

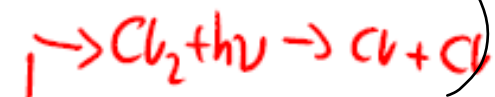
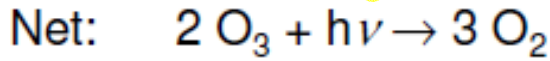
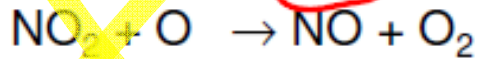
Stratospheric Chemistry in a nutshell III:

Polar Ozone Chemistry: Examples of Catalytic Cycles

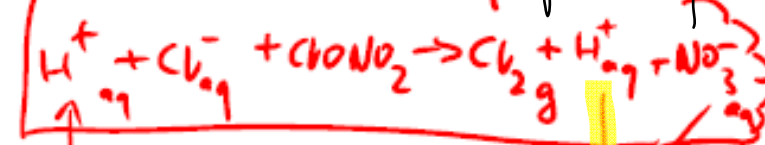
Fasman et al. 1985 → Entdeckung des O₃-Lochs



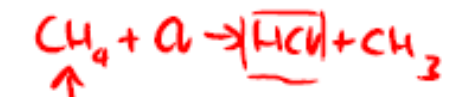
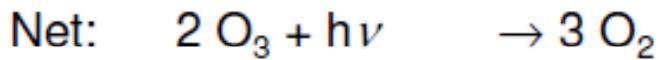
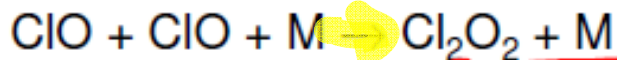
1970 Crutzen



PSC
Solomon et al. 1986: heterog. chemie



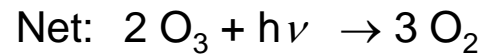
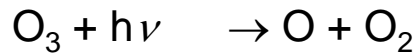
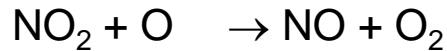
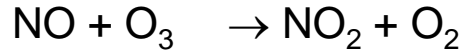
1988 Molina & Molina



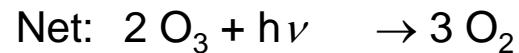
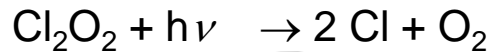
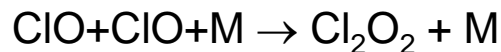
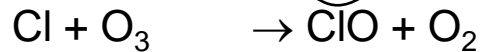
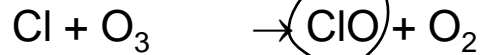
Denitrifizierung

Stratospheric Chemistry in a nutshell IV: Polar Ozone Chemistry (cont')

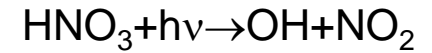
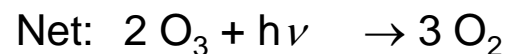
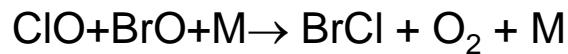
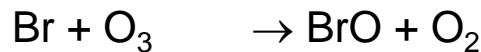
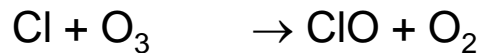
1970 Crutzen



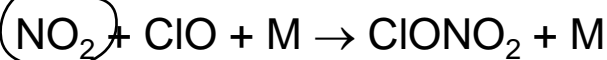
1974 Molina & Molina



1992 McElroy et al.: Halone (Fanzlöcher)

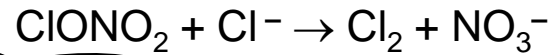


Deactivation



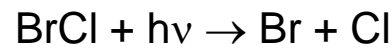
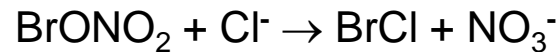
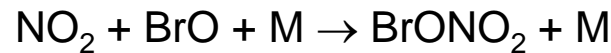
Activation

