THE LEGEND OF CARBON DIOXIDE HEAVINESS

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Abstract: The false legend of carbon dioxide traps resulting from the weight of carbon dioxide gas is disproved. In spite of water-vapor lightness in comparison with air, no water-vapor trap exists on cave ceilings. In fact, underground atmospheres with specific compositions are not related to gravity, but to the absence of any air movement around the gas sources. The process of double diffusion of oxygen and carbon dioxide during organic compound decomposition in still air is shown to be significant. This phenomenon can form atmospheres that are deadly due to oxygen deficiencies and poisonous because of excess carbon dioxide. Carbon dioxide storage behaves like a liquid and can flow or can be poured, as cold air can, but these are typical transient processes with no relation to a cave's foul air formation.

INTRODUCTION

A very common opinion among cavers (and not only cavers, see (Al-Azmi, 2008)) is that dense gases tend to accumulate in depressions, and especially, at the bottom of caves. It is widely accepted that CO_2 accumulates at the bottom of shafts; this concept has been infrequently discussed, but often repeated from paper to paper. In this paper we show that this concept is in fact false and may be regarded as an underground legend (James, 2003; Cigna, 2008). The aim of this paper is to provide a quantitative assessment and details of gas entrapment processes.

GAS DENSITIES

A first indication that those who use the concept of gas density for gas entrapment are simply repeating it, without any understanding of the processes, is the typical statement "the heavier gas accumulates...." Obviously 10 kg of nitrogen are heavier than 2 kg of carbon dioxide, or even of 1 kg of radon. Carbon dioxide is not heavier than oxygen or water vapor, but it is denser than those gases.

Even in papers where the term density is used, the downward increase of carbon dioxide concentration is qualified as normal. Renault (1972) wrote that this phenomenon is predictable from the laws of physics and then noticed that inverse gradients are not so easily explained. In fact, the phenomena are much more complex. In addition, the normal CO_2 gradient that could be attributed to density differences is undetectable on the scale of typical cave dimensions (see Equation (A3) in Appendix A).

Air is composed of many different gases, each one with a different molar mass. Considering an isothermal mass of a gas (temperature T_0, molar mass M_{mol}, density ρ_g), its density really depends on M_{mol}

$$\rho_g = \frac{M_{mol}P}{RT_0} \tag{1}$$

where $R = 8.3142$ J mol^{-1} K^{-1} is the gas constant.

Table 1 shows that, depending on molar mass, gas density changes significantly with water vapor, with methane and hydrogen being less dense than air, while carbon dioxide and radon are much denser. If stratification really does occur, according to the meaning adopted by those who state that heavier gases accumulate in depressions, then we would live in a carbon dioxide atmosphere just a few meters above sea level, in oxygen at the top of mountains, in nitrogen above the mountains, and finally, in water vapor (and rain) in the stratosphere. The Dead Sea and the Caspian Sea would exist in pure radon atmospheres whereas hydrogen would be concentrated in the ionosphere (incidentally, where it actually is, but due to reasons other than stratification). This is an unrealistic scenario.

So do denser fluids sink into less dense fluids? In the case of liquids the answer is complex. It is necessary to take into account many effects connected with the interactions of the molecules involved. For gases, the behavior is much simpler if it is assumed that the gas molecules do not interact with each other (i.e. that the gas molecules behave in an ideal way). Each air molecule is free to diffuse in every direction and it is easy to calculate the atmospheric structure at equilibrium.

GRAVITATIONAL STRATIFICATION

Let us calculate the pressure and density of a gas at constant temperature T_0 stratified in the gravitational field ($g = 9.8$ m s^{-2}) on a flat surface at $z = 0$. The hydrostatic equilibrium imposes a pressure $P(z)$ variation with altitude z (positive upward) as

$$\frac{dP}{P} = -\frac{M_{mol}g}{RT_0}dz \tag{2}$$

Integrating between the surface (z=0, $P=P_0$) and (z, P(z)) yields

$$P = P_0 \exp\left(-\frac{M_{mol}g}{RT_0}z\right) \tag{3}$$

Table 1. Molar mass and density of common gases.

