Review of Atmospheric Ozone Basics

Composition of Air

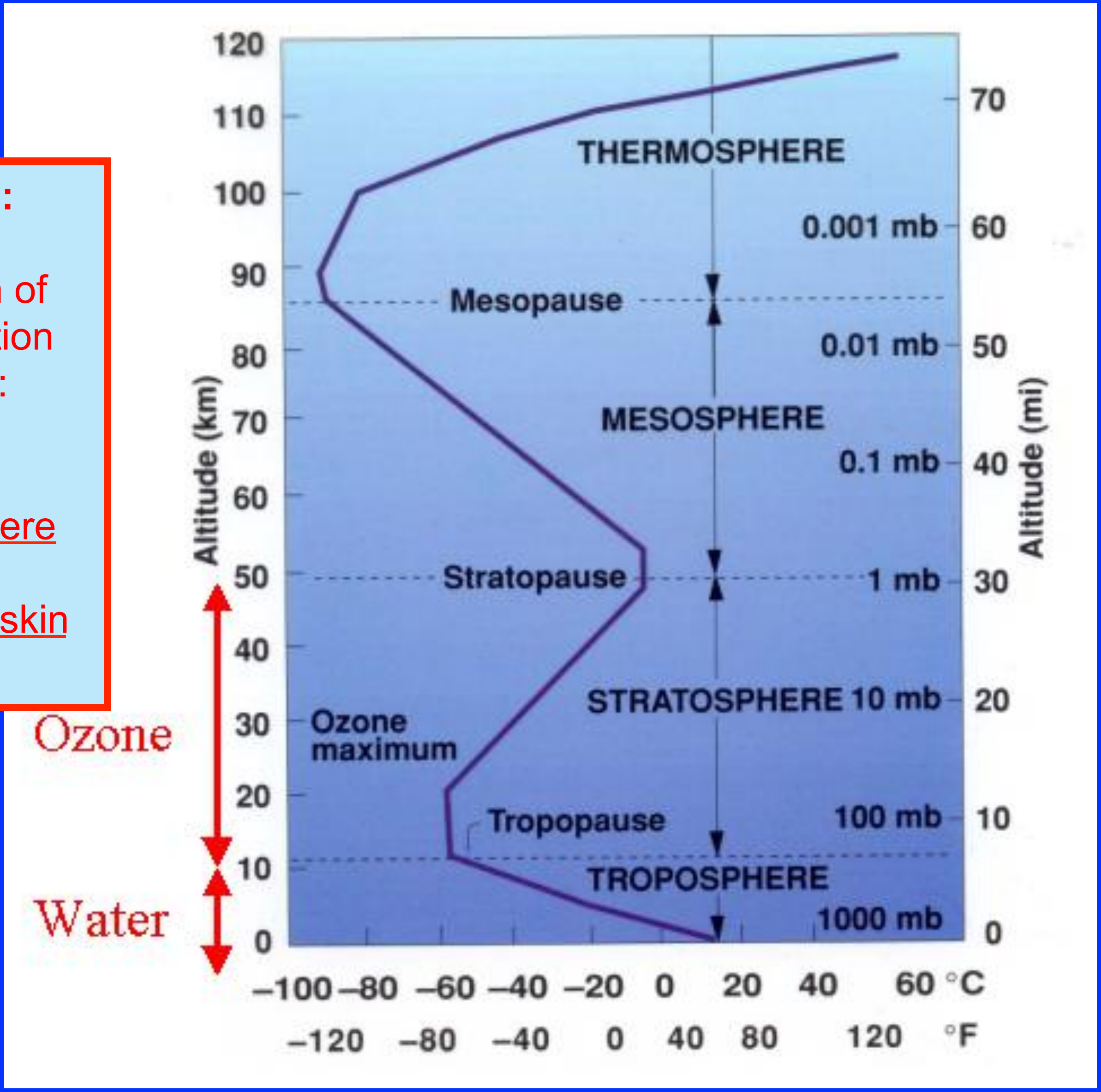
Permanent Gases			Variable Gases			
Gas	Symbol	Percent (by Volume) Dry Air	Gas (and Particles)	Symbol	Percent (by Volume)	Parts per Million (ppm)
Nitrogen	N_2	78.08	Water vapor	H_2O	0 to 4	
Oxygen	O_2	20.95	Carbon dioxide	CO_2	0.036	360
Argon	Ar	0.93	Methane	CH_4	0.00017	1.7
Neon	Ne	0.0018	Nitrous oxide	N_2O	0.00003	0.3
Helium	He	0.0005	Ozone	O_3	0.000004	0.04
Hydrogen	H_2	0.00006	Particles (dust, soot, etc.)		0.000001	0.01–0.15
Xenon	Xe	0.000009	Chlorofluorocarbons (CFCs)		0.00000002	0.0002

