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CLOUDS IN CAVES

Giovanni BADINO

Abstract
Different processes that can create vapour pressure above the equilibrium in the caves atmospheres are considered, quite similar to the processes that give rise to clouds formation in the open atmosphere: ascending air parcels, pressure drop behind bottlenecks, mixing of saturated air parcels at different temperatures and water flow fragmentation.
The difference of adiabatic lapse rate of water and moist air create temperature unbalance between the flowing fluids in deep underground system, leading to thermal and water exchanges, in which the water flow globally subtracts energy to the system.
The usual high purity of caves atmosphere tends to delay condensations that are concentrated where the contact between airflows and wall is tighter.
The rate of condensation on wall of aggressive water is comparable with the external rains and can play a leading role in speleogenesis.

Introduction
The humidity in the cave's atmospheres is generally at the saturation level, due to the usual tight contact between water surface and air in these quasi-closed systems.
Direct measures of fluctuation amplitudes around the equilibrium value are impossible because the usual hygrometers and evaporimeters do not allow so high accuracies.
Nevertheless direct observations show that the water vapour is very often super-saturated. It is a usual experience to see the walls covered by a water film, to find droplets on the surfaces of objects left for some times underground, to see some haze in large halls and aerosols in the air,@.
There are also indirect evidences of condensation processes at work, for instance the so called "degree rule" (the air warmer than the water of some tenths of degree, a fact that *in se* would break not less that the Second Principle...), uniform wall dissolution that extracts insoluble intrusion from rock (a corrosion obviously due to condensation) and other phenomena that can only result from moist air transformation.
For a long time have already been supposed a speleogenetic role of condensation-evaporation processes: Trombe, who assumed condensation processes driven by the thermal unbalances that we have already cited ("degree rule"). We think in fact the contrary (the unbalance coming from condensations) but it does not matter, it is manifest that complex transformation occurs between moist air and its constraints, so clearly that cavers generally estimate active or fossil caves from the perception of water film on walls.
These transformations are energetically fed by the air flux. In fact, as we have already noted @ and we are going to show hereafter, the water *subtracts* energy to the mountain: in the cave digging, the water acts as the chisel but the hammer is the airflow.
The key role of condensed water is due to the fact that they are in equilibrium with local carbon dioxide and are completely unsaturated of salts.
The speleogenetic capability of water flowing inside a cave can be estimated; the annual precipitations are of the order of 1000 mm, then, including evapotranspiration and the fact that the water penetrates underground already charged of salts, we can estimate that only a fraction is