Gas	M_{mol} (10^{-3} kg mol^{-1})	ρ_g at SP, $T = 288$ K (kg m^{-3})
Nitrogen	28	1.19
Oxygen	32	1.36
Air	28.9	1.22
Hydrogen	2	0.08
Methane	10	0.42
Water Vapour	18	0.76
Carbon Dioxide	38	1.61
Radon	222	9.40

Table 2. Comparison of pure gas atmosphere in neutral equilibrium.

Gas	Molar Mass, M_{mol} (10^{-3} kg mol^{-1})	Scale Length, L_z (km)	Pressure at $z = 1$ km $P(z)/P_0$	Pressure at $z = 10$ km $P(z)/P_0$
Nitrogen	28	87	0.89	0.32
Oxygen	32	76	0.88	0.27
Air	289	85	0.89	0.31
Hydrogen	2	120	0.99	0.92
Methane	10	24	0.96	0.66
Water Vapor	18	136	0.93	0.48
Carbon Dioxide	38	64	0.86	0.21
Radon	222	11	0.40	0.000113

The result is an exponential pressure decrease with altitude. Our atmosphere is not isothermal, obviously, but this equation can be used to describe the upper parts of the Earth's atmosphere, from 10 to 80 km where the air temperature is quite constant ($\approx$220 K). It is not correct to use this formula for the lowest portion of the Earth's atmosphere where we live, but the equation still describes the possibility of chemical gas stratification in caves very well because underground the temperature is locally constant. There are some details about the equilibrium of such an atmosphere which are interesting because they touch on the thermal stratification of a cave's atmosphere, but the equilibrium details are not important for our discussion.

The term in brackets in Equation (3) must be dimensionless, which introduces the length scale L_z for gas stratification in a gravitational field

$$L_z = \frac{RT_0}{M_{mol}g} \qquad (4)$$

and allows calculation of the length scale L_z at $T_0 = 288$ K. Atmospheres of pure gases in equilibrium stratify exponentially; meaning that each altitude rise of L_z causes a relative reduction by a factor $e^{-1} = 0.36$ of pressure. For instance, in pure oxygen, we would have to rise 7.6 km to reduce the pressure by 63%. In pure hydrogen, the rise would have to be 120 km, in radon 1.1 km, and so on.

It is then possible to calculate the natural CO_2 gradient enrichment with depth (see Appendix A). The real atmosphere is a gas mixture, but gases are independent of each other. Gases collaborate to create a final total pressure, but the partial pressure of each gas behaves as if the others did not exist.

Hence, the atmosphere can be considered not only a mixture of different gases, but also a mixture of different atmospheres, with each atmosphere composed of pure gas. Table 2 shows that gases have a tendency to separate from each other according to altitude differences of many kilometers. At higher altitudes, the air would be enriched by gases with small molar masses and depleted of those with greater molar masses. As a matter of fact, however, this stratification does not exist because in the real atmosphere the strong vertical mixing in its lower part (called the homosphere, up to 100 km) prevents such separation, and creates a quite uniform chemical composition.

Chemical stratification appears only in the extreme upper layers (heterosphere), where the Earth's atmosphere is arranged into four shells, the lower dominated by molecular nitrogen, the second by atomic oxygen, the third by helium, and finally by hydrogen atoms (Lutgens, 1998). If we cancel the vertical mixing and consider an ideal perfectly calm atmosphere, we could develop differences in chemical composition, but only with large altitude differences because the gases' length scales are around ten kilometers. Table 2 shows that 1 km above sea level, the different gases have essentially the same partial pressure, but in this imaginary situation it would be difficult to detect the different molar weights of the pressures. The chemical stratification would be noticeable only at $z = 10$ km (Table 2).

Stratification could exist, but only in a non-mixing atmosphere with kilometers of drop, whereas on the scale of a few meters, it is impossible to detect any chemical variation, even by measuring radon concentrations. So, water vapor and methane do not concentrate on cave ceilings, but neither does carbon dioxide or radon concentrate on cave floors unless vertical cave dimensions are on the order of many kilometers. The stratification idea, repeated thousands of times from one caving book to another, is absolutely false.

