Announcements

• Read Chapter 17 (all)
• Info on upcoming (extra-credit) talks now by email

Week 2
Chap 17: stratospheric ozone
Mon: ozone basics
   photochemistry
   UV radiation
   atmospheric structure
   terrestrial life
Tues: CFC’s and ozone
   catalytic reactions
   atmospheric cycles
Wed: Antarctic ozone hole
    unexpected couplings
Thurs: global ozone depletion
   ozone protection treaties
   ozone “skeptics”
   lessons from ozone
Fri: tutorial: math and chem

Overview:
Stratospheric ozone illustrates:
• Earth-System
  couplings galore!
  human involvement
  unexpected consequences
• Global environmental problem
  discovery
  explanation
  solution

Forms of oxygen in the atmosphere
Which is most common?

Atmospheric ozone: vertical structure

Definitions
"stratosphere"
• Atmospheric layer above the troposphere, where most ozone is found
• Temperature increases with height

"troposphere"
• Lowest atmospheric layer, where most “weather” occurs
• Temperature decreases with height

Figure source: http://www.al.noaa.gov/WWWHD/pubdocs/Assessment02/Q&As.html
DU: "Dobson Unit"

- Measure of "ozone column depth"
- Literally: thickness of pure ozone atmosphere
- Measure of number of O₃ molecules overhead
- 100 DU = 1 mm at surface

Geographical distribution of ozone column depth

- Thin in the tropics
- Thicker at high latitudes

If you moved from 60N (say, Sweden) to the equator (say, Kenya), how much of a change would you experience in the minimum ozone column depth in a typical year?

From ~300 to ~250 DU or 17% reduction (50/300 = 0.17)

Ozone Chemistry in the Stratosphere

Chapman Mechanism

1. \( \text{O}_2 + \text{UV} \rightarrow \text{O} + \text{O} \) (slow)
2. \( \text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M} \) (fast)
3. \( \text{O}_3 + \text{UV} \rightarrow \text{O} + \text{O}_2 \) (fast)
4. \( \text{O}_3 + \text{O} \rightarrow \text{O}_2 + \text{O}_2 \) (slow)

Production

Destruction

Reactants

Products

KKC Table 17-2

Fast Reactions

1. \( \text{O} + \text{O}_2 \rightarrow \text{O}_3 \) (fast)
2. \( \text{O} + \text{O}_2 \rightarrow \text{O}_3 \) (fast)
3. \( \text{O}_3 + \text{O} \rightarrow \text{O}_2 + \text{O}_2 \) (fast)
4. \( \text{O}_3 + \text{O} \rightarrow \text{O}_2 + \text{O}_2 \) (slow)

The symbol "\( \text{M} \)"

- See KKC Fig. 17-6 for explanation
- To simplify things, let's get rid of it
Ozone Chemistry in the Stratosphere

**Fast Reactions**

production of ozone

(2) O + O₂ → O₃ (fast)

destruction of ozone (photolysis)

(3) O₃ + UV → O + O₂ (fast)

net reaction: add (2)+(3)

net (UV) → heat!

There is no net production or destruction of any chemical species. But, there is a net absorption of UV radiation, which warms the stratosphere.

“photo”: light, “lysis”: splitting

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Stratospheric ozone: Why we care

Ozone “photolysis”

O₃ + UV → O + O₂ + heat

First consequence

- absorption of UV adds heat
  - > get max T at ~50 km altitude (warm fluid on top is stable)
  - > creates “stratosphere” (‘stratified’ layer: little vertical motion; clouds are very rare)

KKC Fig 3-9

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Stratospheric ozone: Why we care

Ozone “photolysis”

O₃ + UV → O + O₂ + heat

Second consequence

- absorption of UV shields the Earth’s surface from UV-B
  - > makes possible life on land

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Role of ozone in Earth history

life on land


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Tuesday April 4

Announcements

- Read Chapter 17 (all)
- Two talks today, 12:30 and 2:30
- HW #4

Today

- UV dose
- oxygen-only reactions
dynamic equilibrium
slow reactions control concentration
- CFC’s and ozone
catalyst
atmospheric lifetime
a very bad prediction (by a very smart man!)
Ultraviolet Radiation (UV)