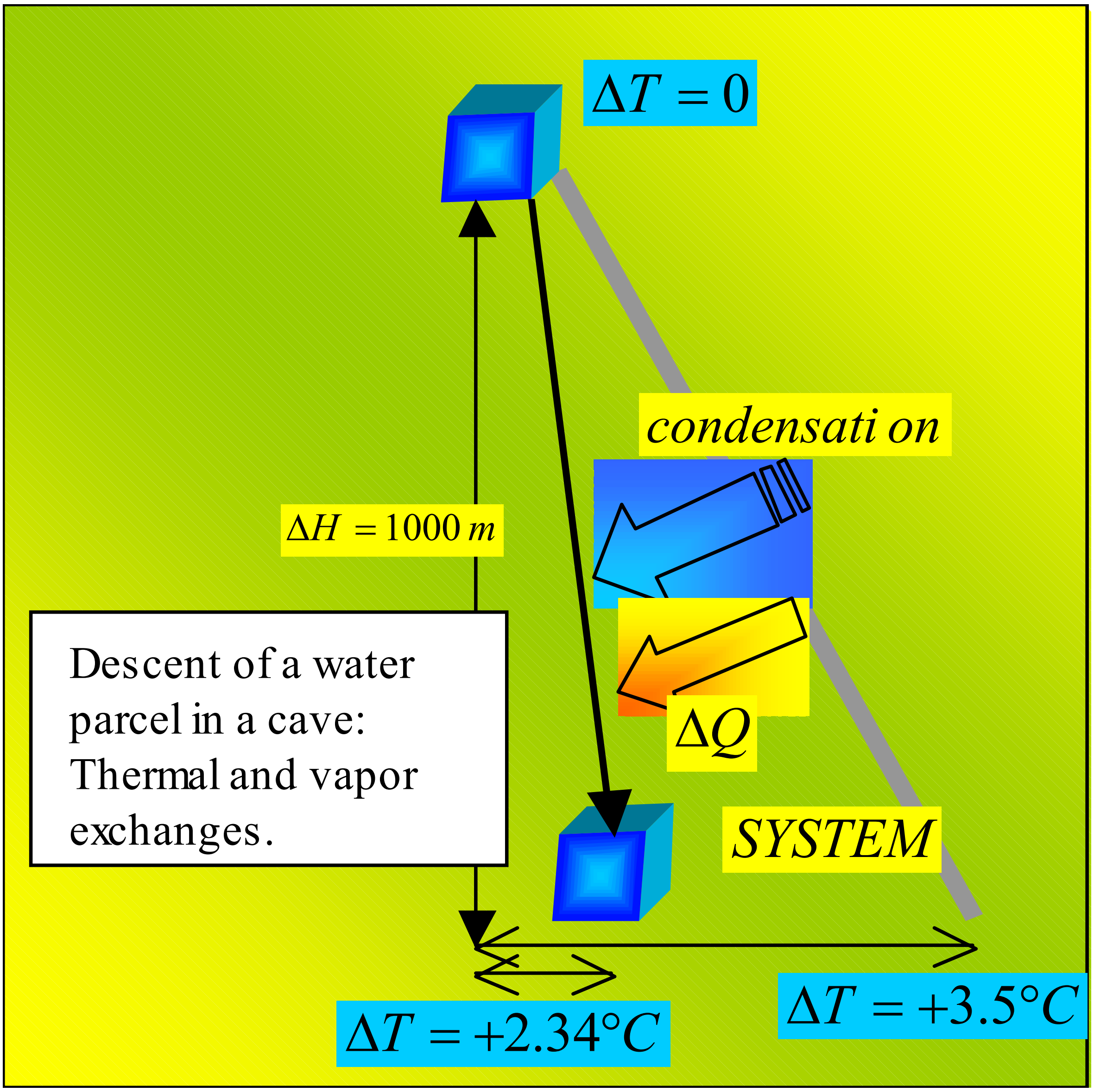
the unsatured water per year, that is around 1-10 mg s^{-1} per square metre of external surface; we are going to compare this figure with the estimated depositions from “underground clouds”.
This paper is a part of a very huge work on general underground climate physics on which we are working, that follow a very introductive work that will be often cited.

The temperature gradient in deep karst

It is well known that the vertical gradient in the atmosphere is, on average, -6.5 °C km^{-1}.
In fact, if we consider an air parcel perfectly dry it is easy to see that in a ideal atmosphere (in hydrostatically neutral equilibrium) the temperature gradient would be –9.7 °C km^{-1}, the so called “dry adiabatic lapse rate”. But if the air parcel contains water vapour this is no longer true, because when the cooling causes a supersaturation some vapour condensate releasing its enthalpy of vaporization, and reducing the cooling.
The lapse rate becomes smaller in absolute value, but it depends on water vapour contents that depend on the temperature and pressure (“moist adiabatic lapse rate”). The table show some values in usual karst conditions.

Moist adiabatic lapse rate [-°C/km] vs. altitude and temperature					
Altitude [m]	100	1000	2000	3000	4000
T=0°C	6.58	6.38	6.14	5.91	5.70
5°C	5.90	5.70	5.50	5.25	
10°C	5.32	5.11	4.89	4.68	
15°C	4.80	4.60	4.40	4.20	
20°C	4.35	4.17	3.98	3.80	
25°C	3.95	3.80	3.65		
30°C	3.63	3.49	3.35		