THE CARBON DIOXIDE TRAPS

There is a problem with the supposed nonstratification of carbon dioxide, however, because the stratification effect does actually appear to exist. Our work in the Tropics finding caves filled with carbon dioxide resulted in the development of specialized shaft equipment for descending into holes where encountering deadly atmospheres was likely (Antonini, 1998).

Carbon dioxide traps do exist, but their classical interpretation is false. The shafts were filled with carbon dioxide not because it is a dense gas, but because carbon dioxide is produced at the bottom of the shaft in an absolutely calm atmosphere. The reason for stratification is not gravitation, but diffusion of gas in gas. Gas traps could also exist in the absence of gravity.

It is worth noting that the false concept of gas stratification depends on the fact that the gas is potentially deadly. If at the shaft bottom there is a lake, the surrounding air is filled with water vapor, which means that the relative humidity is 100%. This high humidity is not a result of the heaviness of water vapor (which is actually less dense than air), but is merely due to the presence of water. The water vapor is concentrated at the water surface.

In exactly the same way, carbon dioxide is concentrated at the carbon dioxide sources and in the same way the gases of upper atmosphere are concentrated at their source. In the ionosphere, the X and UV solar radiations produce atomic oxygen and hydrogen and they accumulate there. This is the reason why radon accumulates in cellars and in lower floors and why methane traps are set at mine conduit ceilings where thermal stratification (hot air) creates relatively quiet bubbles for methane concentration.

Carbon dioxide is generated essentially from the oxidation of organic substances, is much denser than the surrounding air, and tends to accumulate at the lowest cave levels as water often does (although water can potentially flow away whereas dead organic substances cannot). So, carbon dioxide and water vapor tend to accumulate in the depressions that are often humid and sometimes enriched to deadly levels with carbon dioxide.

Worse, but often neglected, are hypoxic conditions. Carbon dioxide is dangerous at high concentrations, but oxygen-poor atmospheres, independent of the presence of other gases, are also deadly. Each carbon dioxide molecule is derived from the reaction of a carbon atom with an oxygen molecule. Therefore, in general, near a carbon dioxide source we can find a deadly presence of carbon dioxide as well as a deadly absence of oxygen.

A CO_2 trap thus represents a two-fold phenomenon. For organic compounds on the left, we have to calculate the oxygen flux from right to left and the carbon dioxide flux from left to right.

GAS DIFFUSION IN GASES

It is quite easy to model carbon dioxide trap formation, but it is necessary to first discuss why and how a gas diffuses in a certain direction. Gas molecules are quite free to move and they do so continuously. For a surface in space, the molecules flow through it in the two possible directions. If the concentration c_1 of a molecule per volume unit near one surface side is the same as c_2 near the other surface side, the net flux is the same and no net gas transfer through the
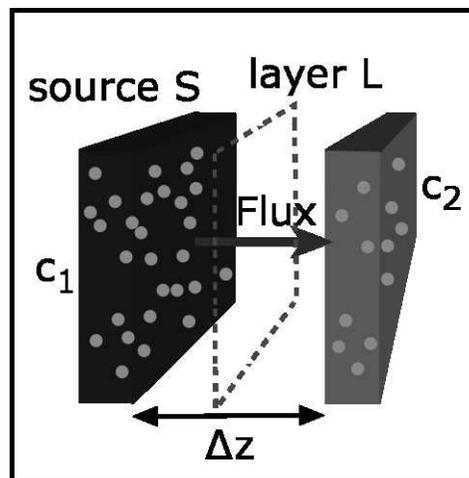

Figure 1.

surface occurs. In this instance, it is commonly stated, incorrectly, that no diffusion occurs when in fact the two diffusions cancel each other. However, if c_1 is greater than c_2, then more molecules will flow from side one than will flow from side two as a result of concentration gradients (Fig. 1). This process is usually described as the gas diffusing through the surface with an intensity proportional to the concentration difference and is known as Fick's law.