PSC



200-mal
weniger Br in
Strat. als Cl

No efficient deactivation

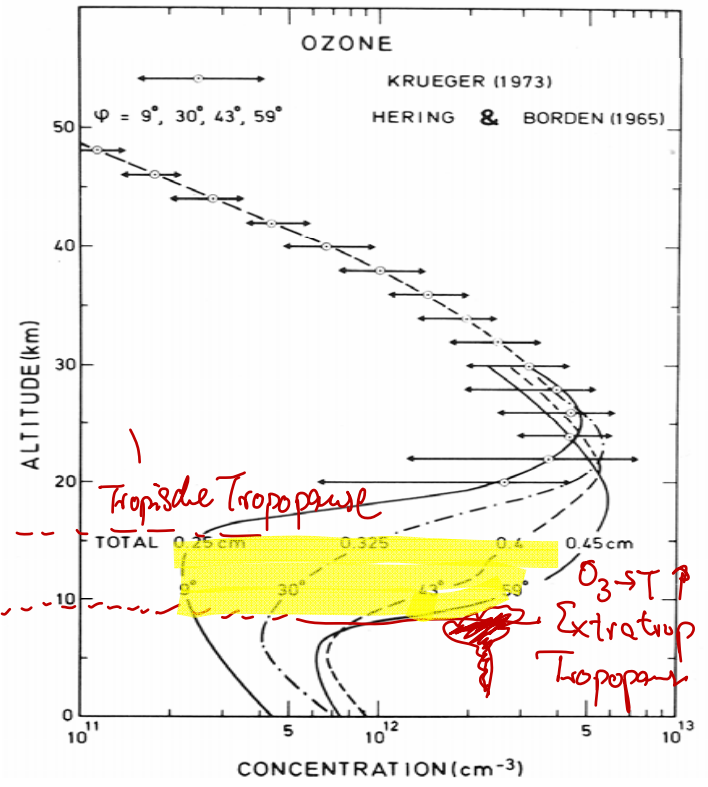
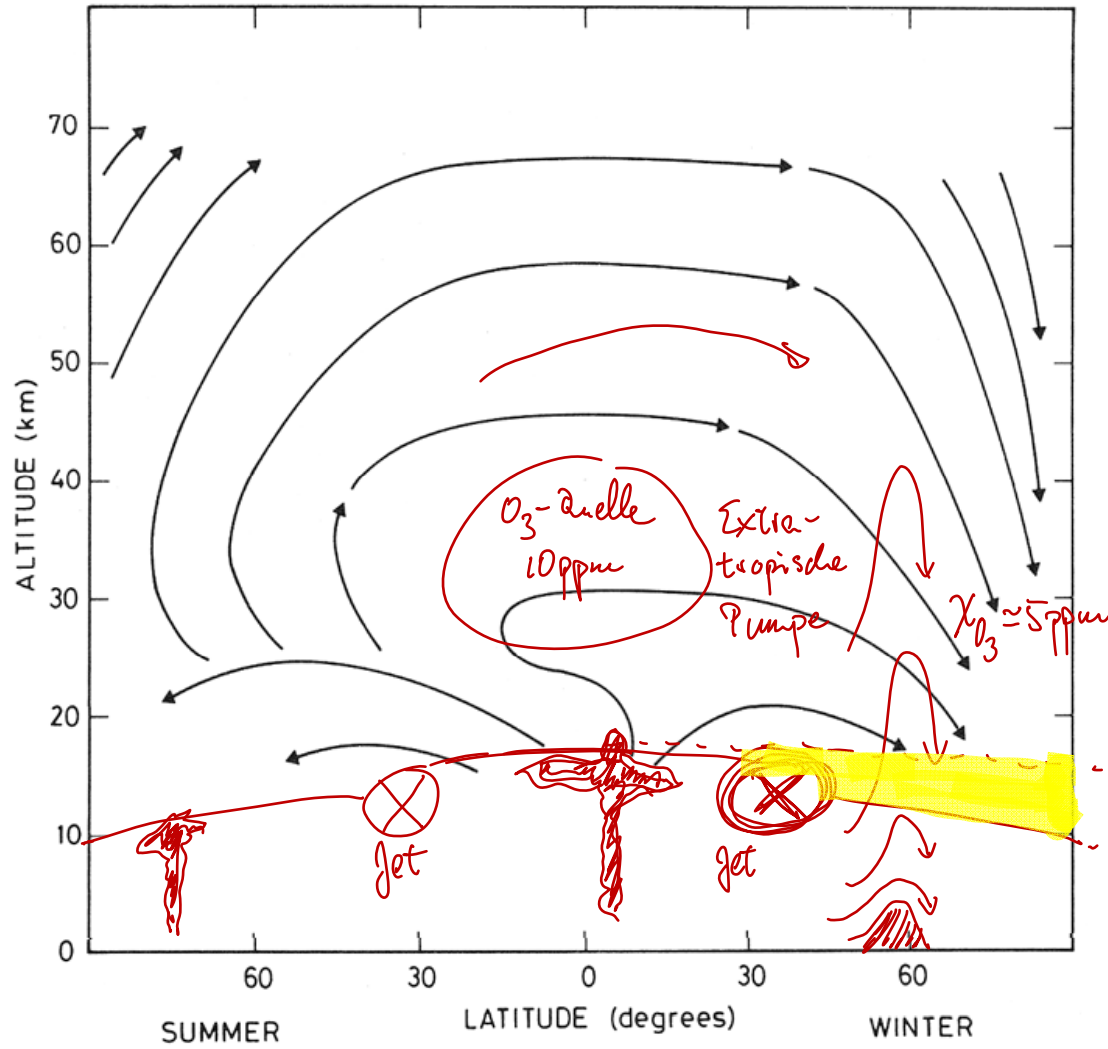