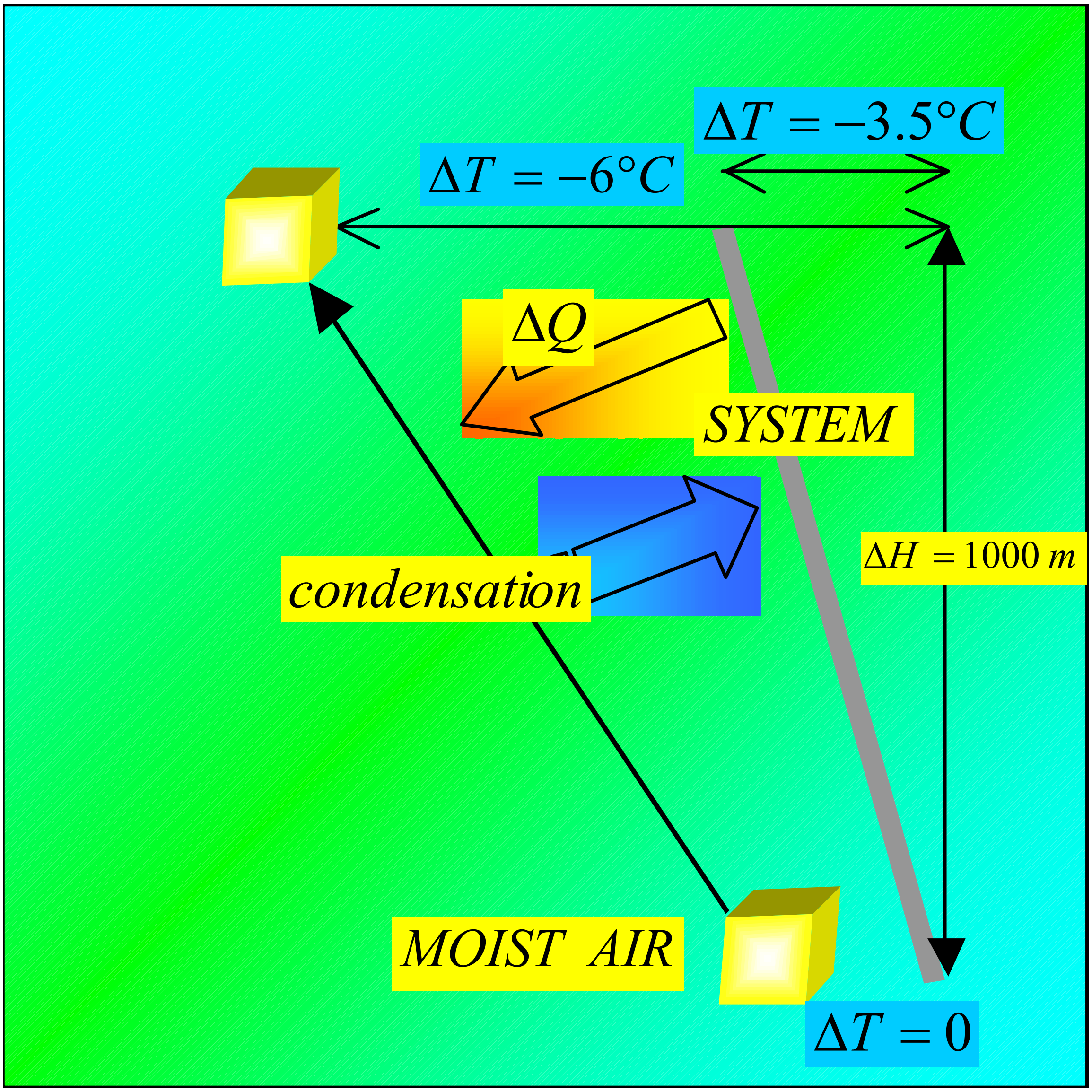
It is then reasonable that the atmospheric average lapse rate is near to the moist adiabatic one and we could expect the same also in caves even more. In fact this is not true, because the cave temperature is mainly established by the water contribution given that, as a rule, the total thermal capacity that enters underground is mainly in the water flux.
It is of paramount importance the fact that the “water adiabatic lapse rate” is completely different from the moist air one. It is easy to show that the complete (adiabatic assumption) transformation of an initial gravitational potential energy in internal energy heats a water parcel of 2.34°C per kilometre of fall. And in fact this would be the asymptotic lapse rate in a cave dominated by water fluxes.



The real situation is intermediate (@), and as a rule we can say that in alpine deep caves the lapse rate is around –(2.8-4)°C km^{-1}, that is quite similar to the water one. Only in very special cases, for instance the quartzite shaft in the Tepui of Venezuela it is possible to measure lapse rate just near to the moist adiabatic one.
We have already noted that this fact has a simple but enormous implication: the water flows out from the deep karst warmer than in adiabatic case, that is, it *subtracts* energy to the mountain.
We want here to give other details on the moist air transformation underground.

