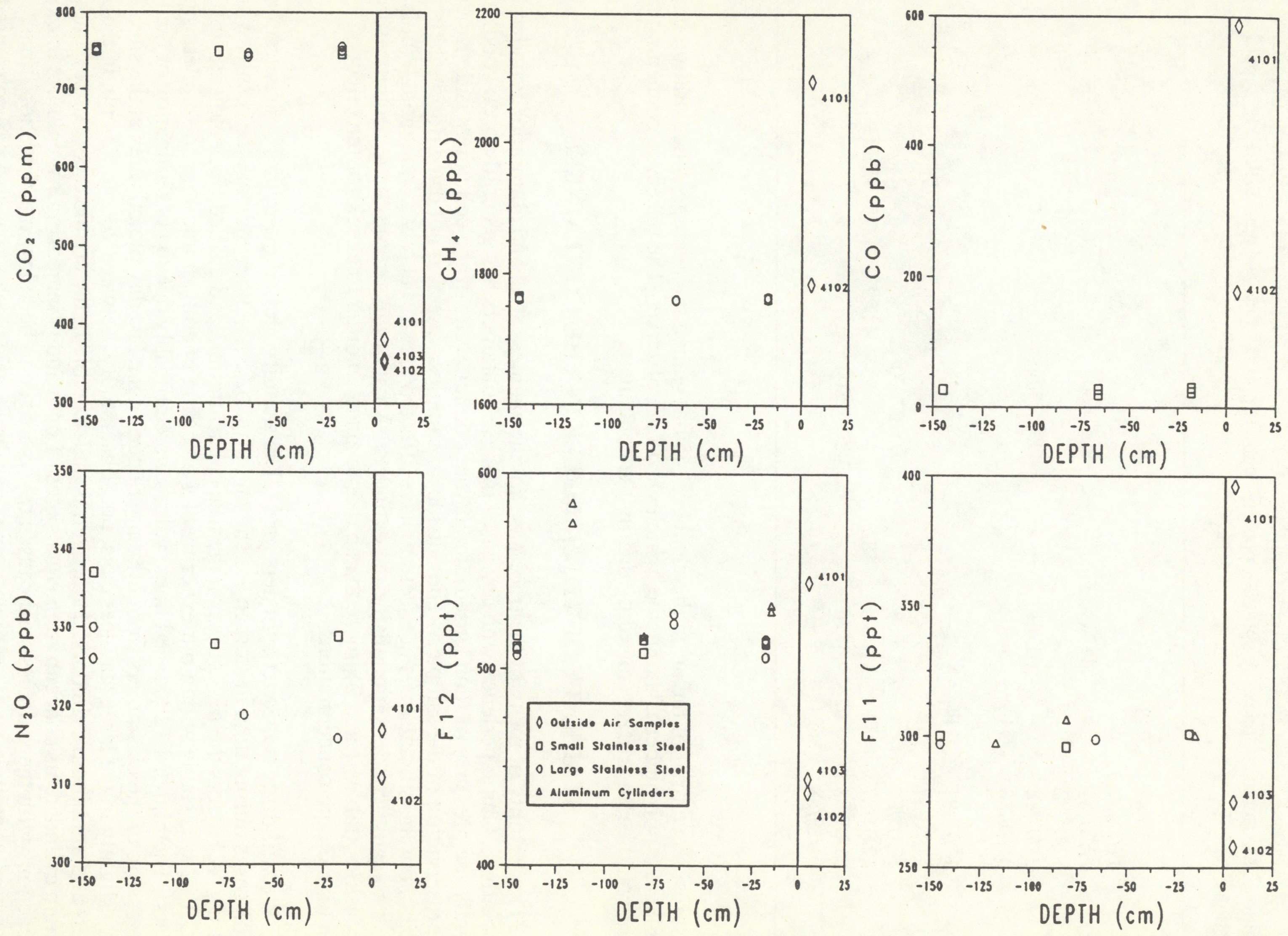

Figure 5. The concentrations of a number of gases inside the boat chamber plotted against depth below the ceiling. For comparison, the concentrations in the outside air samples have been plotted on the right-hand side of each box. ppm = parts per million, ppb = parts per billion, ppt = parts per trillion.