Pro Molekül zerstört Br ca. 60x effizienter
Ozon als Cl

Polar Ozone Chemistry

- In polar regions the destruction of ozone by chlorine species is dominated by formation of Cl_2O_2 dimer, which releases Cl when being photolysed
- Different to mid-latitudes, in presence of sun-light Cl can be rapidly re-activated from the reservoir species ClONO_2 on Polar Stratospheric Clouds (PSCs).
- In presence of temperatures cold enough to form PSCs (typically within the polar vortex in the Winter hemisphere) and of sunlight, polar ozone is most rapidly depleted during the Hemispheric spring (i.e. the time when the sun first reaches the polar stratosphere) → these conditions are required to form the annual observable Antarctic ozone hole
- The re-activation of Cl out of chlorine nitrate leads to ice particles with nitrate. When temperatures are warm enough HNO_3 is evaporating and photolysed to take part again in the NO_x destruction cycle. Yet, at cold temperatures the ice/ HNO_3 particles coagulate by water-uptake. When they are large enough they sediment leading to a permanent NO_x removal. This denitrification slows down the NO_x destruction cycle and enhances the dominance of the ClO_x and BrO_x cycles since the deactivation reactions (reaction with NO_2) are less active.
- Other catalytic cycles are important as well, including reactions with bromine.