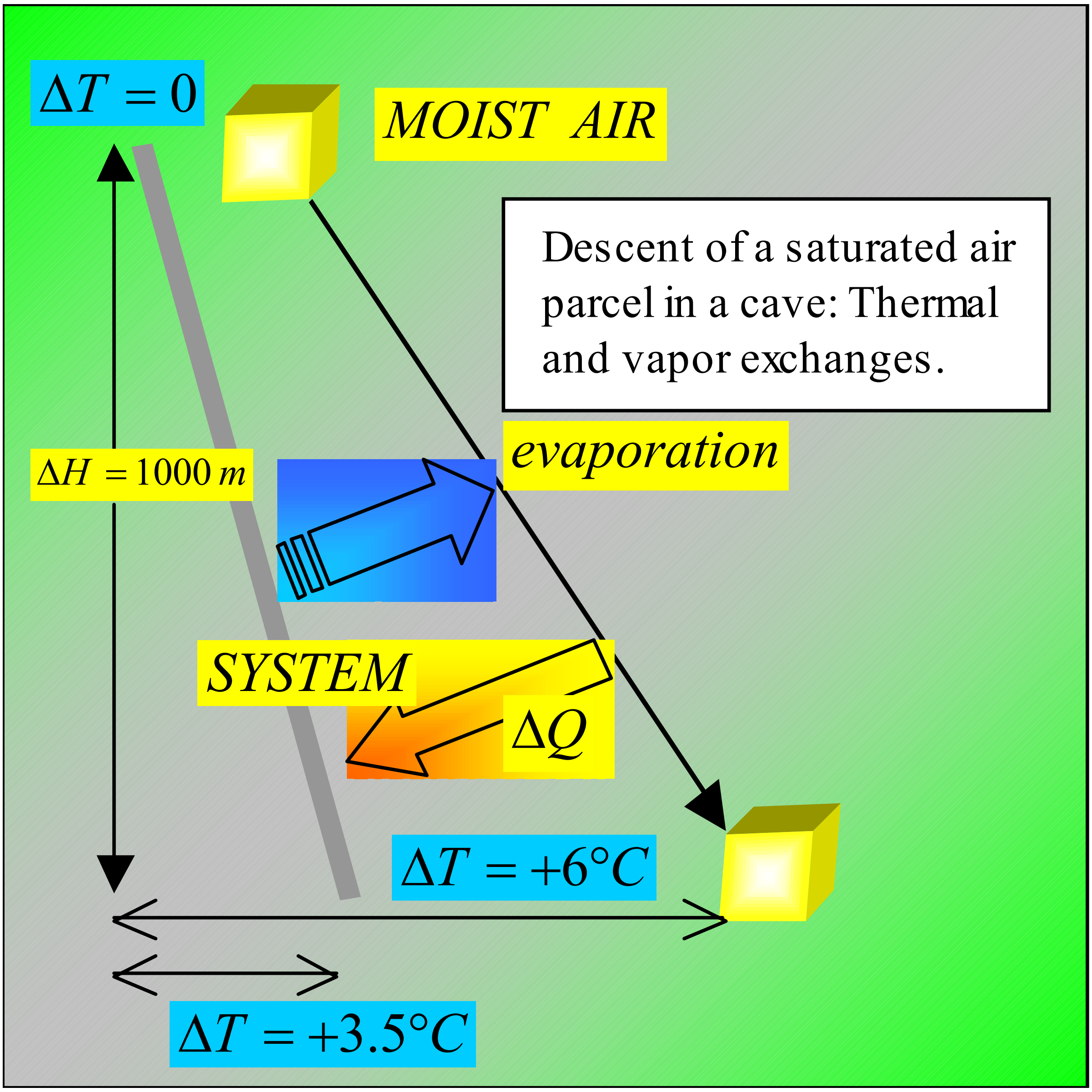
Clouds from ascent of air parcels
The ascent of a saturated air particle is the main process that can create supersaturation conditions in the underground air parcels.