In order to quantify the gas diffusion process, it is necessary to state that the total flux F (kilograms per second per square meter) over some distance Δz that separates two gas volumes with c_1 and c_2 gas concentrations (kilograms per cubic meter) is given by

$$F = D_g \frac{c_1 - c_2}{\Delta z} \qquad (5)$$

where D_g is the gas coefficient of diffusion, which generally depends on the gas viscosity η_g and density ρ_g as

$$D_g = f \frac{\eta_g}{\rho_g} \qquad (6)$$

where f is a factor of order unity. From Equation (6) we can easily obtain the D_g dependence on pressure P and temperature T because

$$D_g \propto \frac{1}{P}$$
$$D_g \propto T^{3/2} \qquad (7)$$

Diffusion processes are, in general, very complex, and only self-diffusion (molecule diffusivity in a gas of identical molecules) is usually described. The real case, in which one gas diffuses inside another, requires consideration of different molecule sizes, asymmetries, masses, and repulsive forces between molecules. A detailed review of the processes may be found in Jost (1952).

Changes in the diffusion coefficient D_g are quite small. Table 3, adapted from Jost (1952), lists this parameter at

Table 3. Diffusion coefficients of common gases.

Gas in Gas	D_g (m^2 s^{-1})
O_2 in O_2	1.89×10^{-5}
N_2 in N_2	1.98×10^{-5}
CO_2 in CO_2	1.04×10^{-5}
O_2 in Air	1.78×10^{-5}
CO_2 in Air	1.38×10^{-5}
H_2O in Air	2.36×10^{-5}

standard temperature and pressure (STP). It should be noted that Equation (5) states that diffusion does not depend, at first order, on gravity. The upward or downward diffusion of a gas in another, heavier or lighter gas, has the same intensity because the buoyancy term is negligible.

The equations describing diffusion processes are the same as those that describe conductive thermal transfer, transient time-dependent processes (Fourier equation), and stationary processes (Laplace equation). Thermal-transfer processes also describe a diffusion process known as thermal-energy diffusion (Badino, 2005). These equations are not easily solved exactly, especially for transient conditions (Nashchokin, 1979), because even apparently simple boundary conditions can cause significant difficulties.

Nevertheless, it is possible to demonstrate that minimal carbon dioxide production in a non-mixing atmosphere can create deadly concentrations close to the source. Consider a reservoir S connected to a free atmosphere by a layer L of Δz thickness of non-mixing air with a continuous carbon dioxide production in S. Assuming in Equation (5) $c_1 = 1.61$ kg m^{-3} and $c_2 = 0$ that is a pure gas in S and nothing at the other side of L, we obtain the maximum gas flux which can be evacuated by diffusion through L

$$F_{\max} = D_{CO_2} \frac{1.61}{\Delta z} = \frac{2.2 \times 10^{-5}}{\Delta z} \qquad (8)$$

If the produced flux is greater than F_{max}, the carbon dioxide concentration in S tends asymptotically to saturation and also accumulates L where the concentration is not linearly decreasing and is time independent. A perfectly toxic atmosphere of almost pure carbon dioxide is obtained because of a very small flux and very calm conditions at the bottom (or at the top) of the cave.

For example, consider a CO_2 source S extended on a flat surface which can be either horizontal or vertical. Suppose that the source is able to release 0.01 kg of CO_2 per day per square meter ($F = 10^{-7}$ kg m^{-2} s^{-1}) that is evacuated by diffusion in a quiet atmosphere L in front of S over a distance of $\Delta z = 10$ m where the gas meets the free atmosphere. Assuming a CO_2 concentration $c_2 = 0$ (actually the average concentration is 383 ppmv and quickly increasing) yields

$$c_1 = \frac{F \Delta z}{D_g} = \frac{10^{-7} \times 10}{1.4 \times 10^{-5}} \approx 0.07 \qquad (9)$$

In this case, given such a minimal flux, the carbon dioxide concentration at equilibrium and near the source reaches roughly 5% in volume, a value that is already dangerous. The F_{max} is now 2.2×10^{-6}.

Increasing the flux $F = 10^{-5}$ kg m^{-2} s^{-1} one hundred times stronger than in the previous example, the equation would yield a meaningless value of 7 kg m^{-3}. The reason for this is that the assumption of a linear decrease in z of concentration at equilibrium cannot be satisfied for transfer of such high fluxes over such long paths and $F > F_{max}$. For these conditions, at the first few meters in front of S, the CO_2 concentration would be extremely high, and only near the free atmosphere would the concentration decrease almost linearly to zero.