The Ozone Layer: meridional and seasonal aspects



The Ozone Layer: meridional and seasonal aspects

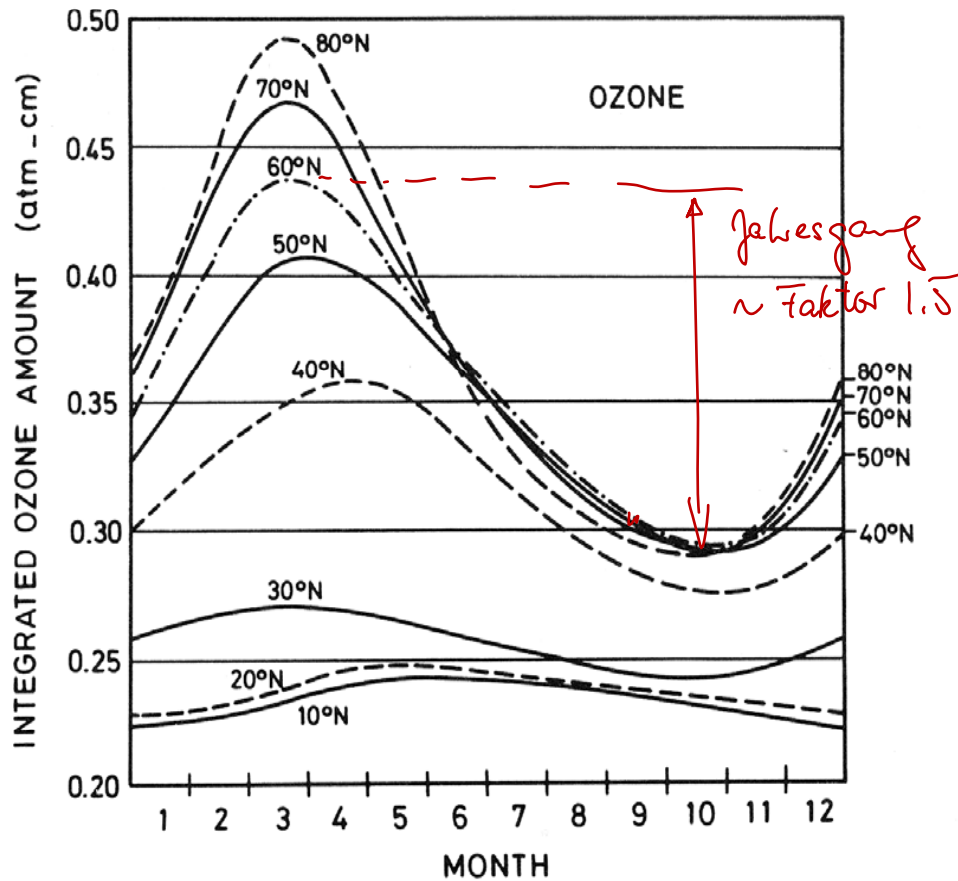
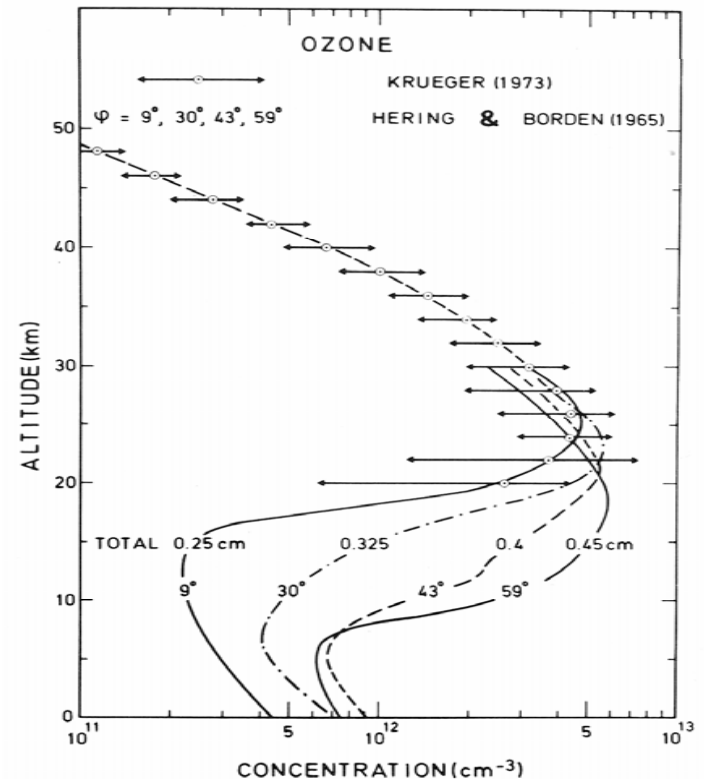


