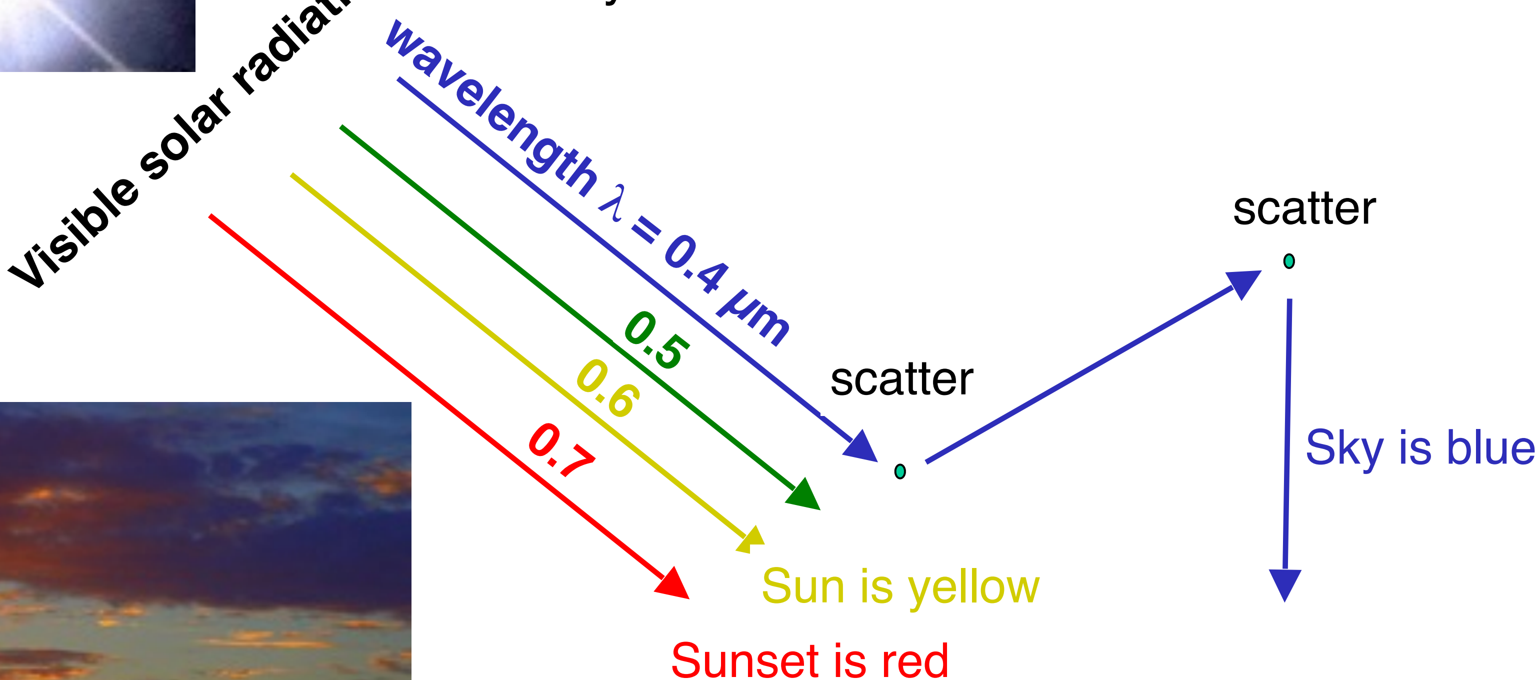
1. MEASURES OF ATMOSPHERIC COMPOSITION

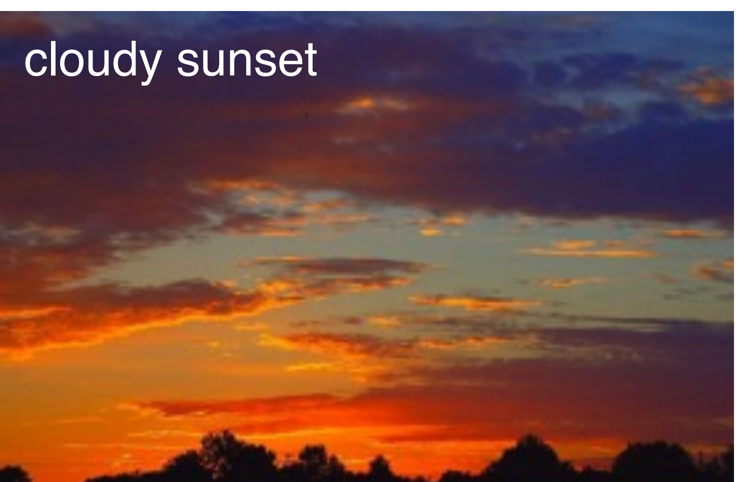
The atmosphere: gas envelope surrounding the Earth

The atmosphere seen from the space shuttle

Sun seen from space shuttle

- Size of air molecules $\approx$ 0.3 nm << λ
  $\Rightarrow$ scattering is inefficient and $\sim \lambda^{-4}$
- Absorption at visible wavelengths is also very weak



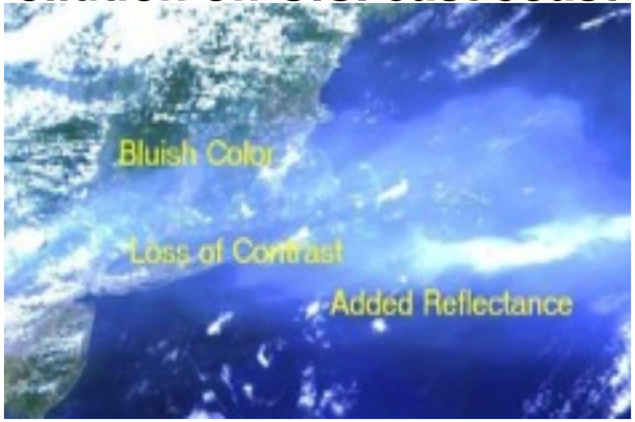


Aerosols and clouds: the visible part of the atmosphere

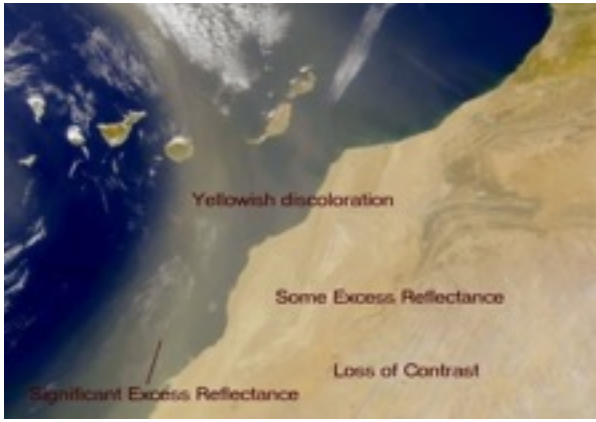
Aerosols are suspended solid or liquid particles, typically 0.1-1 μm in size

California fire plumes

Pollution off U.S. east coast



Dust off West Africa



Cloud droplets (1-100 μm in size) form by condensation on particles when relative humidity exceeds 100%