- Ultraviolet means "beyond violet"
  - Shorter wavelength than violet
  - Not visible to humans
- Highly energetic
  - Drives photochemical reactions
  - Causes harm to life (sunburn, genetic damage, cancer)
- 3 classes: A, B, C
  - A not harmful
  - C extremely harmful, but none reaches surface
  - B is the big concern

UV dose

UV dose: the amount of UV-B radiation received at the surface

Two factors control UV dose
- Ozone column depth
- Solar zenith angle

Stratospheric Ozone Chemistry: Outline

1. Oxygen-only reactions
2. Catalytic destruction by halogens (Cl and Br)
3. Antarctic ozone hole (Wednesday)
   - Discovery
   - Explanation (surface catalyzed reactions)

Key Concepts
- Rate of reaction
- Odd-oxygen
- Coupled reactions -> net reaction
- Dynamic equilibrium
- Catalyst (speeds up a reaction)

Motto

"No law that says nature has to be simple!"

Oxygen-only reactions

1. \( \text{O}_2 + \text{UV} \rightarrow \text{O} + \text{O} \) (slow)
2. \( 2\text{O} + 2\text{O}_2 \rightarrow 2\text{O}_3 \) (fast)
3. \( \text{O}_3 + \text{UV} \rightarrow \text{O} + \text{O}_2 \) (fast)
4. \( \text{O}_3 + \text{O} \rightarrow \text{O}_2 + \text{O}_2 \) (slow)

Ozone production in the stratosphere

1. \( \text{O}_2 + \text{UV} \rightarrow \text{O} + \text{O} \) (slow)
2. \( 2\text{O} + 2\text{O}_2 \rightarrow 2\text{O}_3 \) (fast)

Step 1, the slow reaction is the rate-limiting step.
(Production rate depends entirely on rate at which Step 1 occurs.)
Ozone production in the stratosphere

Production depends entirely on rate of Step 1 . . .

What controls the rate of Step 1?

- Concentration of O₂ (molecular oxygen)
- Solar luminosity

Consequence:
Average rate of ozone production for current climate on Earth is pretty much fixed (i.e. essentially constant).

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Oxygen-only reactions

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) O₂ + UV --&gt; O + O</td>
<td>(slow)</td>
</tr>
<tr>
<td>(2) 2O + 2O₂ --&gt; 2O₃</td>
<td>(fast)</td>
</tr>
<tr>
<td>(3) O₃ + UV --&gt; O + O₂</td>
<td>(fast)</td>
</tr>
<tr>
<td>(4) O₃ + O --&gt; O₂ + O₂</td>
<td>(slow)</td>
</tr>
</tbody>
</table>

"Dynamic equilibrium":
- lots of activity, but no net production or destruction

Since production rate is essentially fixed, equilibrium concentration of O₃ depends on (4)

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Catalyst definition

catalyst
• a substance that accelerates the rate of a reaction without itself being consumed

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Catalyst example

Calculate the NET reaction…

(a) O₃ + X --> XO + O₂
(b) XO + O --> X + O₂

(\text{net}) O₃ + O --> O₂ + O₂

• Species X facilitates the destruction of ozone (and atomic oxygen) but is not itself consumed.
• Do you recognize the net reaction? Have you seen it before?

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Catalytic ozone destruction

A new model of ozone equilibrium:

\begin{align*}
1) & \quad O₂ + UV \rightarrow O + O \\
2) & \quad 2O₂ + 2O \rightarrow 2O₃ \\
3) & \quad O₃ + UV \rightarrow O₂ + O \\
4*) & \quad O₂ + O \rightarrow O₂ + O₂
\end{align*}

*the 4th reaction from the oxygen-only cycle is catalyzed by species X.

Result will be a lower equilibrium concentration of O₃ (due to more efficient removal).