The karstic temperature gradient is intermediate between the water and moist air adiabatic lapse rates and this implies that the two fluids in the vertical transfers into the mountain undergoes transformations that are not adiabatic: there is a continuous thermal exchange between the two and the transformation can be considered “at constant temperature gradient”@.
Let us consider at first an air parcel ascent (one cubic metre) with vapour at the equilibrium (from hereafter “saturated” air parcel, for simplicity, but about the inaccuracy to use the word “saturation” instead of “equilibrium” see BOHREN).



Suppose, for instance, that the rise is 1 km, in a cave with an internal lapse rate of –3.5°C km^{-1}. From the energetic point of view we can divide the general transformation in two steps: an adiabatic ascent to the final altitude and an isobaric transformation to the local condition. The adiabatic ascent gives a total cooling of –5°C (suppose to be at 10°C) and a condensation of

roughly 5 g of water vapour. The subsequent transformation to the local condition requires a heating of 1.5°C and the vaporization of 1.5 g of water. In fact, this shows two things:
1) The air parcel has absorbed thermal energy to the internal surroundings
2) It has released 3.5 g of water.
In the real case the energy and water exchanges are distributed along the path. Generally the ascent of air parcel happens during cold season, but it is necessary to note that the mechanism can work in the case of ascending trench of a globally descending flux. This means that the underground rainy season in general is winter, but locally can be summer...



The descending air parcel obviously tends to evaporate water and to dry the cave, probably with a tendency to create thermal unbalance and sedimentations in the region already dried. For instance if, on the conduit roofs, there is not so much water to evaporate, the flowing air parcel tends to warm more and to stay "trapped" in the upper parts of galleries: thermal sedimentation can occur.

Underground banner clouds

Banner clouds are the clouds that sometimes appear leeward of large picks. Their phenomenology is not completely understood, but they appear to be the result of a sudden (i.e.: adiabatic) air expansion that locally cools the gas below the dew point.

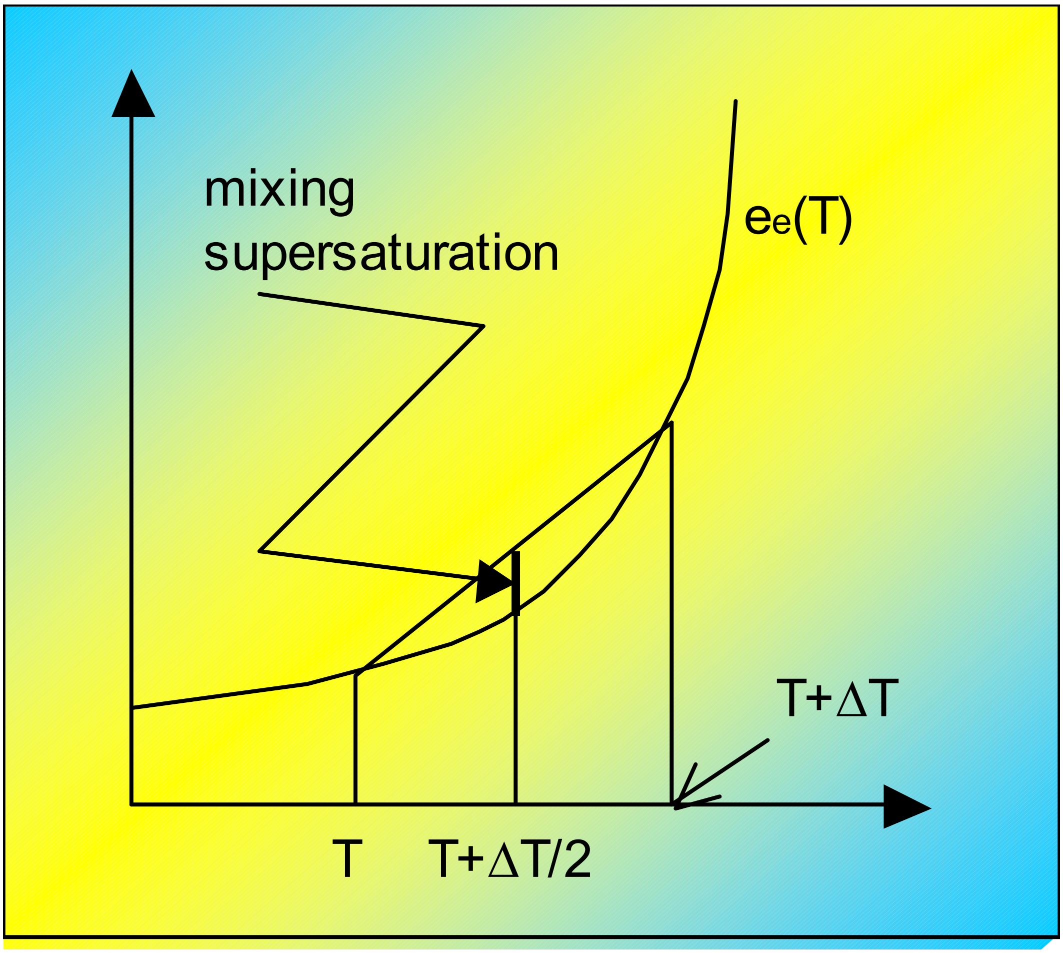
Let us now consider the airflow in a cave system; the flux through a mountain, as a whole, can be considered a Joule-Thomson expansion (note that it is locally "expansion" either for ascent or descent of air parcels) because in fact the air particle is "throttled" through the cave. The general transformation is then isenthalpic, as the flow through a single narrow passage.