Atmospheric gases are "visible" too… if you look in UV or IR

radiation
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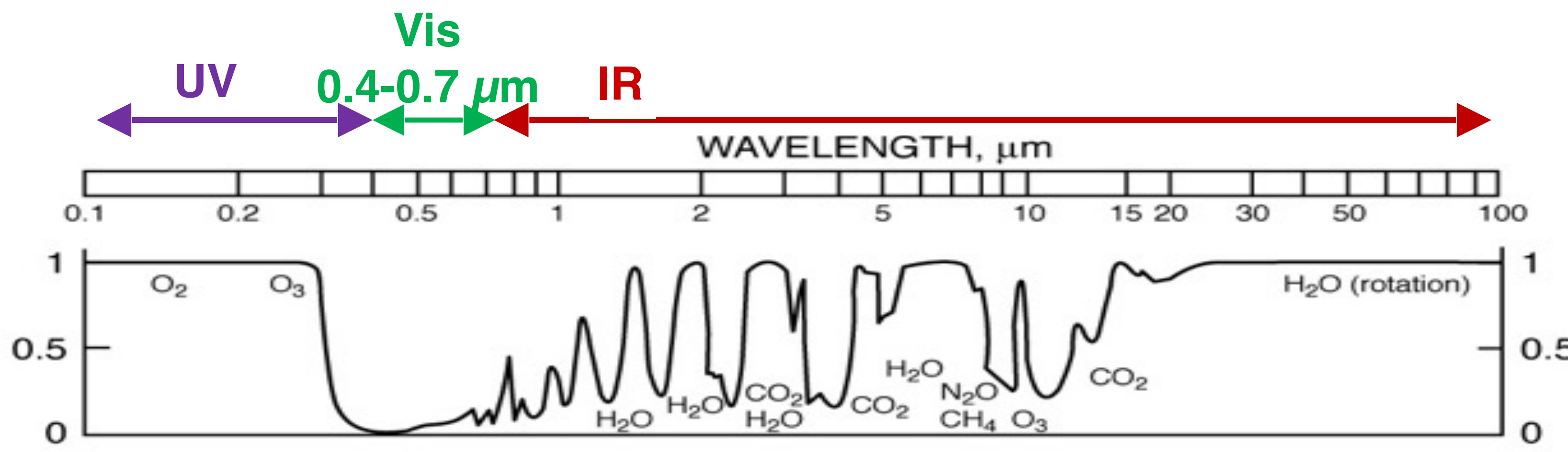
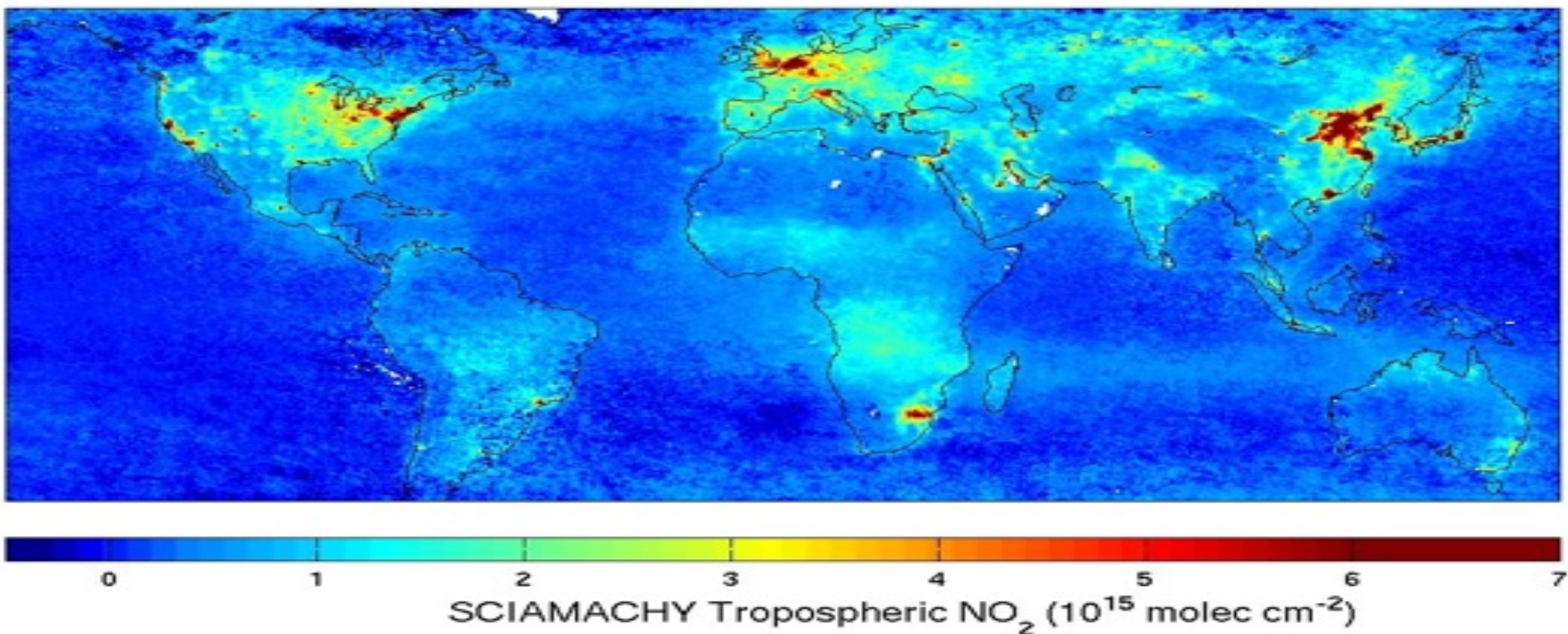


Nitrogen dioxide (NO_2) observed by satellite in the UV



Relative concentration: mixing ratio a.k.a mole fraction C_X [mol mol^{-1}]

$$C_X = \frac{\#\text{ moles of X}}{\text{mole of air}}$$

remains constant when air density changes

$\Rightarrow$ **robust measure of atmospheric composition**

SPECIES	MIXING RATIO (dry air) [mol mol^{-1}]
Nitrogen (N_2)	0.78
Oxygen (O_2)	0.21
Argon (Ar)	0.0093
Carbon dioxide (CO_2)	400×10^{-6}
Neon (Ne)	18×10^{-6}
Ozone (O_3)	$(0.01\text{-}10)\times10^{-6}$
Helium (He)	5.2×10^{-6}
Methane (CH_4)	1.8×10^{-6}
Krypton (Kr)	1.1×10^{-6}

Trace gases (Carbon dioxide through Krypton)

Air also contains variable H_2O vapor (10^{-6}-10^{-2} mol mol^{-1}) and aerosol particles

Trace gas concentration units:

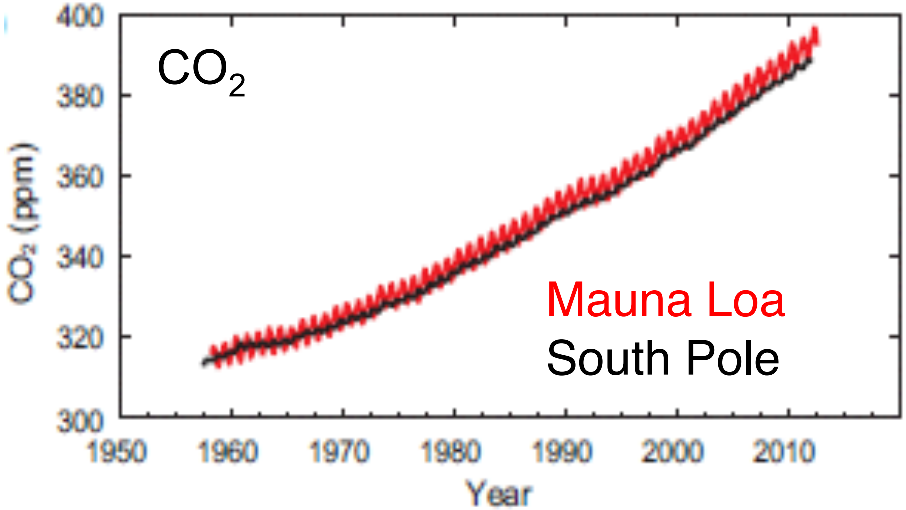
1 ppm = 1 μmol mol^{-1} = 1×10^{-6} mol mol^{-1}

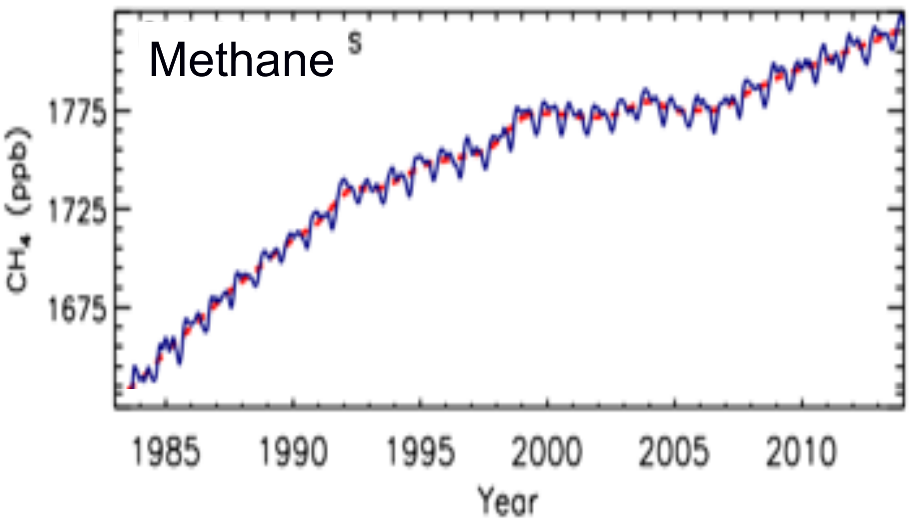
1 ppb = 1 nmol mol^{-1} = 1×10^{-9} mol mol^{-1}