The weight (density) of carbon dioxide does not matter. Exactly the same approach can be used for oxygen or nitrogen (or methane, in coal mines) sources to obtain almost pure gas atmospheres near the source. The same could be said for a water-vapor source, but this gas is far from perfect at room temperature (i.e., its behavior is highly complicated by processes like saturation, condensation, enthalpy releases, eddies, etc.). The problem of water-vapor diffusion in stable atmospheres is very complex.

The key point in creating a CO_2 trap underground is the thermal uniformity of cave atmospheres that hampers air movements and which can create traps of quiet cold air. No heavy gas stratifiation occurs, but thermal stratifiation does. Ek and Gewelt (1985) includes several incorrect comments on the role of gravity and normal gradient increasing downward, but the importance of thermal stratifiation is correctly noted. Ek and Gewelt also note the apparently surprising fact that "…in a single room or gallery the pCO_2 is frequently higher near the roof than near the ground."

Double Diffusion

There are many studies explaining carbon dioxide enrichment in caves (see, for example James, 2003 and references therein). The main, and most dangerous, reason for carbon dioxide enrichment in caves is the oxidation of organic compounds in motionless atmospheres (Ek and Gewelt, 1985). This leads to another underground legend: that carbon dioxide is able to extinguish flames.

Oxidation and degradation of any long organic molecule causes an entropy increase in one direction. Each carbon atom and each hydrogen atom in an organic waste will bind to oxygen to flow away and return as wood, skin, milk, etc. In open-air, the process is generally very fast and is helped by countless types of creatures (fungi, bacteria, birds, jackals, human beings, etc.) that live off the degradation of these dead structures, and are able to quickly distribute it to

surrounding life. However, when the organic compounds stay in a very stable situation, far from the degradation workers, as in a cave, only the Second Law of Thermodynamics can work, and it works slowly by diffusion, by slow air draughts, and by minimal temperature differences.

In general, a carbon dioxide source does not exist, but some organic residues (i.e., vegetable matter) are in contact with air. It is possible to see that if (1) the oxygen and carbon dioxide just diffuse in the same surrounding atmosphere without any draught and (2) the oxidation rate is proportional to the oxygen concentration (see Appendix B). There is then a correspondence between the oxygen and carbon dioxide concentrations around the organic storage as shown by

$$c_{CO_2,0} = 1.17(0.28 - c_{O_2,0}) \qquad (10)$$

Calling F_{id} the oxidation rate of S in free atmosphere when the oxygen concentration is $c_{O,1} = 0.28$ kg m^{-3}, the actual oxidation rate is slower due to the lower oxygen concentration

$$F = F_{id} \frac{1}{\left(1 + \dfrac{F_{id}\Delta z}{0.28 D_{O_2}}\right)} = \varepsilon F_{id} \qquad (11)$$

The reduction factor ε depends on the geometry of diffusing atmosphere. It is directly connected with the oxygen concentration near the deposit, given by

$$c_{O,0} = 0.28\varepsilon \qquad (12)$$

Returning to the previous example and assuming that the flux used, 10^{-7}, is F_{id}, it is possible to calculate new values that result from the effect of double diffusion to give

$$F = 0.85 F_{id}$$
$$c_{O_2,0} = 0.85 c_{O_2,1} \qquad (13)$$
$$c_{CO_2,0} = 0.06$$

The oxidation flux is reduced in comparison to free atmosphere, and correspondingly, the concentrations of oxygen and carbon dioxide are reduced. For extreme conditions and if F_{id} is very high, F cannot increase over the maximum value given by:

$$F \approx \frac{5.0 \times 10^{-6}}{\Delta z} \qquad (14)$$

with concentrations:

$$c_{O_2,0} \approx 0 \qquad (15)$$

$$c_{CO_2,0} \approx 0.35 \qquad (16)$$

This means that in the case of oxidative processes, the maximum carbon dioxide concentration around the source is approximately 21% in volume as oxygen in free air.