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Catalytic ozone destruction

Figure source: http://www.a1.noaa.gov/WWW/HD/pubdocs/Assessment02/Q&As.html
Catalytic ozone destruction

Species X can be: NO (odd-nitrogen)  
Cl (chlorine)  
Br (bromine)

Reactions when X = chlorine...

(a) \( \text{O}_3 + \text{Cl} \rightarrow \text{ClO} + \text{O}_2 \)
(b) \( \text{ClO} + \text{O} \rightarrow \text{Cl} + \text{O}_2 \)

(net) \( \text{O}_3 + \text{O} \rightarrow \text{O}_2 + \text{O}_2 \)

NO, Cl, and Br have all been greatly enhanced in the stratosphere due to human activities.

Origin of CFC’s

In 1929, 100 people were killed in a hospital in Cleveland due to a leak in the refrigeration system.

Refrigeration systems require a “working gas” to transfer heat via compression and expansion cycle.

Traditional working gases - sulfur dioxide and ammonia - are highly toxic.

The invention of chlororfluorocarbons (CFCs) in the 1930s was a great step forward for public safety. These gases are totally “inert” - meaning totally non-toxic.

Soon, many other uses were found for CFCs and related bromine compounds known as halons.

Origin of CFC’s

Because CFCs are chemically inert, there is no mechanism by which they are removed from the atmosphere. They accumulate.

1970: Jim Lovelock invents electron capture device, allowing CFC’s in open atmosphere to be measured.

1973: Lovelock deduces that essentially all CFC’s ever produced are still in the atmosphere.

Quote from Lovelock’s 1973 article:

“The presence of these compounds constitutes no conceivable hazard” (Jim Lovelock, 1973).

CFC lifetimes

atmospheric lifetime (or “residence time”):
The average length of time a substance spends in the atmosphere.

<table>
<thead>
<tr>
<th>name</th>
<th>other name</th>
<th>chemical formula</th>
<th>atmospheric lifetime</th>
</tr>
</thead>
<tbody>
<tr>
<td>CFC-12</td>
<td>Freon-12</td>
<td>CCl₂F₂</td>
<td>100 yrs</td>
</tr>
<tr>
<td>CFC-11</td>
<td>Freon-11</td>
<td>CCl₃F</td>
<td>45 yrs</td>
</tr>
</tbody>
</table>

CFC destruction

CFC lifetime’s in atmosphere are long, but not infinite.

How do you think they (eventually) get destroyed?

Answer:

Slowly diffuse into the stratosphere.

There, they encounter UV radiation.

Photolysis breaks off chlorine atoms.

Emissions of all these compounds were greatly reduced in about 1990. Which compound has the longest atmospheric lifetime? Which has the shortest? Explain.

a) CFC-11  \( t = 45 \) yrs  
b) CFC-12  \( t = 100 \) yrs  
c) carbon tetrachloride  \( t = 26 \) yrs  
d) methyl chloroform  \( t = 5 \) yrs

Longest (responds most slowly)

Shortest (responds most quickly)

KKC Fig 17-8
Wednesday April 5

Announcements
- Novak, Hansen, Science

Today
Antarctic ozone hole
- "reactive" vs "unreactive" chlorine
- role of theory vs discovery in science
- high-tech embarrassment
- weighing the evidence for CFC (i.e. human) causation
- science (and policy) in normal times vs unusual times

Global trends in stratospheric ozone

Science, 24 Mar 2006

Vertical distribution of chlorine species

CFC cycle in atm:
- source in tropo; well-mixed
- sink in strato; decreases with height

Three categories:
- source gases (CFCs, etc)
- unreactive forms in strato
  - HCl and ClONO2
- reactive form in strato: ClO

Only the reactive form is a catalyst and a danger to stratospheric ozone

effect of 6-m sea level rise

[Graph: Question 8 from WMO, Answers to Twenty Questions]

Ozone & CFC recap

Ozone level governed by dynamic equilibrium. Loss rate via step (4) is key.