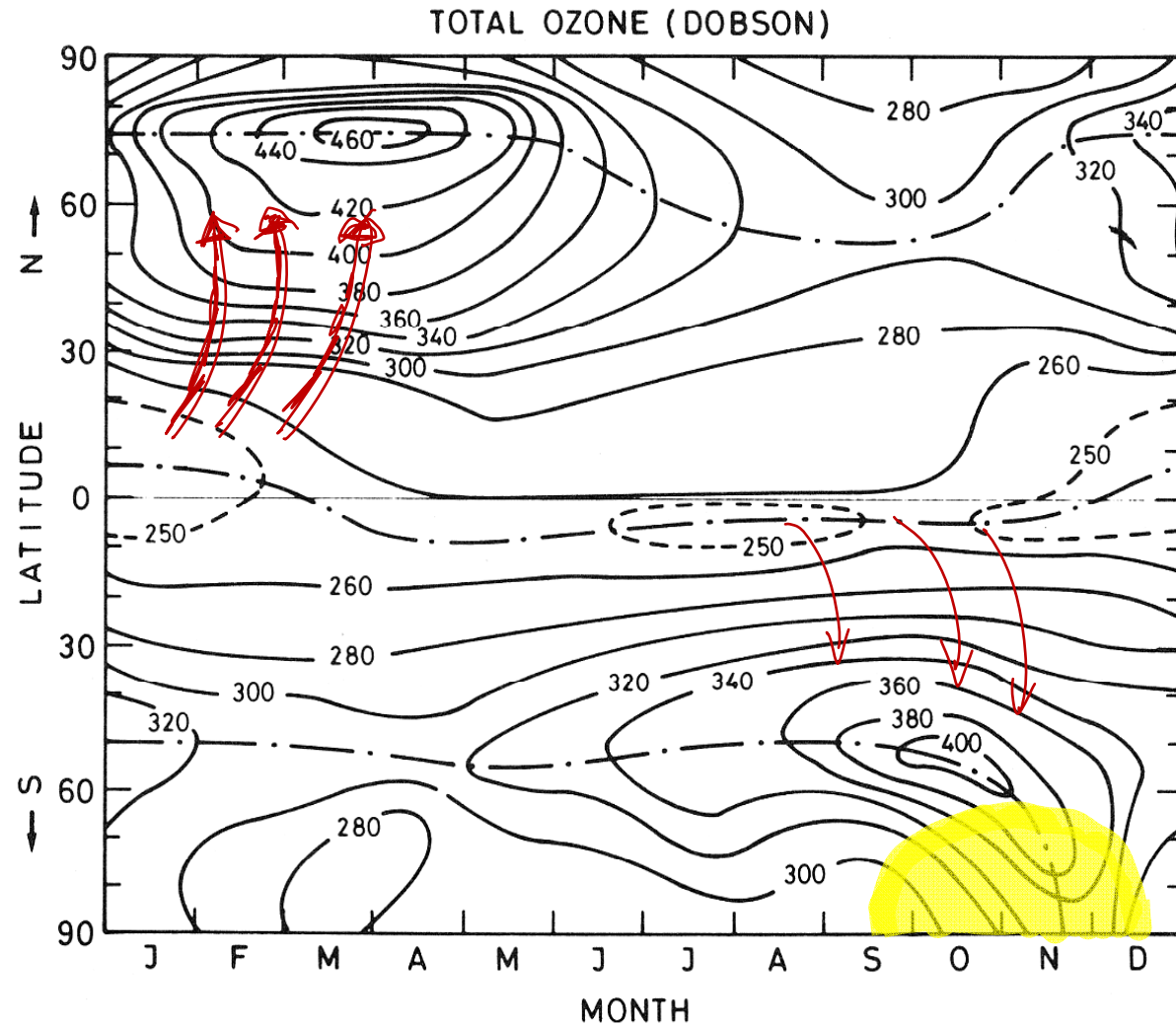
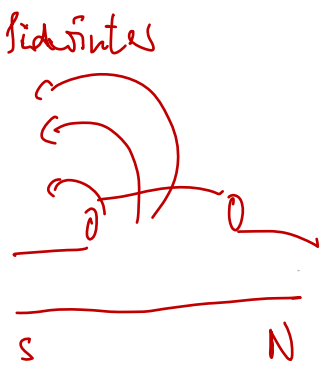
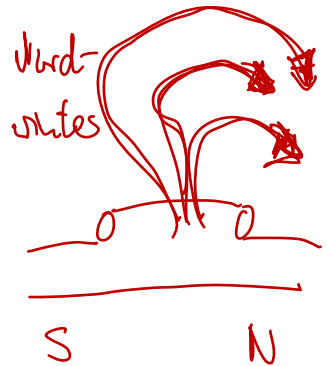
Fig. 5.5. Mean trend of the total ozone abundance during the year at different latitudes in the northern hemisphere. From Dobson (1968). (Copyright by Clarendon Press).