1 ppt = 1 pmol mol^{-1} = 1×10^{-12} mol mol^{-1}

Atmospheric increases of greenhouse gases

Intergovernmental Panel on Climate Change (IPCC), 2014

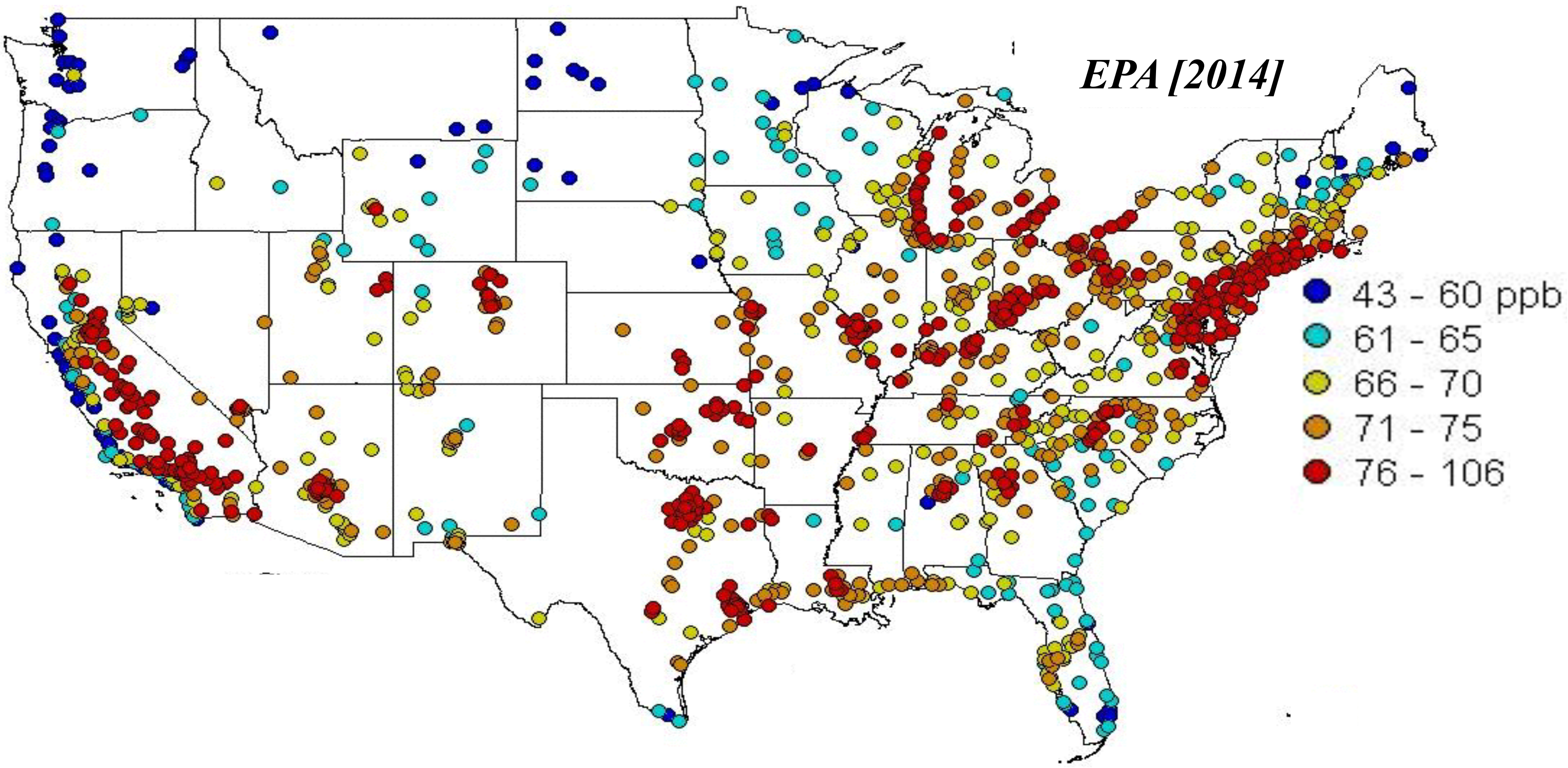




Concentration units: parts per million (ppm) and parts per billion (ppb)

CO_2 and methane concentrations are measured as mixing ratios

4^{th}-highest annual maximum surface ozone, 2010-2012



EPA air quality standard: 70 ppb

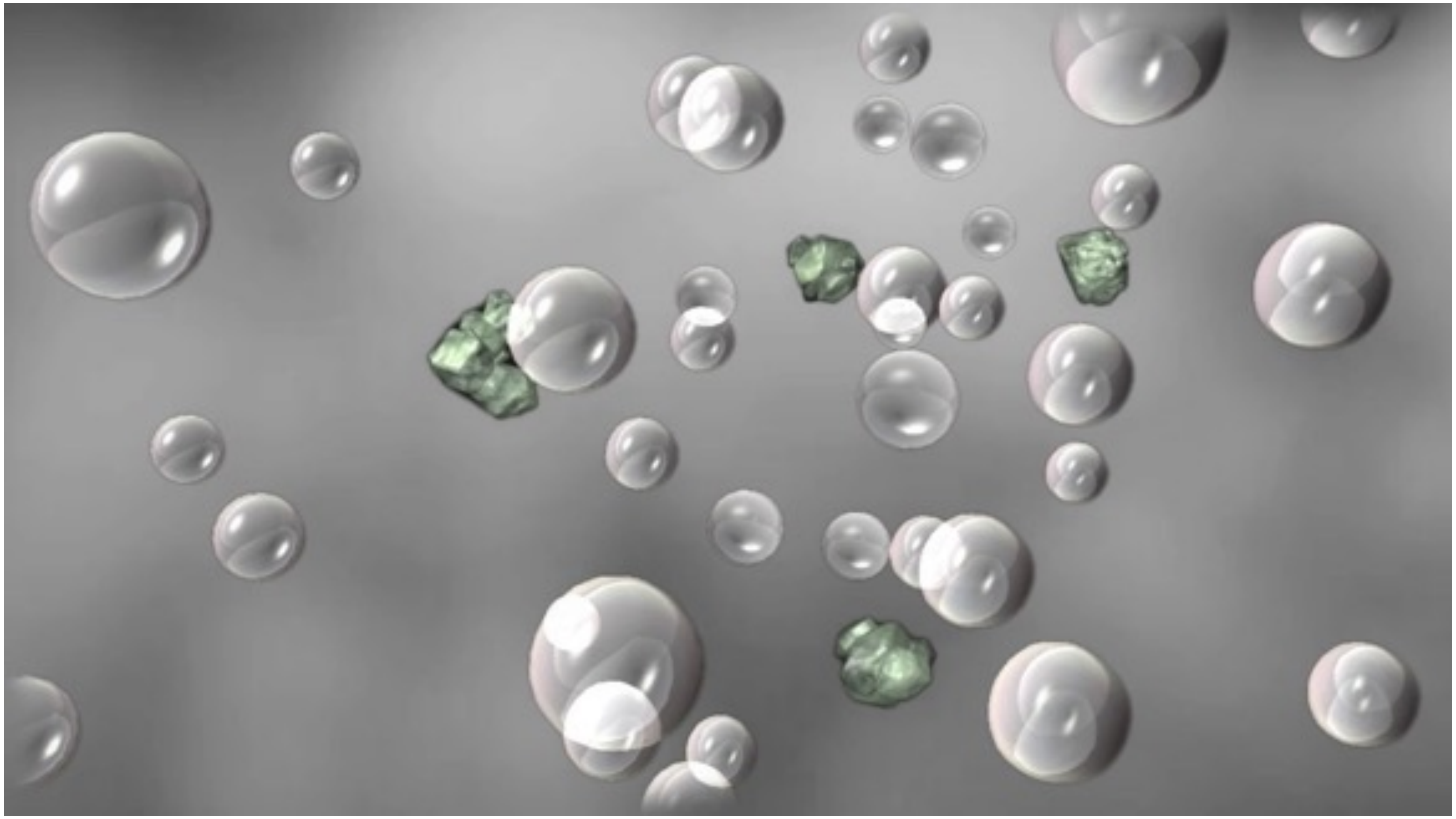
Questions

1. Oxygen has a fixed mixing ratio in the atmosphere. How would you expect its number density measured in surface air to vary between day and night?