These are typical conditions in which a flame will extinguish, not because of the high carbon dioxide concentration (which does not take part in combustion, as does not nitrogen), but because of low oxygen partial pressure. Flames burn only if there is a sufficient oxygen concentration. In fact, if carbon dioxide does not come from oxidation, as it usually does, but from other sources like reaction of sulphuric acid with carbonates or volcanic gases, the atmospheres can be very dangerous and the flames burn very well (Mucedda, 1998).

ENTHALPY RELEASE AND TRAP STABILITY

The logic of a very stable atmosphere around S is an issue. Oxidation always involves enthalpy releases and temperature increases causing convective processes that transfer air much more efficiently than does diffusion.

The reaction of organic substances with oxygen produces typically 3×10^7 J kg^{-1}. As previously demonstrated, the reaction of 1 kg of matter releases 3.1 kg of carbon dioxide, with a consequent energy release of 10 MJ kg^{-1} of carbon dioxide. For a flux F (kilograms of carbon dioxide per square meter per second) we then have

$$I_{O_2} \approx 10^7 F; \quad [\text{Wm}^{-2}] \qquad (17)$$

Water molecules that are produced during the reaction form a gas, and in general, have to release the vaporization enthalpy L_w where it condenses on S or on farther walls to obtain:

$$I_w = \frac{1.3}{3.1} F L_w = 10^{-6} F; \quad [\text{Wm}^{-2}] \qquad (18)$$

where I_w is significantly smaller than I_{O_2}.

The flux assumed in the previous examples ($F = 10^{-7}$ kg m^{-2} s^{-1}) releases an energy flux approximately 1 W m^{-2}. This energy flux can increase the temperature of air and then force gas migration more efficiently than diffusion to transfer carbon dioxide and oxygen, but the rate of temperature increase and gas evacuation depends on the shape of the system. For example, a similar energy release is able to increase in a day 100 kg of air by 1 K, or 100 kg of moist vegetables of about 0.2 K, but it can only evaporate 0.04 kg of water. In general, this is a very small energy release and its effect is dependent on the system shape, such as organic deposit orientation, reactivity and depth, water presence in the deposit, and heat exchanges. If the temperature differences between the organic deposit and the cave are around 0.1–0.5 K, they force air convections of a few centimeters per second, which are much more efficient than diffusion to evacuate such small fluxes of carbon dioxide.

The situation that appears most favorable to use this energy to trigger convective movements is when S is on a vertical wall. The heated air form eddies in front of S, and

at the same time, the water flows away from it to reduce its cooling role.

The least favorable situation use of this energy occurs when S is on the ceiling (or, more reasonably, in a closed ascending cave branch). The energy released creates a thermal sedimentation that traps air in the hot bubble and only diffusion can evacuate gases from there, even if the entrance is quite large. The escape route from a similar trap is downward and it is then quite easy to get away from it with little effort and without the need for intense breathing. The presence of water thus allows for a relatively isothermal reaction and contributes to system closure, because the temperature differences are not sufficient to create eddies. In any case, it appears that extremely low air fluxes are sufficient to prevent the formation of carbon dioxide-rich or oxygen-poor atmosphere inside caves. In actuality, these conditions are quite rare.

Transient Conditions

The preceding discussion covered steady-state situations in which the parameters do not depend on time and quiet conditions. For those systems, it was shown that even when essentially at equilibrium, it is possible to create exotic micro-atmospheres.

A sudden gas emission of one cubic kilometer of carbon dioxide from Nyos Lake is not a process at equilibrium (Sigvaldason, 1989; Tazieff, 1989; Evans et al., 1993), and it is very similar to the cold air bubble that falls on our legs when we open a refrigerator. These are typical transient situations. A carbon dioxide-filled cup is very similar to a hot stone, which is going to cool, slowly, according to a similar diffusion law.