A much more accurate discussion would be necessary (it is necessary to talk about constant, periodic or transient flows, rock surface role and so on) but roughly we can say that downstream the air parcel undergoes a sudden expansion that locally (in time and space) can be considered adiabatic and then with a resulting temperature drop.

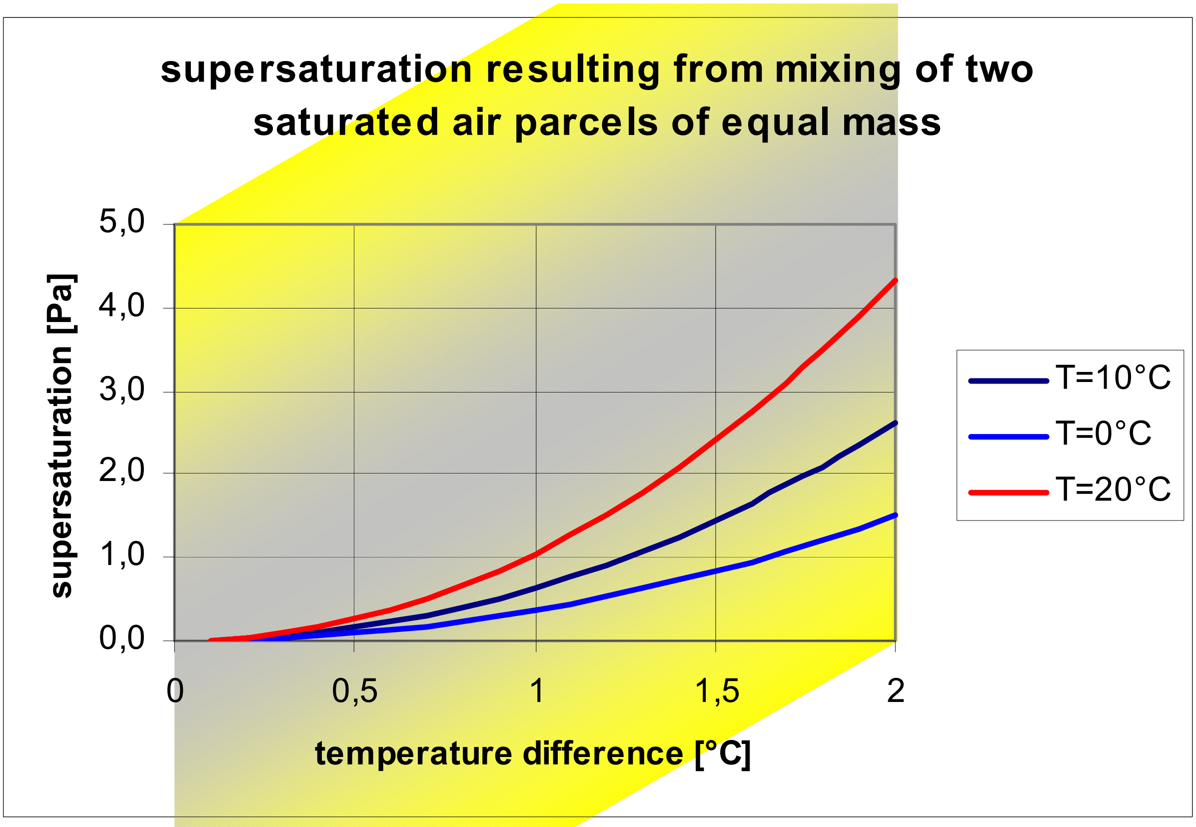
The pressure drop, roughly proportional to the square of velocity in the "throttle" is quite small, as then the temperature decrease: for example, a velocity of 5 m s^{-1} corresponds to a pressure decrease of about 10 Pa, equivalent to an ascent of one metre and then to a temperature drop of 5 mK. The supersaturation level would then be of the order of 0.05%, directly not measurable but able to create condensation on walls; the estimation is then 5 mg per cubic metre flowing.