1. Give a rough order of magnitude for the number of molecules present in a typical 1 micrometer aerosol particle.

Shape of aerosol particles

- Liquid particles are always spherical (minimizes surface tension)
- Solid particles can have any shape



Absolute concentration as amount per unit volume: general notation [X]

- **Number density n_X [molecules cm^{-3}]**

$$n_X = \frac{\text{\# molecules of X}}{\text{unit volume of air}}$$

Proper measure for
- **reaction rates**
- **optical properties of atmosphere**

$$\text{Column concentration } \Omega_X = \int_0^\infty n_X(z)dz$$

Proper measure for absorption or scattering of radiation by atmosphere

n_X and C_X are related by the ideal gas law:

$$n_X = n_a C_X = \frac{Ap}{RT} C_X$$

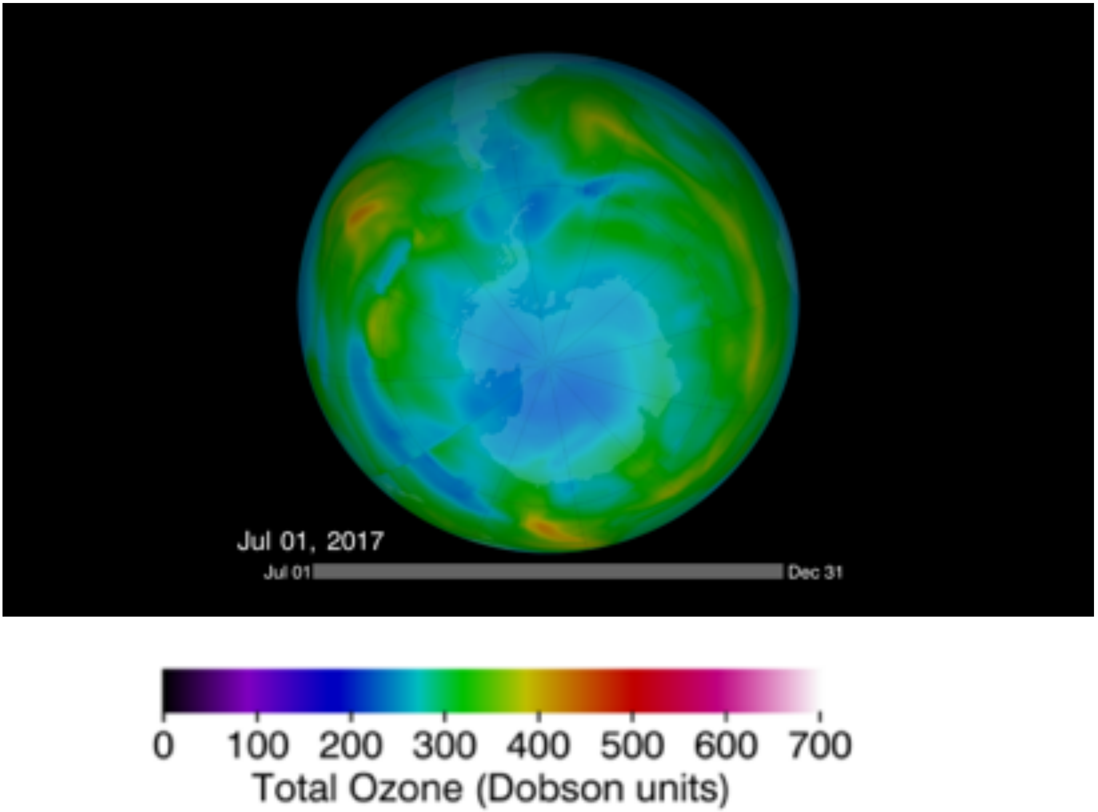
n_a = air number density
A = Avogadro's number
p = pressure
R = Gas constant
T = temperature
M_X = molar mass of X

- **Mass concentration (g cm^{-3}):**

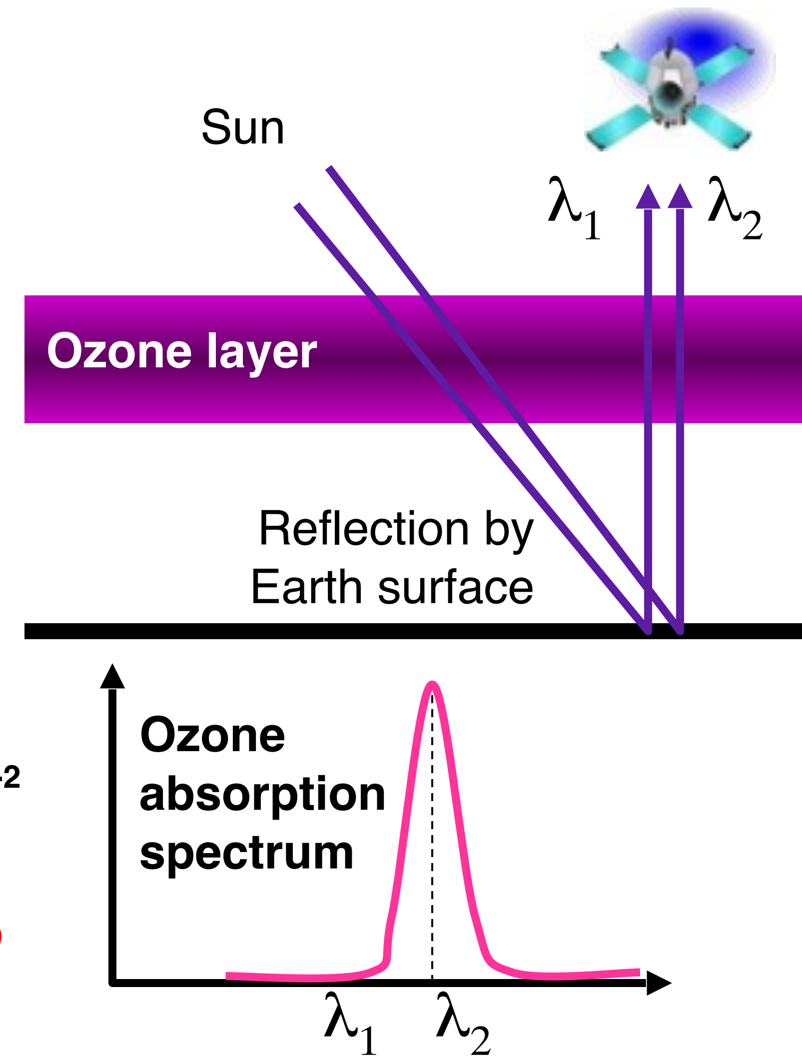
$$\rho_X = \frac{\text{mass of X}}{\text{unit volume of air}} = \frac{M_X n_X}{A}$$

Monitoring the ozone column from satellite

http://ozonewatch.gsfc.nasa.gov/



Method: UV solar backscatter

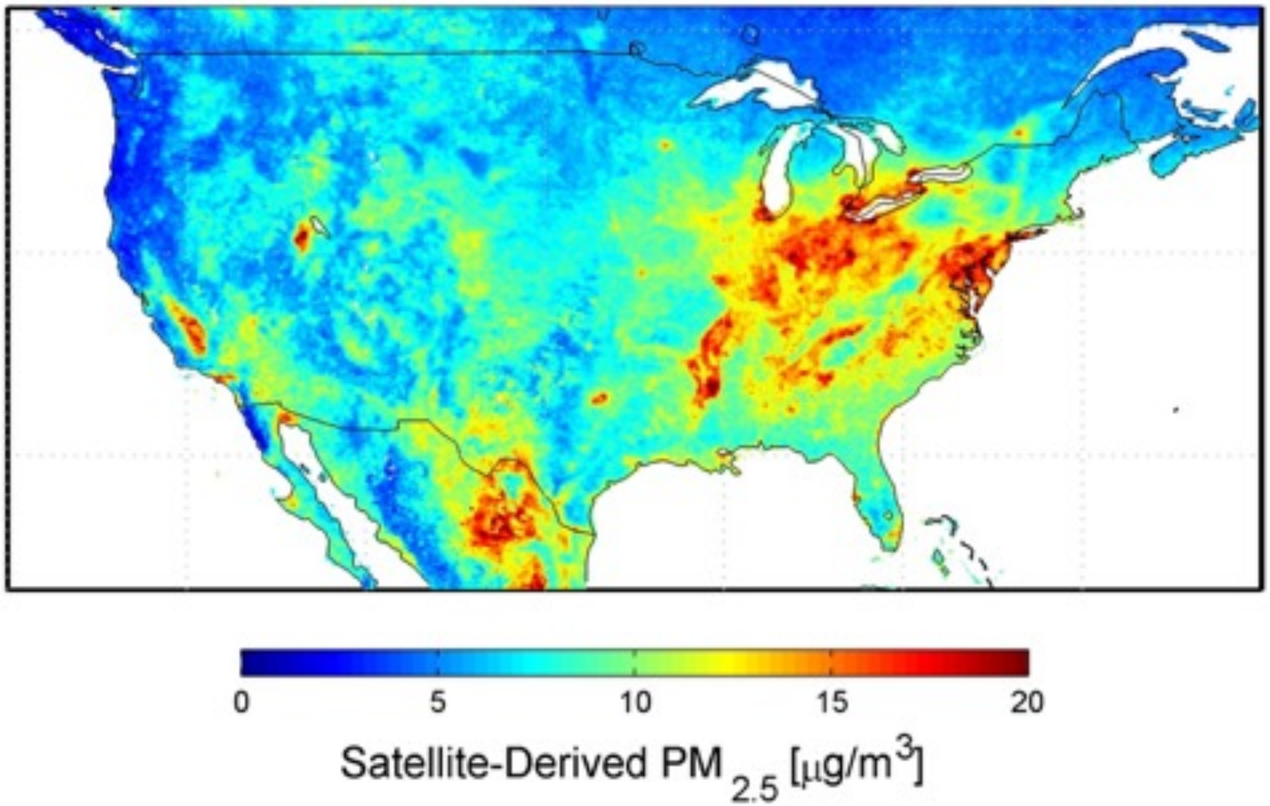


1 "Dobson Unit (DU)" = 2.69×10^{16} molecules cm^{-2}

THICKNESS OF OZONE LAYER IS MEASURED AS A COLUMN CONCENTRATION

Surface concentration of aerosol a.k.a. particulate matter (PM)