RECALL--Layers of the Atmosphere

NOTE:

Absorption of UV radiation by ozone:

- causes stratosphere
- prevents skin cancer



The Ozone Hole Story

The Ozone Hole:
A Story of Dynamics, Clouds and Chemistry

Ozone in the stratosphere is important because it absorbs ultraviolet radiation at wavelengths less than 0.3 µm. This short wavelength radiation can break apart organic molecules. Ultraviolet radiation can damage animals and plants and cause skin cancer in humans. Additionally, the absorption of energy by ozone warms the stratosphere. The warming creates a warm layer above a cold layer making the stratosphere stably stratified. The stable stratification of the stratosphere inhibits vertical mixing and helps create conditions for horizontal transport of materials over large distances in the direction from the equator to the poles (Figure 1).

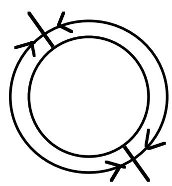


Figure 1. Equator to pole transport in the stratosphere

Ozone is produced by a set of photochemical reactions. The following reactions reach a steady state in the stratosphere. (Notes: M is a catalyst that removes energy from the system. Typically M is a N_2 molecule. $h\nu$ represents a photon.)

$O_2 + h\nu \rightarrow O + O$ absorbs radiation between 0.18 - 0.24 µm

$O + O_2 + M \rightarrow O_3 + M$

$O_3 + h\nu \rightarrow O_2 + O$ absorbs radiation between 0.20 - 0.30 µm

$O + O_3 \rightarrow O_2 + O_2$

The more photons are available, the more ozone is produced. Thus most of the ozone in the stratosphere is produced in the tropics. However, measurements indicate that the highest concentrations of ozone are at high latitudes. Stratospheric ozone is produced at the equator and is transported to the poles.

In the mid 1970's, it was discovered that chlorofluorocarbons (CFCs) and chlorofluoromethanes (CFMs) can trigger runaway destruction of ozone. CFCs and CFMs can yield Cl by photodissociation. Cl can react with O_3 to produce ClO. Cl and ClO are key catalyst molecules in a set of reactions that destroy ozone.

$ClO + O \rightarrow Cl + O_2$

net reaction: $Cl + O_3 \rightarrow ClO + O_2$

$O + O_3 \rightarrow O_2 + O_2$

These reactions are able to occur repetitively because of a unique combination of factors that prevail during the Antarctic winter and early spring. Since 1976, measurements taken over the south pole have shown a decline in ozone concentration during October, the southern hemisphere early spring.

During the Antarctic winter, it is dark for several months. A circumpolar current of air called the polar vortex isolates the air over the south pole by blocking the usual equator to pole transport in the stratosphere. When these conditions prevail no ozone is produced and none can be transported in. Additionally, it is particularly cold (190 ^oK) in the stratosphere over the south pole during the winter. A special type of ice clouds, called Polar Stratospheric Clouds, (PSC's) forms. The ice particles that make up the PSC's are sites for reactions that release Cl_2 and tie up NO_2. NO_2 is important since it can react with Cl and ClO and thus prevent them from reacting with ozone. At the end of winter there is more Cl_2 and less NO_2 than at other times of the year.

When the sun comes out in the spring, photodissociation reactions produce Cl.

$$Cl_2 + h\nu \rightarrow Cl + Cl$$

$$CFCs + h\nu \rightarrow Cl + other things$$

These reactions increase the concentrations of Cl and ClO. With much less NO_2 to tie up Cl than usual and more Cl and ClO available, the catalytic destruction of ozone takes place. The polar vortex keeps the south pole area isolated so that no ozone can come in from other areas to replenish what is destroyed. The rapid destruction of ozone without replenishment creates the ozone hole, which reflects a sharp reduction in local concentration of ozone.