Ozone climatology and seasonal cycle

- Highest mixing ratios can be found in the lower stratosphere in the Tropics for all seasons.
- Brewer-Dobson-Circulation increases ozone mixing ratios at the winter pole in the middle stratosphere. In the lower stratosphere ozone decreases.
- This can also be observed for individual stations (e.g. Payerne). The increase at the surface in summer months is due to photochemical chemistry (see tropospheric chemistry).

O₃-Klimatologie (London 1980)



Extretrop.
 Pumpe
 (Wellenantrieb)
 ist effizienter
 nach Norden
 als nach
 Süden
 (=> Berge,
 Land-Wasser-
 Verteilung)

Fig. 5.6. Variation of total ozone with latitude and season. From London (1980).

Total Ozone Climatology

- The climatology by London (1980) represents the mean state for the pre-ozone hole period. Today's values are much more reduced, especially in the spring hemisphere. In the Southern Hemisphere the Antarctic ozone hole develops where minimum values as low as 100 DU are observed.
- Due to the Brewer-Dobson-Circulation (residual circulation with ascending branch over the Tropics, transport towards Winter Pole and descending branch over the Winter Pole) the seasonal variation of Total Ozone is largest at the Poles whereas at the Tropics this remains almost constant throughout the year.
- The biggest variations among northern/southern high latitudes occur for spring, where Total Ozone climatology shows a very steep meridional gradient. Over the Arctic the descending transport of air masses is larger than over the Antarctic. Hence the maximum of total ozone values (in spring) in the northern high latitudes exceeds those in the Southern Hemisphere