Mixing clouds

The mixing clouds in caves are so common that are almost not perceived: the clouds that cavers create with breath or moist dresses are typical mixing clouds. BOHREN discusses the mixing clouds formation mechanism and its common misinterpretation: to believe they are formed "because the warm breath is cooled..." and so on. "Heating and cooling per se are irrelevant... mixing clouds are formed by mixing different parcel of air... because of the shape of the saturation vapour pressure curve two parcel can mix to form a supersaturated parcel".



It is in fact a mechanism connected with the non-linearity of Clapeyron curve, and essentially the same as the "Boegli's corrosion by water mixing".
Temperature drop in caves are quite common due to different "histories" of water and air columns flowing along different branches, often characterized by different temperature gradient along the flow but mainly by different temperature at the entrance @.
Temperature drops of 1°C and more between different branches are quite common in alpine karst, especially with external topographies very steep. Calling T and T+ΔT the absolute temperature of the two air parcel, with equal mass, e_s the equilibrium vapour pressure at T, it is quite easy to calculate from Clapeyron equation the supersaturation, given in the graphic.

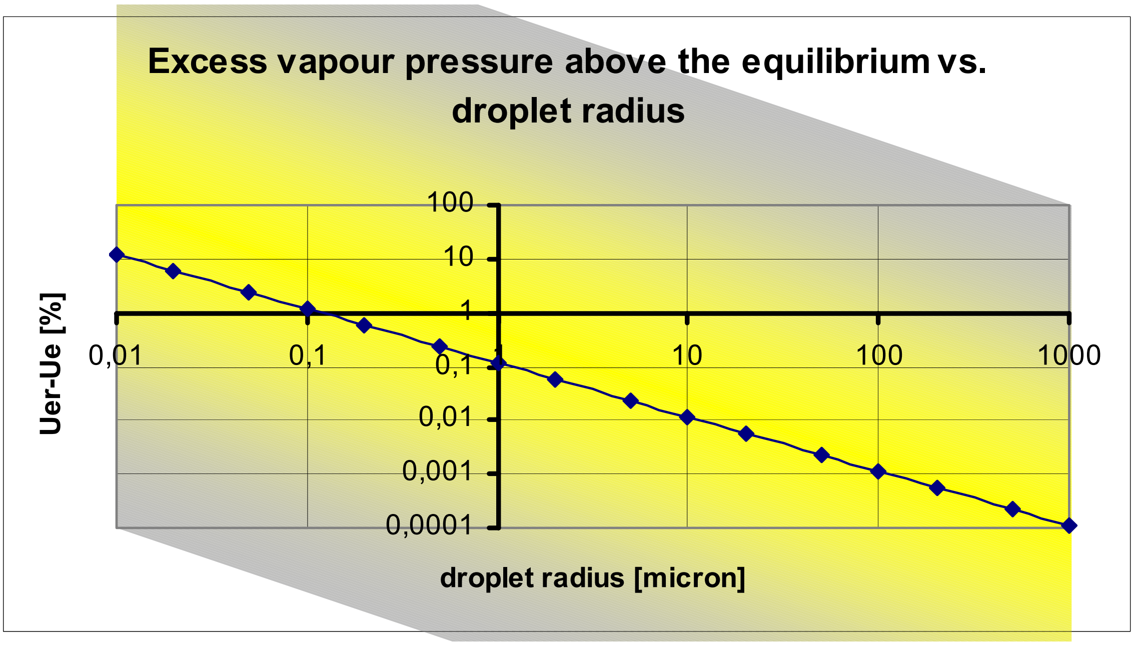


The equation that gives the relative supersaturation is given by

$$\frac{\Delta e_s(T,\Delta T)}{e_s(T)} = 3.7\times10^6\left(\frac{\Delta T}{T^2}\right)^2$$

It is easy to see that the supersaturations are quite low, 0.01-0.1%, what nevertheless corresponds to a total release of some milligrams per cubic metre of air coming at the mixing point.