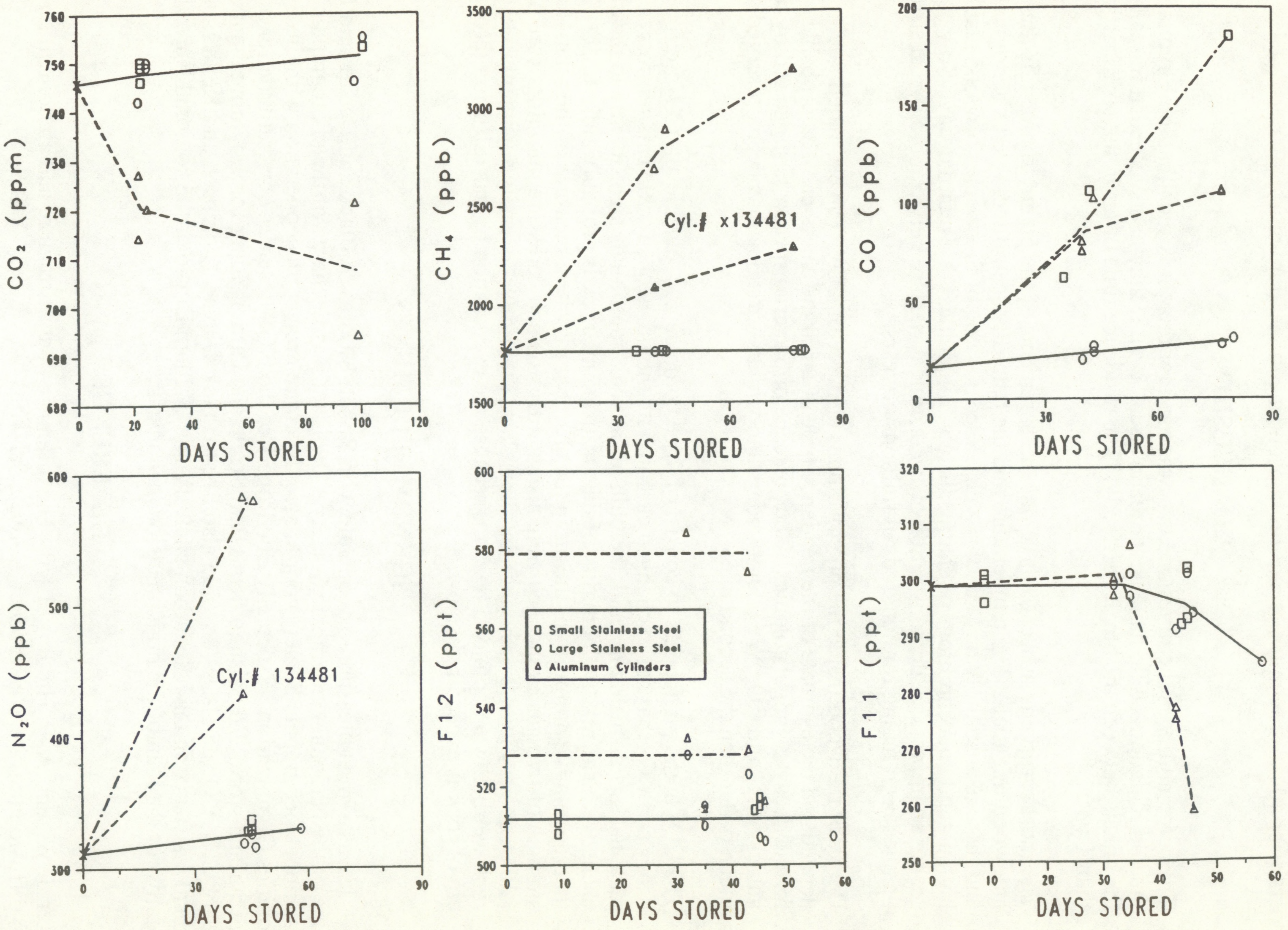

Figure 6.--Stability of the trace gases, CO_2, CH_4, CO, N_2O, F12 and F11, of the "wet" tomb samples in both stainless steel and aluminum cylinders as a function of time (in days) stored after sampling.

num cylinders but not in the stainless steel cans; in fact, the cylinder that lost the most CO_2, and gained the most CH_4, thereby suggesting a chemical reduction of CO_2 enhanced by the walls of the treated aluminum cylinder. F11 is decreasing in both the stainless steel and aluminum cylinders after 40 days, with the greatest loss occurring in the aluminum cylinders.

CONCLUSIONS

1. The permeability of the limestone that was used for this pit is such that the Egyptians of the Old Kingdom could have never made a seal, even if they had succeeded in sealing all the cracks between the blocks perfectly. The residence time of air in the chamber is less than 1 year.

2. The most surprising aspect to us of our measurements of the pit environment is that there is any wood left at all. The temperature and the humidity seem favorable to biological decay, and there is absolutely no lack of oxygen. Cedar is one of the species of wood that has high natural concentrations of chemicals (e.g. fungicides) that retard decay. So we may be seeing an impressive demonstration of the chemical warfare between biological species, that has been raging for hundreds of millions of years.

3. Decay of the wood inside the pit constitutes a source of CO_2. The estimated rate of decay depends on the estimate of the residence time of air in the chamber. The probable agent for the decay is fungal colonies. The presence of bacterial species is suggested by the low values of H_2 and CO. We do not understand why the first boat has been preserved so much better than the second one.

4. The CO_2 in the pit appears to consist of three components: outside air, CO_2 from wood decay and CO_2 that has exchanged carbon with the limestone rock. This reinforces the idea that gas diffusion through the bulk of the rock contributes significantly to the air exchange. The relative humidity of the air inside the rock is probably close to 100%, so that the relative humidity of the air in the chamber may be a measure of the relative strength of two gas exchange mechanisms: diffusion and "pressure pumping" (see p. 8). Although very low, the annual rainfall in Cairo (25 mm/yr) is easily sufficient to keep the rock wet below a depth of a few cm, because the evaporation by gas diffusion through 1 cm of rock is exceedingly slow.

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