$PM_{2.5}$ ≡ concentration of aerosol particles < 2.5 μm diameter



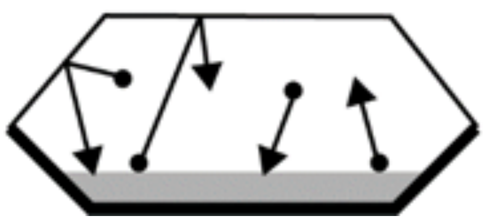
EPA air quality standard: 12 μg m^{-3} (annual mean)

Absolute concentration as partial pressure p_x [Pa]

Dalton's law: $$p_X = C_X p$$ **Proper measure for phase change (such as condensation of water vapor)**

Evaporation of liquid water from a pan:

No lid: water molecules escape from pan to atmosphere (evaporation)



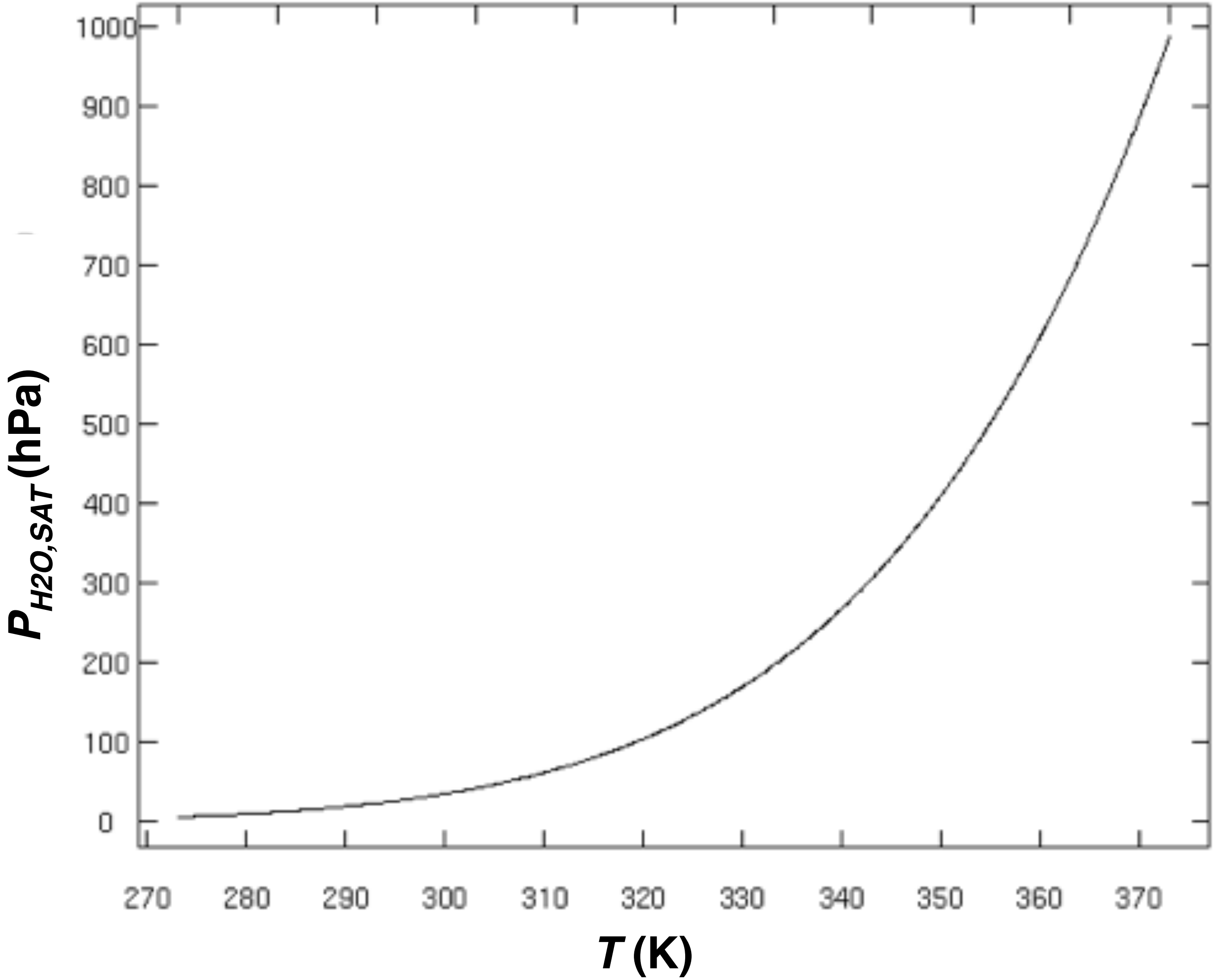
Add a lid:

- **escaping water molecules collide on lid and return to surface; collision rate measures p_{H2O}**
- **eventually, flux escaping = flux returning : saturation ($p_{H2O,SAT}$)**
- $T \nearrow \Rightarrow p_{H2O,SAT} \nearrow$

CLAUSIUS-CLAPEYRON EQUATION: $p_{H2O,\,SAT} = f(T)$

$$p_{H2O,SAT} = A\exp[B(\frac{1}{T} - \frac{1}{T_o})]$$

A = 6.11 hPa
B = - 5310 K
T_o = 273 K



Phase rule of physical chemistry

The number *n* of independent variables determining the equilibrium partitioning of *c* species between *q* phases is given by

$$n = c + 2 - q$$

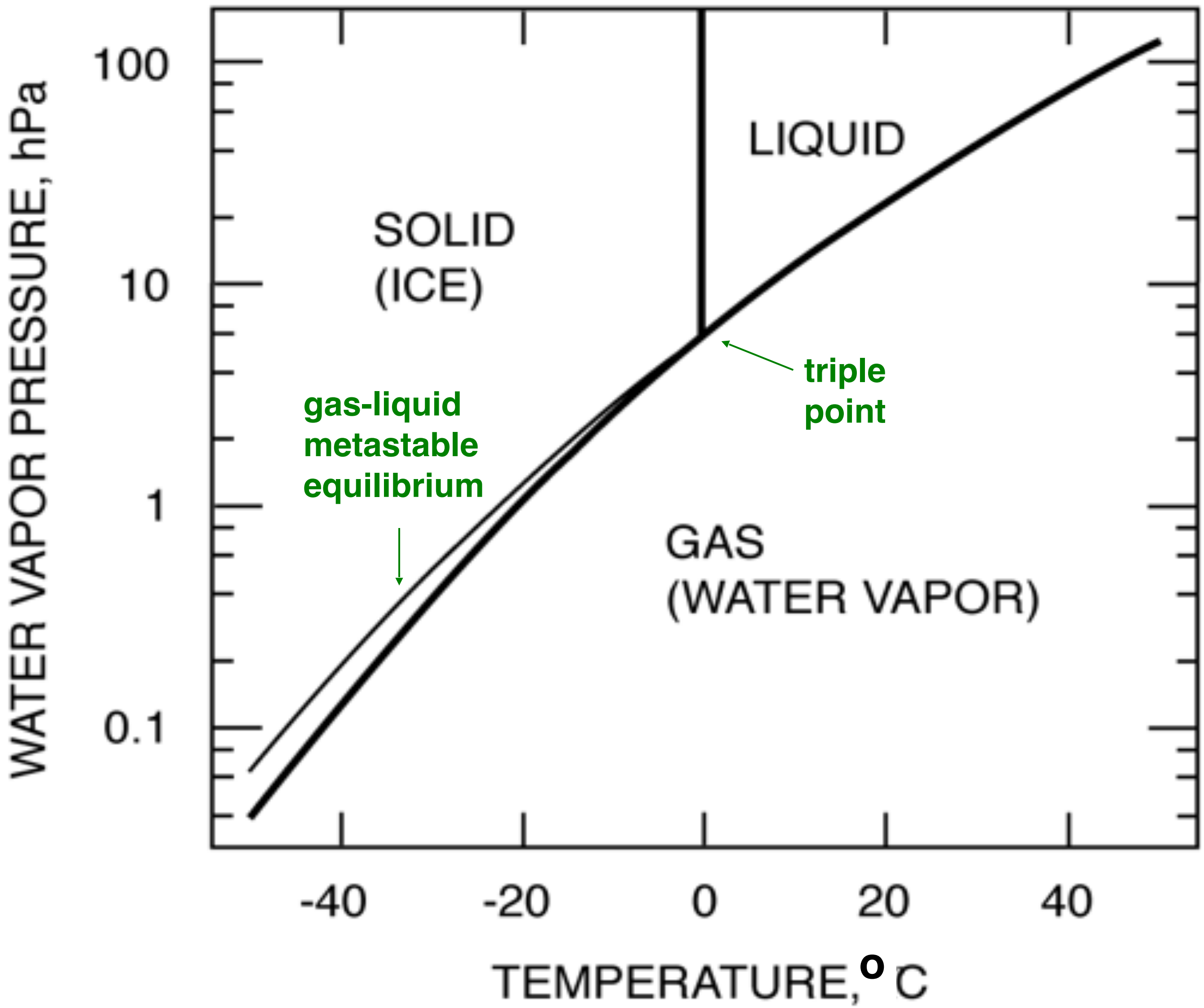
Consider pure H_2O system:

- **One species $\Rightarrow$ $c = 1$**
- **Two variables: p_{H2O} and T**

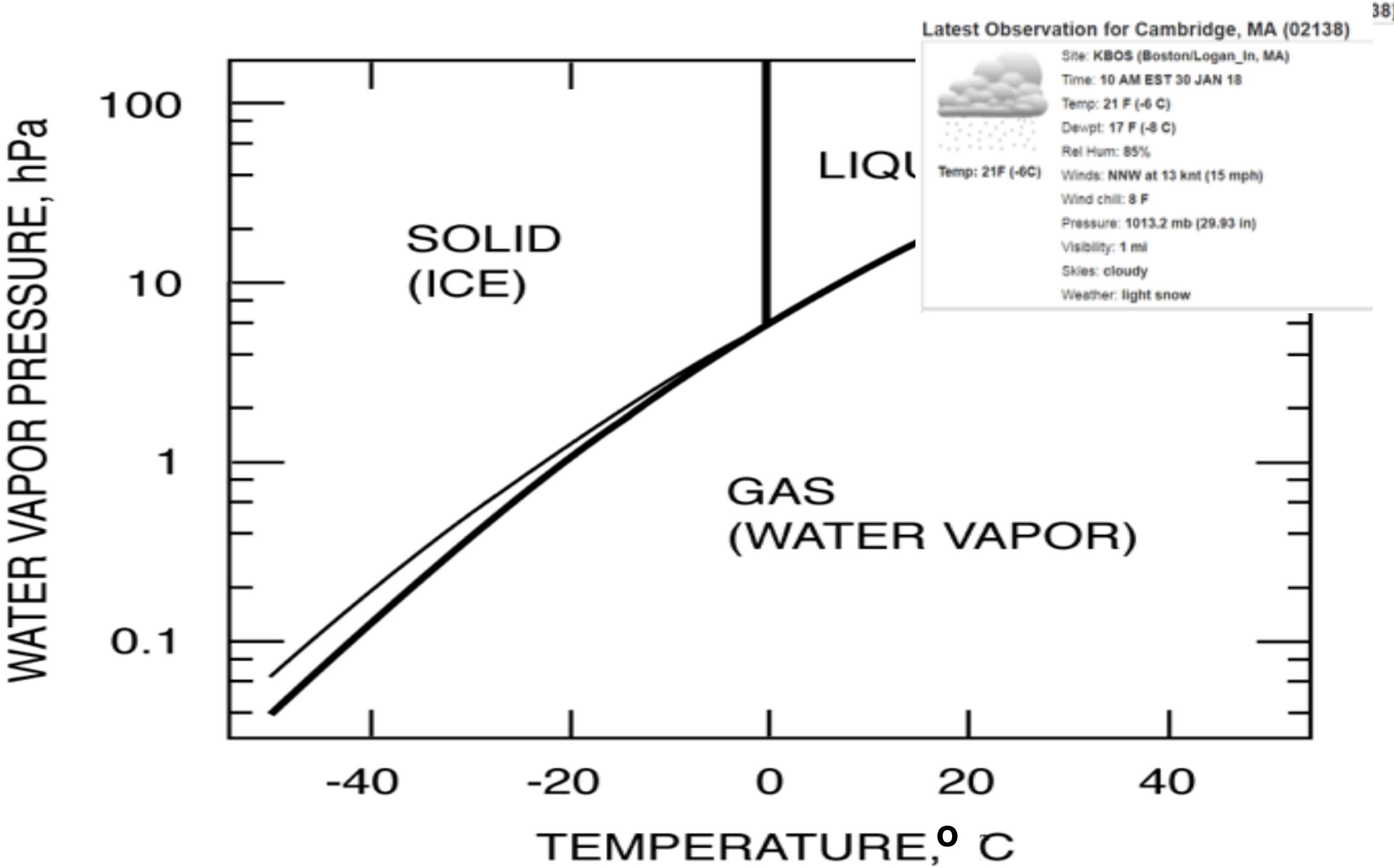
For water vapor at equilibrium with liquid water, $q = 2 \Rightarrow n = 1$

$\Rightarrow$ at given T there is only one p_{H2O} at which you have equilibrium

Phase diagram for water



Working with the phase diagram: current Cambridge weather



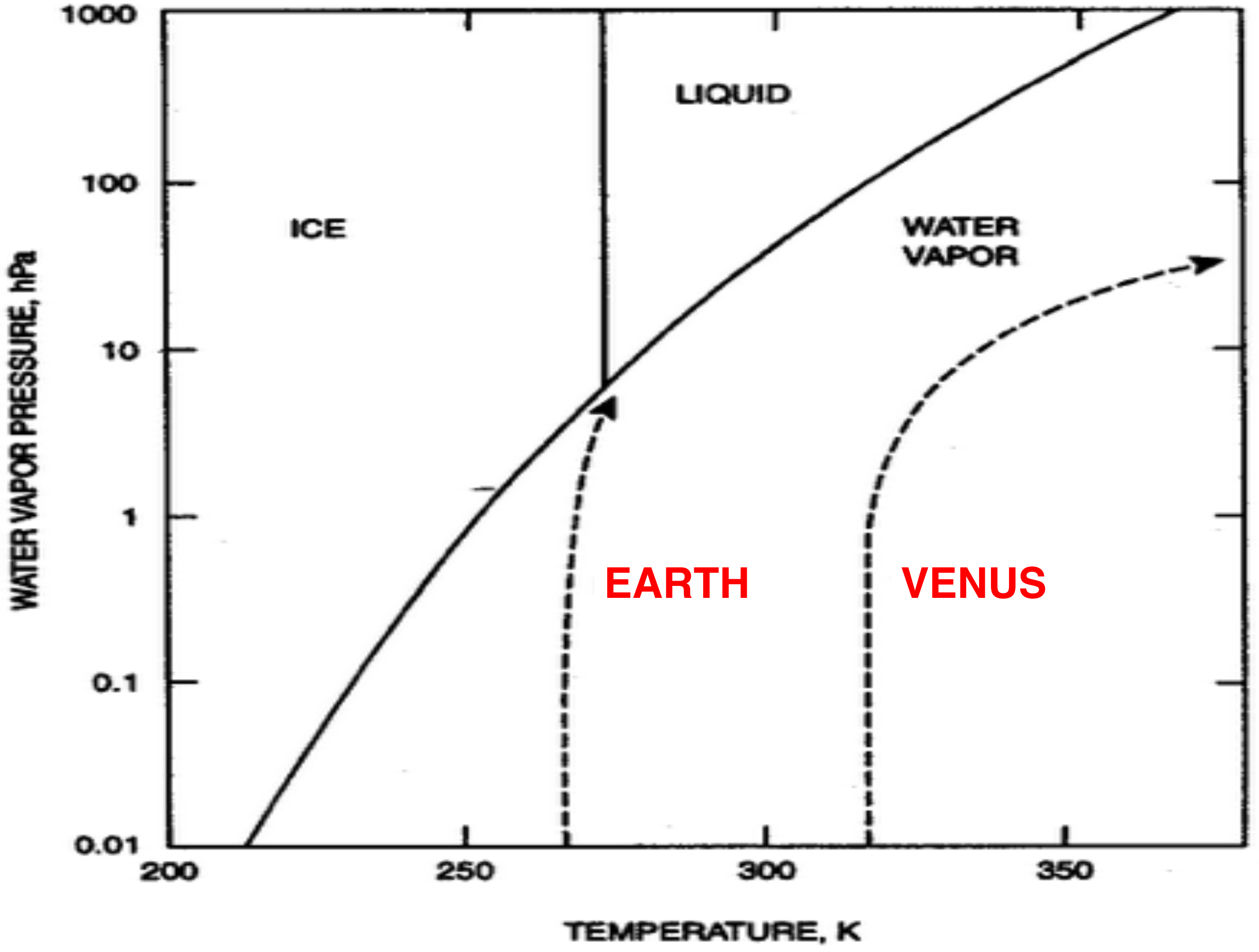
Relative humidity (%) = 100($p_{H2O}/p_{H2O,SAT}$)