When the polar vortex weakens in mid spring mixing with the rest of the atmosphere is again possible. More NO_2 is brought in and reacts with Cl and ClO. The air in the region of the ozone hole mixes with air in the rest of the stratosphere and the ozone depletion is spread out over a wide area so that it is not as obvious.

1987 Montreal Protocol - international agreement to restrict production and phase out CFCs

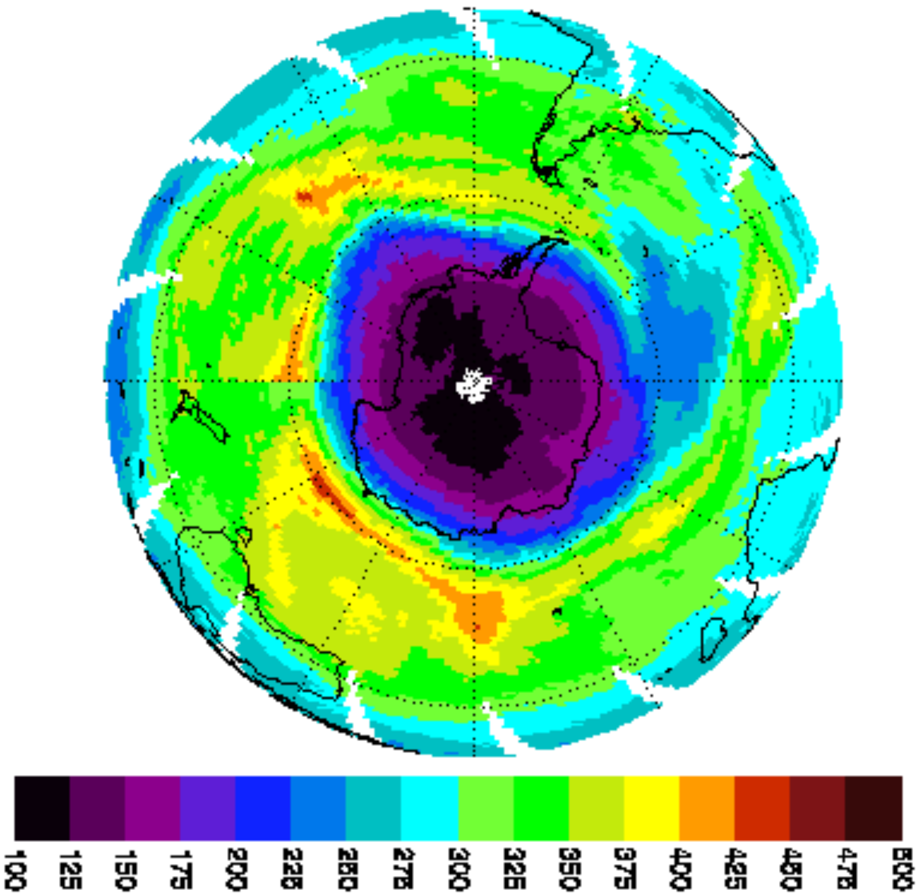
1988 Dupont agrees to phase out CFCs eventually