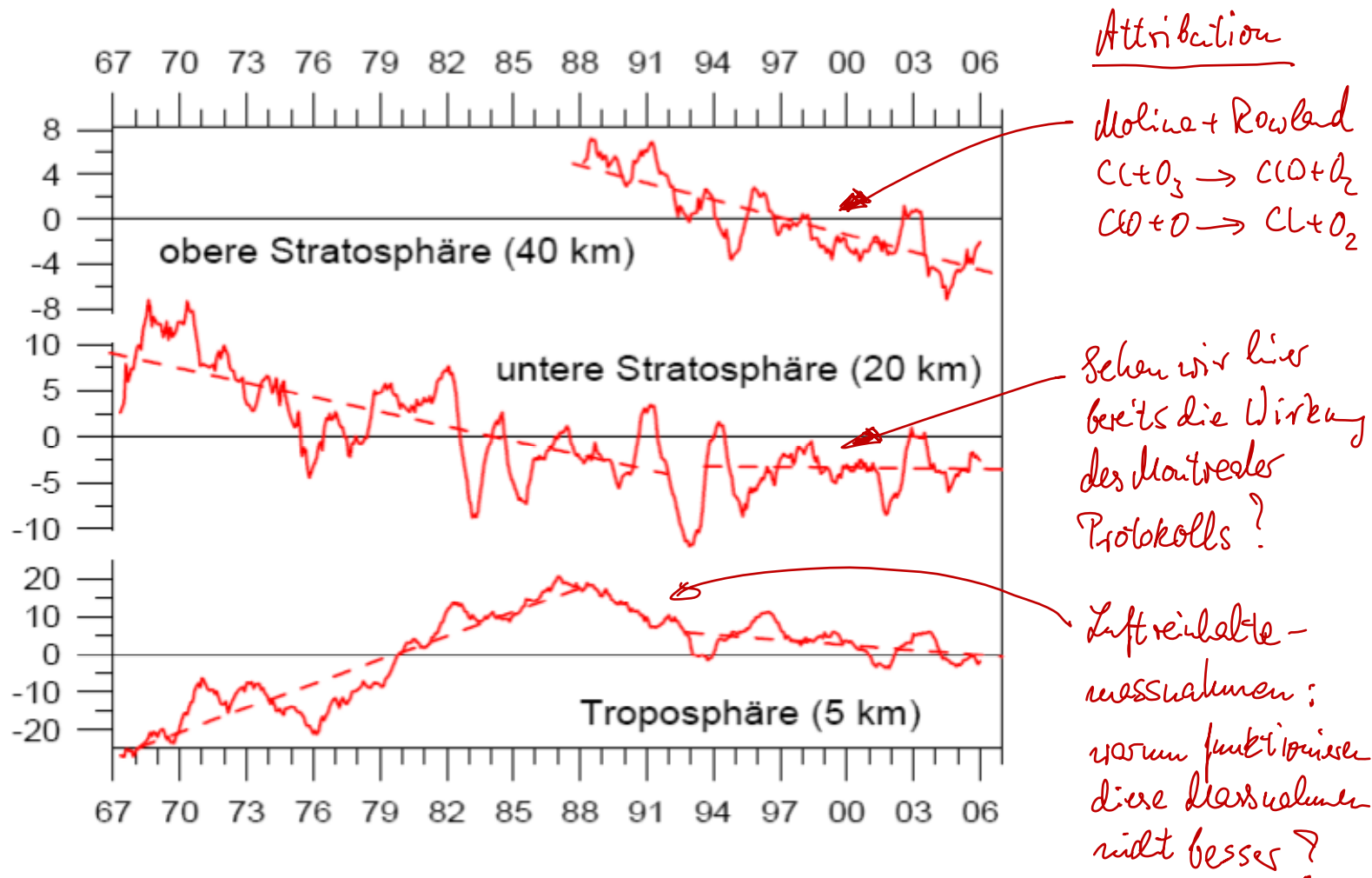


Abb. 3: Prozentuale Ozonabweichung für drei ausgewählte Höhenbereiche über Hohenpeißenberg, gemessen durch Ballonsonden (5 und 20km) und Laser-Radar (40km). Die Abweichungen wurden durch Subtraktion der Monatsmittel von den Langzeit-Monatsmitteln ermittelt und geglättet (13-monatiges, gleitendes Mittel).

Natürliches

Stratosphärisches NO_x :

① Blitze \rightarrow geringer Beitrag

② Böden \rightarrow $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$
Verbrenung $\text{M} + \text{NO}_2 + \text{OH} \rightarrow \text{HNO}_3 + \text{M}$ } fast kein Beitrag
Auswaschen

③ $\text{N}_2\text{O} + h\nu \rightarrow \text{N}_2 + \text{O}$

$\text{N}_2\text{O} + \text{O}(\text{^1D}) \rightarrow \text{NO} + \text{NO}$ \leftarrow Hauptquelle stratos. NO_x
oder $\rightarrow \text{N}_2 + \text{O}_2$

Natürliches stratos. ClO_x :