Dew point: Temperature T_d such that $p_{H2O} = p_{H2O,SAT}(T_d)$

RUNAWAY GREENHOUSE EFFECT ON VENUS

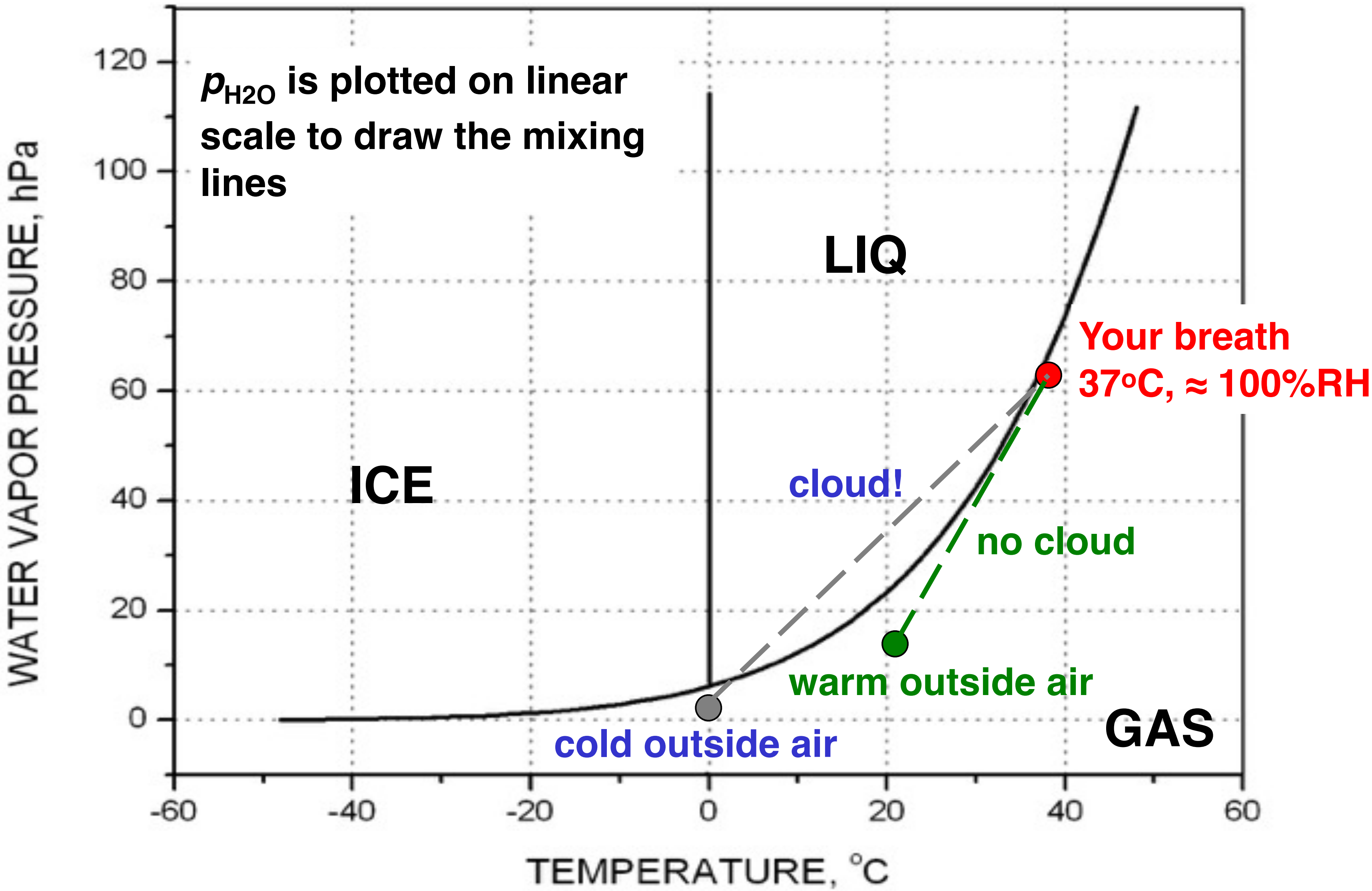
due to accumulation of water vapor from volcanic outgassing early in its history

…did not happen on Earth because farther from Sun; as water accumulated it reached saturation and precipitated, forming the oceans



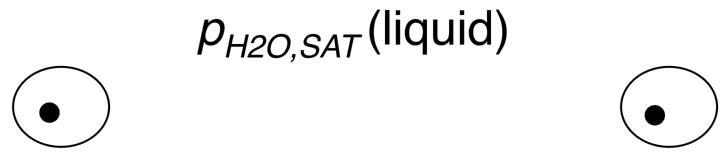
WHY CAN YOU SEE YOUR BREATH ON COLD MORNINGS?

Draw mixing lines (dashed) to describe dilution of your breath plume w/outside air

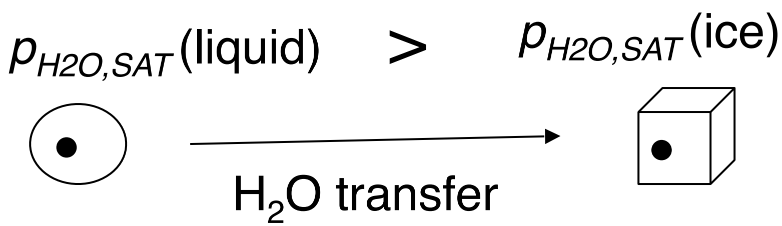


Precipitation induced by cloud freezing

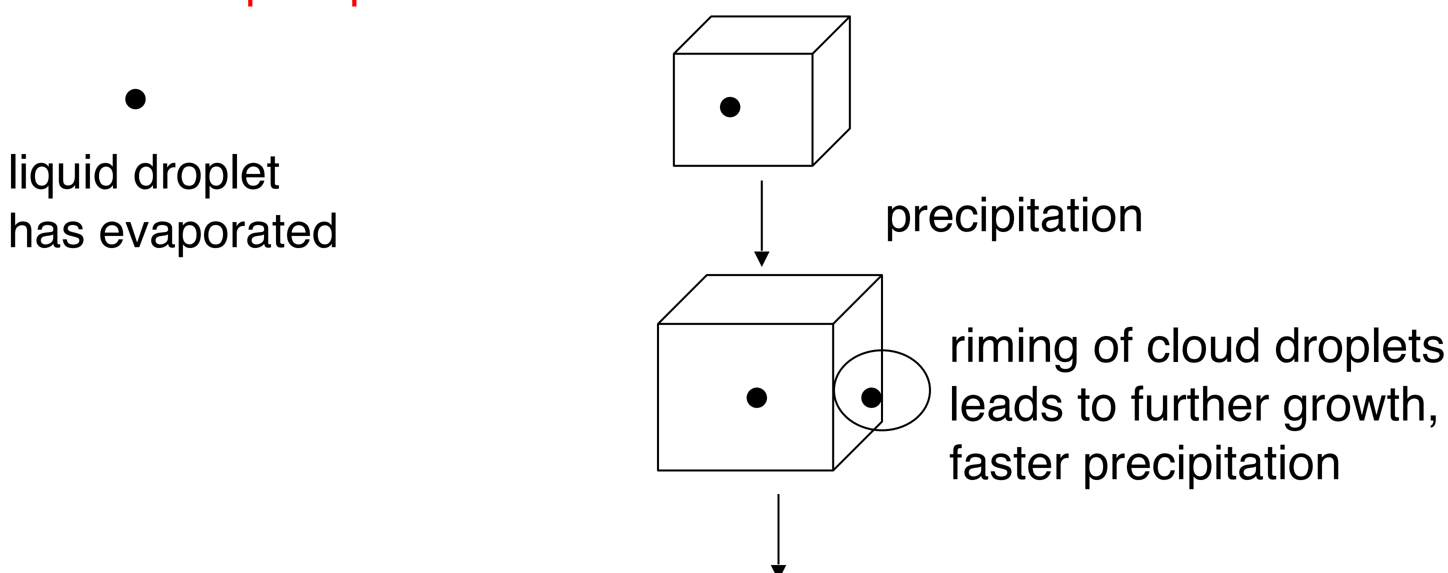
1. Liquid cloud at temperature < 0 °C



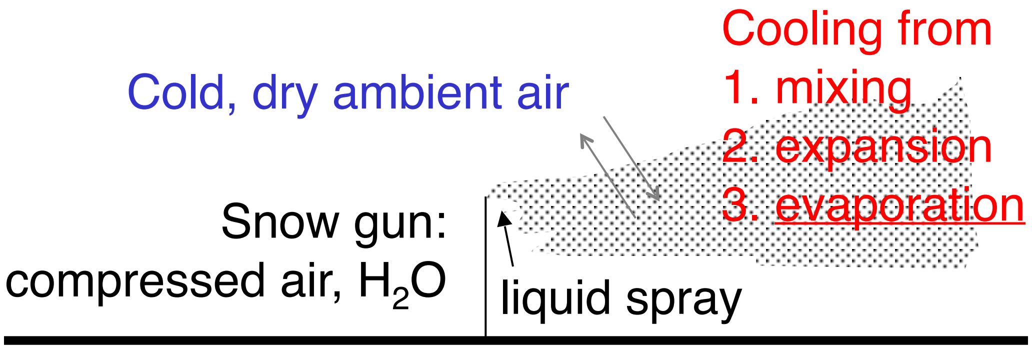
2. A few droplets freeze and grow at expense of the liquid droplets