A hot stone is not stable in the long term because it is in a state of disequilibrium and will eventually reach a final stable state over a relatively long period of time. A carbon dioxide reservoir behaves in a similar way. Over a long time scale, it is unstable and tends to diffuse into the atmosphere within an altitude of a dozen kilometers. On a much shorter time scale than the time scale of equilibrium drift, the general behavior changes. The Fourier (not the Laplace) equation has to be used and our approach to study the asymptotic state does not describe the process. This means that if we produce, in some way, the filled cup, its gas will remain there for some period of time, like the cold air in a supermarket freezer, but the situation is unstable. Just like the freezer situation is usually stabilized by continuous air-cooling, the carbon dioxide trap can be stabilized by a gas source resulting in a return to stationary physics. However, if these sources are absent, the systems evolve to the maximum entropy state, with one progressing to uniform temperature, and the other progressing to complete gas mixing. In this case, gas will then diffuse away to fill the Earth's atmosphere very slowly, but it can be poured like a liquid or flow along a gallery floor.

Conclusions

Confusion between stationary and transient conditions has created a false underground legend of gas entrapment, which obscures recognition of the true processes that produce carbon dioxide, methane, and radon traps in caves and mines. The basic concepts have been further confused by the fact that if carbon dioxide is produced by oxidation near its source, there is not only high carbon dioxide concentration, but also a very low oxygen concentration, which leads to the occurrence of flame extinctions and similar evidences of poor atmospheres.

The traps are essentially due to accumulation near a source (whatever the origin) in motionless atmospheres. The up-down gradients are generally due to (1) preferred point of organic accumulation and (2) air thermal stratifiation that creates a motionless trap of cold or warm air.

Structure, periodicity, and intensity of traps depend on organic matter inflow, thermal stratification, and shape of the cavity.

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Appendix A

The Natural Carbon Dioxide Gradient

The air pressure in an isothermal atmosphere, in neutral equilibrium, at height h [km] as given by Equation (5) and Table 2, leads to

$$P_{air} = P_0 \exp\left(-\frac{h}{8.5}\right) \qquad (A1)$$

Similarly, in a pure CO_2 atmosphere the pressure behaves according to

$$P_{CO_2} = P_0 \exp\left(-\frac{h}{6.4}\right) \tag{A2}$$

The ratio between P_{CO_2} and P_{air} in the previous equations gives the ideal carbon dioxide impoverishment with altitude so that we can then obtain:

$$\frac{P_{CO_2}}{P_{air}} = \exp\left(\frac{h}{8.5} - \frac{h}{6.4}\right) = \exp\left(-\frac{h}{26}\right) \tag{A3}$$

The scale length of reduction of carbon dioxide concentration due to buoyancy is then around 26 km. For these conditions and with a carbon dioxide concentration of 3% at the floor, it is necessary that the ceiling be located at 10.4 km of altitude to reach 2% concentration. This is in fact the true natural CO_2 gradient under ideal conditions.

APPENDIX B

DOUBLE DIFFUSION

Using an organic deposit S and some mass M per square meter, the chemical composition of organic matter is very roughly C_nH_{2n}. Putrefaction (oxidation) of these molecules eventually is

$$\frac{3}{2}O_2 + CH_2 \Rightarrow CO_2 + H_2O \tag{B1}$$
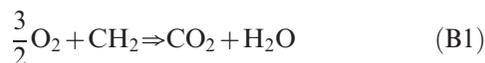
which in term of reacting masses gives

$$(3.4M)_{O_2} + M \Rightarrow (3.1M)_{CO_2} + (1.3M)_{H_2O} \tag{B2}$$
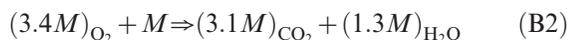
Volumetrically, this means that putrefaction of one kilogram of vegetable mass needs the oxygen in about 12 cubic meters of air and emits two cubic meters of carbon dioxide. Most importantly, it needs an oxygen supply.

It is reasonable to assume that the oxidation rate of a compound is proportional to the local oxygen concentration in S. Therefore the produced flux of CO_2 is given by:

$$F = K_{O_2} c_{O_2,0} \tag{B3}$$

where $c_{O_2,0}$ is the oxygen concentration near the compounds.

The proportionality depends on exposed surface, compound type, reactivity, temperature, presence of bacteria, total mass of S, etc. Calculation of K_O is basically impossible, but some K_O does exist. We can assume that the free atmosphere that feeds oxygen to S is also the same atmosphere that evacuates carbon dioxide (it is not an obvious assumption, but in general, it is true), so we can also assume that the free atmosphere is at a distance Δz from S. At equilibrium, system parameters do not depend on time (the system is stationary) and the rate of CO_2 molecules

evacuation must equal exactly the incoming oxygen molecules, as well as the carbon dioxide production.