1989 Cl and PSCs seen in Artic, not as cold as south pole so less PSCs, and not as strong a vortex.

1991 Preliminary reports from measurements taken in early October indicate a particularly severe ozone hole this year.

Example of the Seasonal Progression of the Ozone Hole

EP/TOMS Total Ozone for Oct 1, 2001



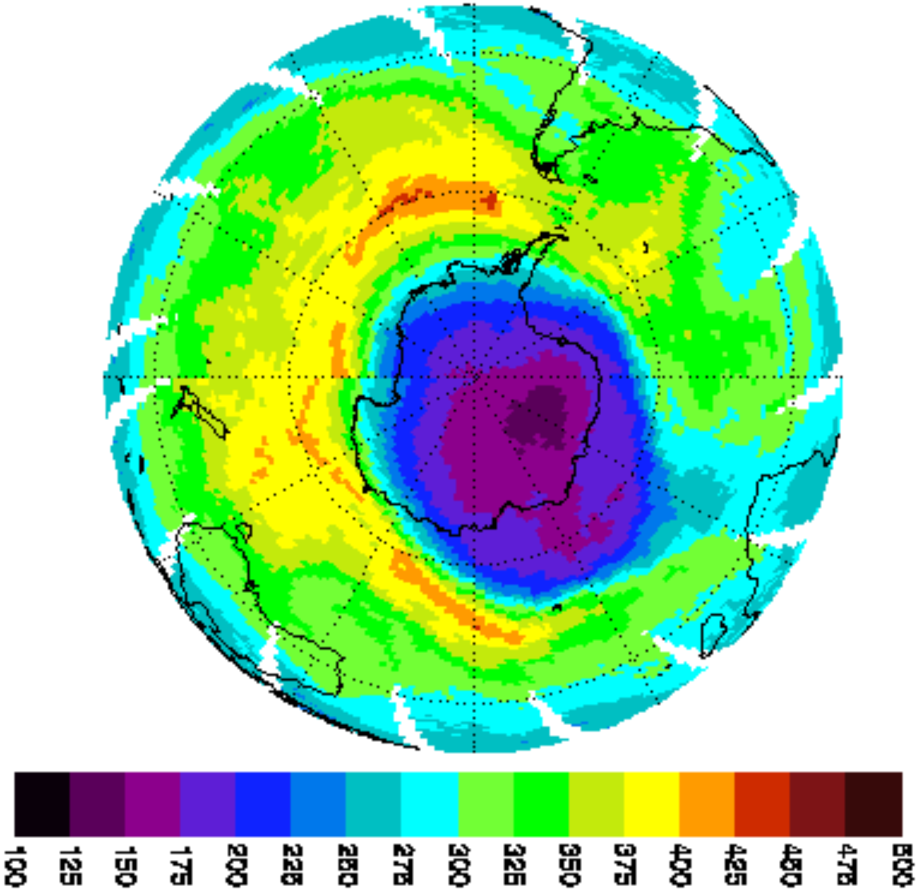
Dobson Units

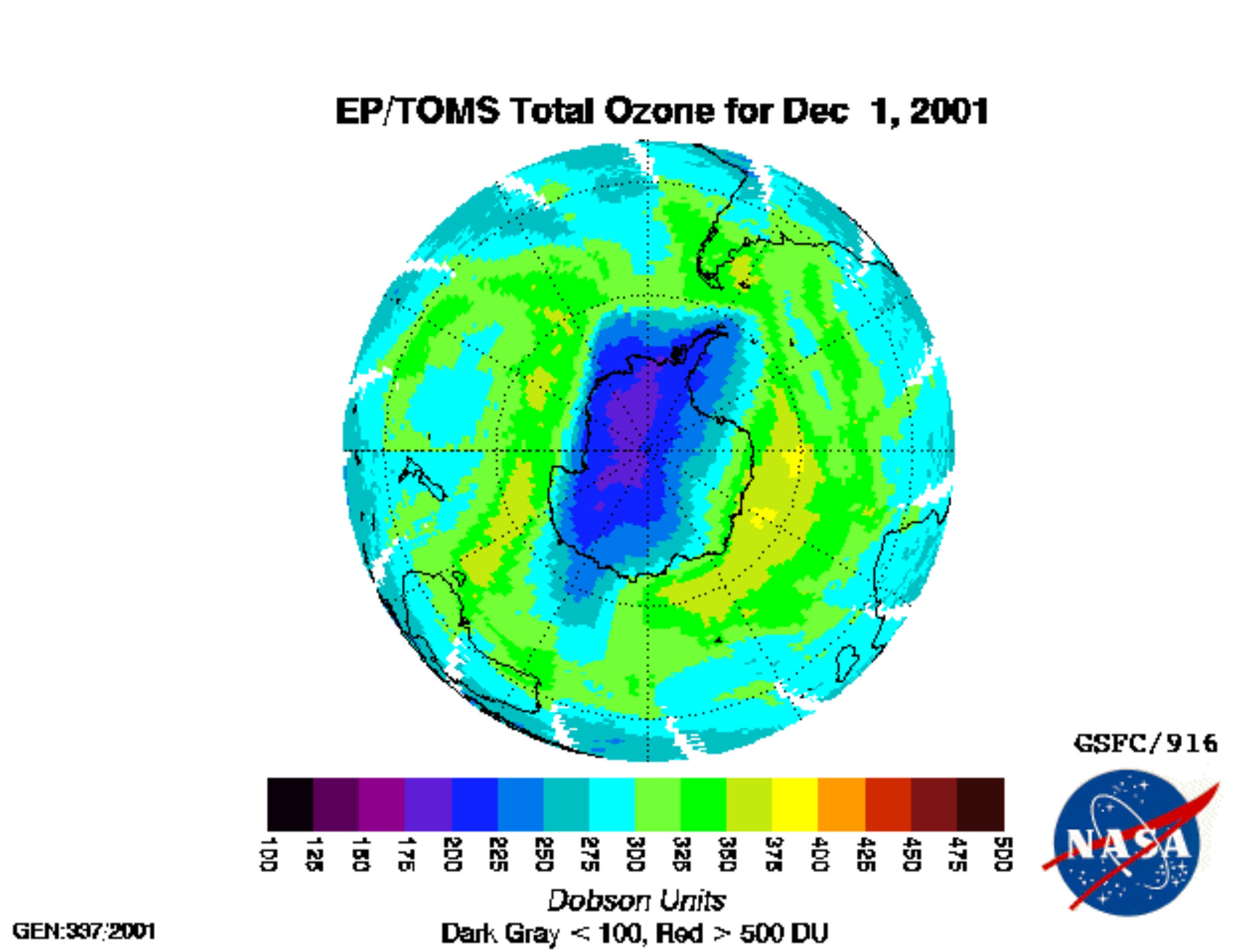
Dark Gray < 100, Red > 500 DU

GSFC/916

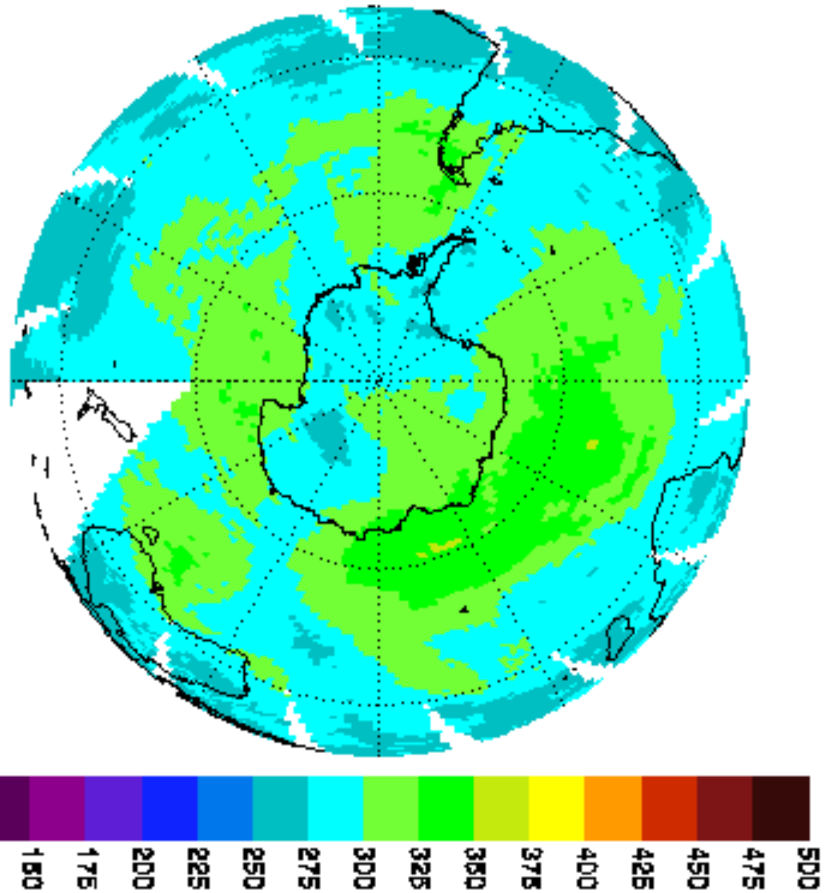
GEN:276:2001