3. Ice crystal growth results in precipitation



The science of snowmaking



SWISS VALLEY SKI AREA SNOWMAKING TEMPERATURE GUIDE

AIR TEMP °F	% RELATIVE HUMIDITY 20%	30%	40%	50%	60%	70%	80%	90%	100%	SNOW QUALITY
	WET BULB TEMPERATURE °F									IDEAL / POOR / FORGET IT!
14.0	9.9	10.4	10.9	11.5	12.0	12.4	12.9	13.5	14.0	IDEAL SNOWMAKING CONDITIONS
15.8	11.3	11.8	12.4	12.9	13.5	14.0	14.7	15.3	15.8	
17.6	12.7	13.3	13.8	14.5	15.1	15.8	16.3	16.9	17.6	
19.4	14.0	14.7	15.4	16.0	16.7	17.4	18.0	18.7	19.4	
21.2	15.4	16.2	16.9	17.6	18.3	19.0	19.8	20.5	21.2	
23.0	16.9	17.6	18.3	19.0	19.9	20.7	21.4	22.3	23.0	MARGINAL SNOWMAKING CONDITIONS
24.8	18.2	19.0	19.8	20.7	21.6	22.3	23.2	23.9	24.8	
26.6	19.6	20.5	21.4	22.1	23.0	23.9	24.8	25.7	26.6	
28.4	20.8	21.9	22.8	23.7	24.6	25.5	16.6	27.5	28.4	
30.2	22.3	23.4	24.3	25.3	26.2	27.3	28.3	29.3	30.2	FORGET ABOUT IT GET OUT THE BIKE!
32.0	23.7	24.6	25.7	26.8	27.9	28.9	30.0	30.9	32.0	
33.8	25.0	26.1	27.3	28.4	29.5	30.6	31.6	32.7	33.8	
35.6	26.4	27.5	28.8	29.8	31.1	32.2	33.3	34.5	35.6	
37.4	27.9	28.9	30.2	31.5	32.5	33.8	35.1	36.7	37.4	
39.2	29.1	30.4	31.6	32.9	34.2	35.4	36.7	37.9	39.2	
41.0	30.6	31.8	33.1	34.5	35.8	37.0	38.5	39.7	41.0	
42.8	31.8	33.3	34.7	36.0	37.4	38.8	40.1	41.5	42.8	

AIR POLLUTION HAZE

Views of Acadia National Park

http://www.hazecam.net/

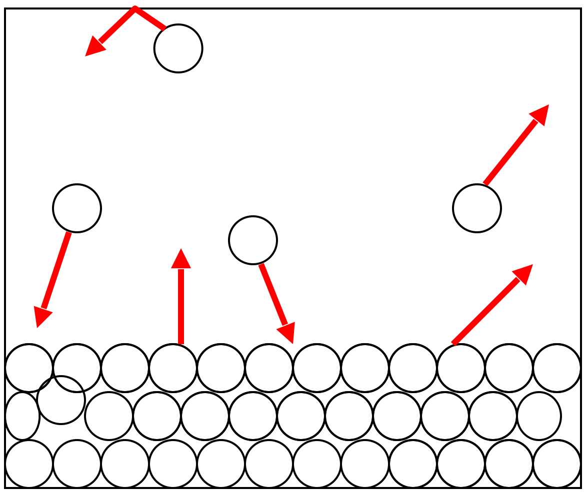
"clean" day

"moderately polluted" day

Visibility is limited by high concentrations of aerosol particles that have swollen to large sizes due to high (but <100%) relative humidity

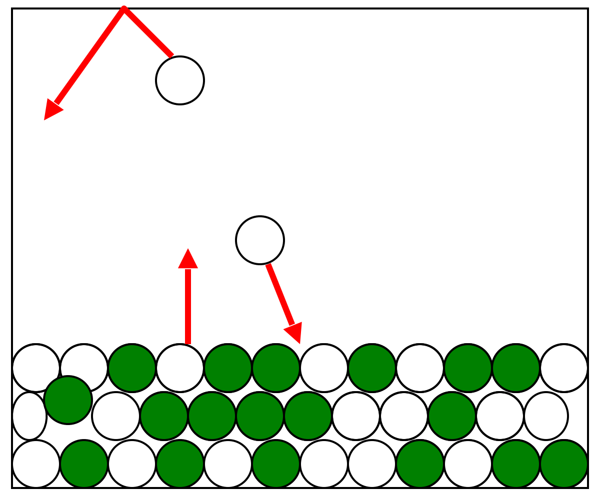
RAOULT'S LAW

$$p^{o}_{H2O,SAT}$$



water saturation vapor pressure over pure liquid water surface

$$p_{H2O,SAT} = x_{H2O}\, p^{o}_{H2O,SAT}$$



solute molecules in green

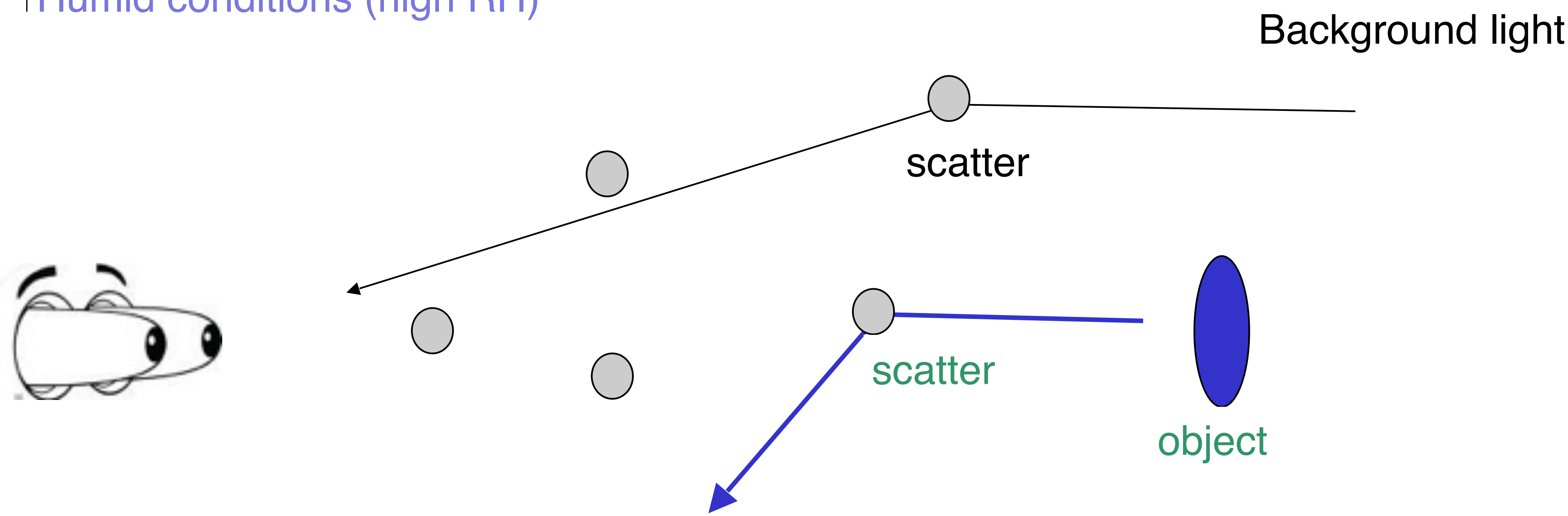
water saturation vapor pressure over aqueous solution of water mixing ratio x_{H2O}

An atmosphere of relative humidity *RH* can contain at equilibrium aqueous solution particles of water mixing ratio

$$x_{H2O} = \frac{p_{H2O,SAT}}{p^{o}_{H2O,SAT}} = \frac{RH}{100}$$

Visibility decrease under hazy (humid) conditions

Humid conditions (high RH)



As particles swell by taking up water, their cross-section for scattering background and object light increase

Questions

1. In an atmosphere with fixed mixing ratio of water vapor, what two processes can cause an increase in relative humidity?

2. At a given temperature below freezing, and for a given total amount of water in an air parcel, will a cloud contain more condensed water if it is liquid or solid?