The concentrations $c_{CO_2,0}$ and $c_{O_2,0}$ are the gas concentrations in S, and the concentrations $c_{CO_2,1}$ and $c_{O_2,1}$ are those in the free atmosphere. We must also account the for the different masses involved, and assuming that the flux is not so strong as to destroy the linear distribution, we have

$$F_{CO_2} = D_{CO_2} \frac{c_{CO_2,0} - c_{CO_2,1}}{\Delta z} \tag{B4}$$

for the diffused carbon dioxide flux from S to $z > 0$, and

$$F_{O_2} = D_{O_2} \frac{c_{O_2,0} - c_{O_2,1}}{\Delta z} \tag{B5}$$

for the flux of diffused oxygen to S. The mass balance shown in Equation (B2) gives

$$F_{O_2} = \frac{3.4}{3.1} F_{CO_2} \tag{B6}$$

At sea level we can assume that

$$c_{O_2,1} = 0.28 \text{kgm}^{-3}$$
$$c_{CO_2,1} = 0 \text{kgm}^{-3} \tag{B7}$$

so that we can then obtain a relation between the carbon dioxide and oxygen in S

$$D_{O_2} \frac{0.28 - c_{O_2,0}}{\Delta z} = \left(\frac{3.4}{3.1}\right) D_{CO_2} \frac{c_{CO_2,0}}{\Delta z} \tag{B8}$$

Then, with numerical values

$$c_{CO_2,0} = 1.17(0.28 - c_{O_2,0}) \tag{B9}$$

setting F_{id} the oxidation rate of S in free atmosphere (i.e., when the oxygen concentration is $c_{O_2,1} = 0.28$ kg m^{-3}). We expect that the real oxidation rate to be slower due to the lower oxygen concentration which is proportional to K_{O_2}

$$F_{O_2} = K_{O_2} c_{O_2,0} = F_{id} \frac{c_{O_2,0}}{c_{O_2,1}} \tag{B10}$$

Combining and rearranging

$$F = F_{id} \frac{1}{\left(1 + \dfrac{F_{id}\Delta z}{0.28 D_{O_2}}\right)} = \varepsilon F_{id} \tag{B11}$$

$$c_{O_2,0} = c_{O_2,1} \frac{F}{F_{id}} = 0.28\varepsilon \tag{B12}$$

The carbon dioxide concentration in S is simply

$$c_{CO_2,0} = \frac{F\Delta z}{D_{CO_2}} = \varepsilon \frac{F_{id}\Delta z}{D_{CO_2}} \tag{B13}$$

That is, carbon dioxide concentration is also reduced by a factor ε when compared with the concentration that we would obtain in the case of single diffusion.

We found a reduction factor ε that takes into account the limited transfer possibilities due to the double diffusion which showed that the actual flux ratio F/F_{id} only depends on the oxygen transfer capacity of local atmosphere. If $D_{O_2}/\Delta z$ is very large (that is, the gases diffuse very easily) in comparison with F_{id}, then $\varepsilon = 1$ and F is near F_{id} as it must be. The equations then reduce to the conditions for single diffusion. So, the limiting behavior of double diffusion need only be considered when dealing with high reactivity and, correspondingly, with high CO_2 concentrations.

It is easy to show that for these conditions, oxidation rate tends to zero, there is no oxygen near the source (hypoxic atmosphere), and flames smother.

Equation (B11) can be rewritten as

$$F = \frac{1}{\left(\dfrac{1}{F_{id}} + \dfrac{\Delta z}{0.28 D_{O_2}}\right)} \tag{B14}$$

and if F_{id} is high, F reaches its maximum value according to

$$F \approx \frac{5.0 \times 10^{-6}}{\Delta z} \tag{B15}$$

$$c_{O_2,0} \approx 0 \tag{B16}$$

$$c_{CO_2,0} \approx 0.35 \tag{B17}$$

which means that in the case of oxidative processes, the maximum carbon dioxide concentration around the source is approximately 21% in volume.