EP/TOMS Total Ozone for Nov 1, 2001



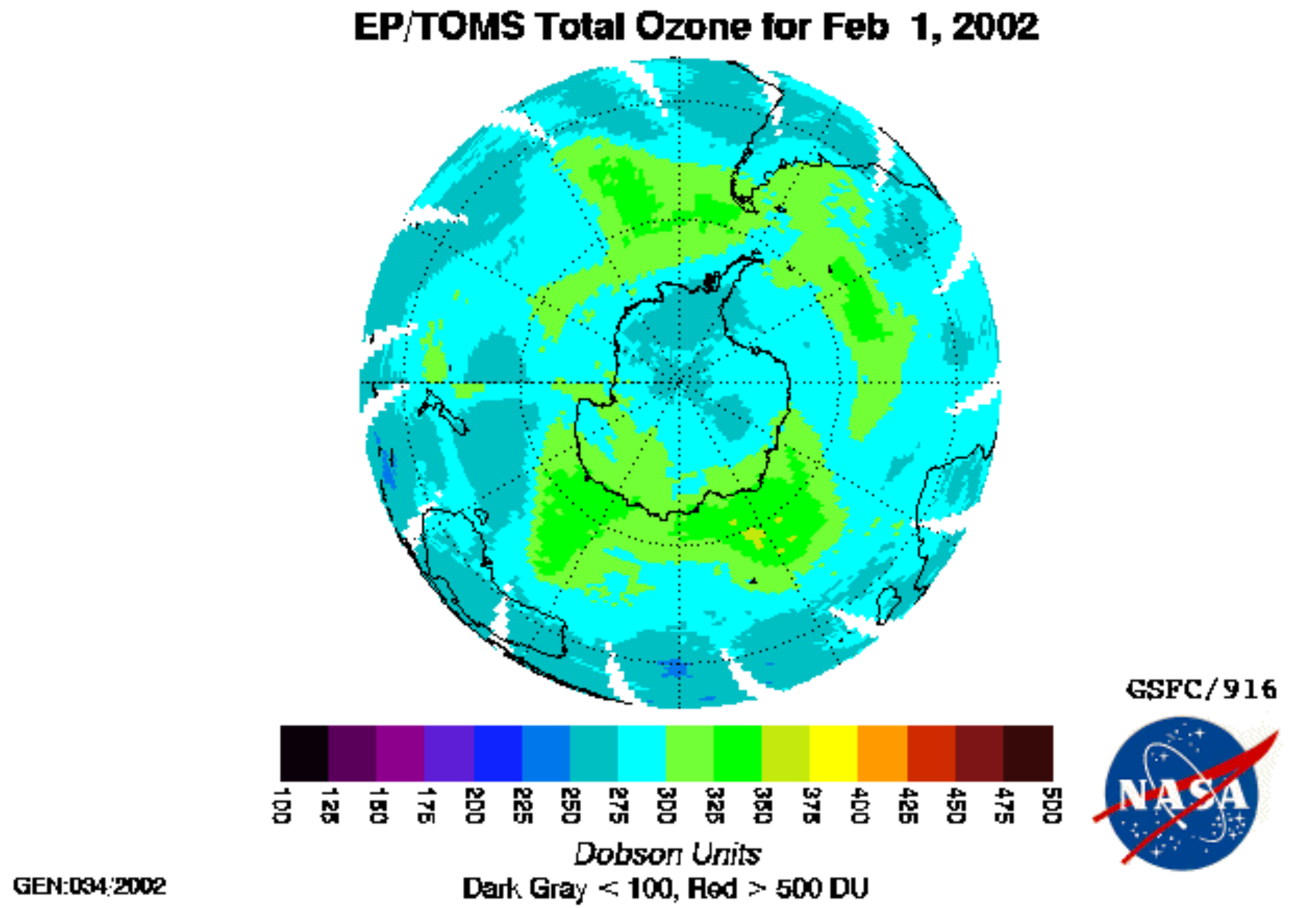

EP/TOMS Total Ozone for Dec 1, 2001
100 125 150 175 200 225 250 275 300 325 350 375 400 425 450 475 500
Dobson Units
Dark Gray < 100, Red > 500 DU
GEN:337/2001
GSFC/916
NASA