Fragmentation clouds
The processes that generate clouds from fragmentation of cascades do exist obviously outside but their role in the open atmosphere is perfectly negligible. In the case of closed or semi-closed water draining systems, like caves or canyon, this is no longer true.
The key point is that the Clapeyron law describes the equilibrium pressure above a flat water surface. If the surface has radius of curvature comparable with the intra-molecular interaction lengths large correction have to be done. In practice, a molecule on the surface of a small droplet is less bent to the liquid than in a flat surface and its tendency to evaporate is stronger. The equilibrium pressure is then higher.
The equation that connect the e_s on a flat surface and the e_{sr} in a droplet is given by the Kelvin equation.



The graphic shows the supersaturation that a moist air in equilibrium with droplets of radius r has then when it arrives to a flat water surface. Incidentally we note that the presence of a stable aerosol in a cave atmosphere is then a direct evidence of a supersaturation state of moist air.
A droplet falling in the air, moves at a constant velocity, established by the equilibrium between viscous and gravitational forces. If the droplet is sufficiently small it moves in laminar regime, but if its radius is larger than 0.5 mm the Reynolds number associated with its motion becomes higher than 2000 and the regime becomes turbulent.
The dissipated power increases and lee eddies appear, transmitting oscillations to the droplet. In practice, large drop tends to become unstable and to divide in droplets with size smaller that the critical one. It would be very important to have measures, but meanwhile we can then suppose that the fragmentation during fall creates droplets, mainly with a quite large size and then with small supersaturation associated.
The final fragmentation on rock or water is more efficient in the droplets splitting because it is only contrasted by the surface tension; if we assume that the final kinetic energy is spent in large part creating drop surface we obtain a typical size of 10 μm.
The fragmentation is then able to mechanically create a cloud, which has to be in equilibrium with the surrounding air. The surface rocks around are then washed not only by the falling drops and aerosol but also by the condensation of super-saturated air. It is easy to see that also in this case the mechanism produces supersaturation of some 0.01%, again an excess water content of milligrams per cubic metre, that are going to be released to walls when the air parcel eventually flow on it.
The Kelvin equation is useful also for negative radius of curvature, which is for concave surface. In this case the surface needs a smaller vapour pressure to be in equilibrium and then it becomes

a preferred condensing point for surrounding air in equilibrium with flat surface. This means that small fissures tend to fill with condensed water.

Condensation nuclei

It is well known that supersaturated air particle can condensate only in presence of "condensation nuclei", that is, air impurities. From one side we can see why the cave's atmospheres are so pure: the supersaturation (ascents, eddies, mixing, expansions...) is able to capture and precipitate air dust on the floor. From the other we have to remember that the rock surfaces are excellent condensation "nuclei". Then the local air super-saturation can become quite high due to the almost absolute air purity, but it will condensate ("supersaturation reset") as soon as it enters in contact with rocks. It is easy to understand that the points where the super-saturation is reduced are those where the conduit sizes are smaller: the smallest cave parts along the water column flow are preferred points for condensation, they integrate the supersaturation formed in large region upstream, and this has obvious consequences on speleo-genesis.

Conclusions

Our discussion has outlined general processes, without trying to enter in details that would be able to transform this short note in a book.

Nevertheless many point are too shortly discussed: the main is probably the energy balance of supersaturation formation that leads to thermal unbalances between the aerosols and the air, but we have not discussed other important points like the kinetic of evaporation and droplets formation, thermal sedimentation in air, presence of dissolved salt in fragmented water, dynamics of air flow on walls, dynamic of aerosol size-spectra and so on.

We have already analyzed in part these problems, but the extreme calculation complexities and, above all, the lack of measures have suggested us to write this brief, qualitative treatment in order to suggest new observations.

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