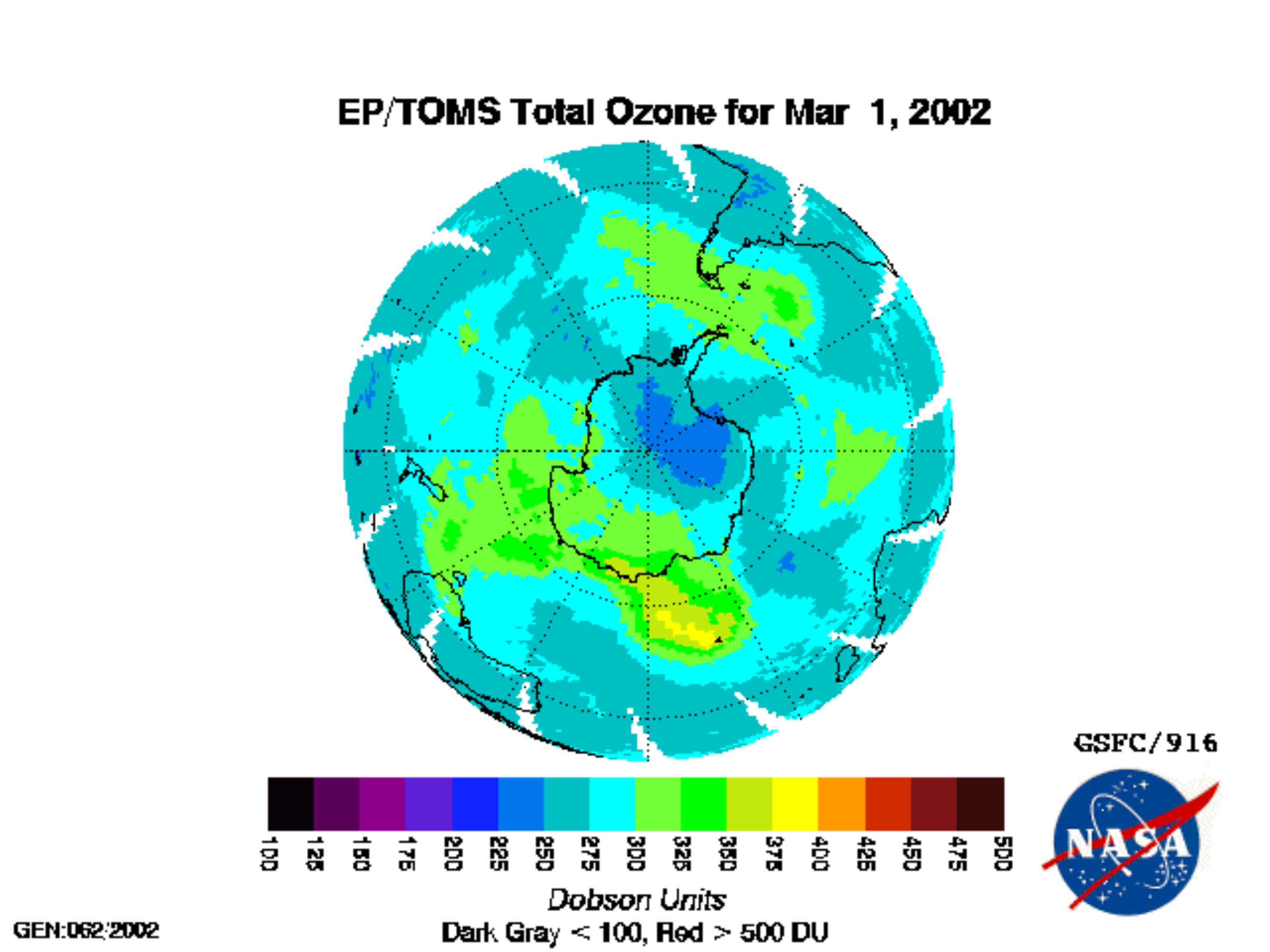
EP/TOMS Total Ozone for Jan 1, 2002



GSFC/916

GEN:003:2002


EP/TOMS Total Ozone for Feb 1, 2002
GSFC/916
100
125
150
175
200
225
250
275
300
325
350
375
400
425
450
475
500
Dobson Units
Dark Gray < 100, Red > 500 DU
GEN:034/2002



EP/TOMS Total Ozone for Mar 1, 2002
GSFC/916
100 125 150 175 200 225 250 275 300 325 350 375 400 425 450 475 500
Dobson Units
Dark Gray < 100, Red > 500 DU
GEN:062 2002