Understanding in 1970s and early 80s
- Cl can catalyze reaction (4)
- Cl in stratosphere is increasing due to CFCs but most Cl in stratosphere is locked up in unreactive forms thus, CFCs should cause only modest losses of ozone (predicted 7% loss by 2100)

then came Farman et al., 1985...

1985: Ozone Hole Discovery
- Total ozone over Halley Bay, Antarctica in October.
- Farman et al., (1985) long-term, ground-based measurements (circles)
- later confirmed by TOMS satellite measurements (squares)
1987: State of Knowledge

Antarctic Ozone Hole
see also KKC Fig 1-5

- Satellite view of ozone hole
- TOMS: Total Ozone Mapping Spectrometer
- TOMS launched in 1979
- Ozone hole developed over Antarctica in the early 1980’s
- So, naturally, the TOMS satellite discovered it, right?

WRONG! Low values were rejected by the TOMS computer as instrumental error.

Science and Policy

NORMAL TIMES (theory-driven)
- 1974 Molina and Rowland propose catalytic destruction of stratospheric ozone by CFC’s. They predict 7% loss over the next 50-100 years (Nature, 249, 194-196).
- 1978 US bans CFC use in aerosol sprays.
- 1979 NASA launches TOMS satellite to monitor global ozone.

UNUSUAL TIMES (event-driven)
- 1987 Montreal Protocol calling for strict limits on CFC emissions is signed by 59 nations, including U.S. (under Reagan).
- 1987 Cause of ozone hole is still in question. The leading theories are:
  - dynamics and natural variability
  - nitric oxide (NO) and sunspots
  - CFC’s and polar stratospheric clouds

Stratospheric "Ozone Hole": Explanation

Four years (1985-1988) of frantic research and debate led to definitive consensus that the CFC/PSC explanation was correct (KKC 17:353-356). Outline of that explanation:

1. polar vortex (extremely cold conditions)
2. formation of polar stratospheric clouds (PSCs)
3. heterogeneous reactions (reactions on surfaces)
4. removal of NO and H
5. liberation of Cl (normally tied up via bonding with NO and H)
6. massive, catalytic destruction of O

Vertical distribution of chlorine species

Only the reactive form of Cl is a catalyst and a danger to stratospheric ozone.

Almost all Cl, esp. in lower stratosphere, is bound up in unreactive forms.

Reactions on crystal surfaces of polar stratospheric clouds (PSCs) sequester NO2 and H and liberate Cl.

These heterogeneous reactions were left out of the early models that calculated modest ozone destruction from CFCs.

Heterogeneous Reactions: The Key

harmless chlorine

catalytic chlorine

source: Turco (1987)
Earth Under Siege

Prediction: Ozone destruction should correlate with regions with high concentrations of activated chlorine (Cl and ClO)
Smoking gun: Correlation from aircraft

**Question:** What is the ratio of ClO to O₃ within the ozone hole?

- 1 ppt
- 1 ppb

\[ \frac{1 \text{ ppt}}{1000 \text{ ppb}} = 1/1000 \]

Not much ClO, but it has big effect.

**Nowadays we can see the same correlation from satellites**

Figure source: http://www.al.noaa.gov/WWWHD/pubdocs/Assessment02/QnAs.html

Global trends in ozone

The "ozone hole is serious, but very limited in extent
- mainly in October
- mainly over Antarctica

Have CFC's caused a reduction in stratospheric ozone at the global scale?

**Global trends in ozone**

Global ozone correlates with solar luminosity.

*Change (%) in mean ozone column depth, 40N-40S, after removal of seasonal cycle, QBO, and long-term trend.

**Correlation with sun...**

Step 1 (ozone production) is controlled by...

- Concentration of O₂ (molecular oxygen)
- Solar luminosity

**Global trends in ozone**

Trends at mid-latitudes are small and hard to pick out due to large seasonal variability.

Hohenpeissenberg, Germany (KKC Fig 17-11)
**Global trends in ozone**

Despite all this, a modest downward trend in global ozone is apparent.

![Schematic of the North-to-South Ozone Depletion: 1970-1987](image)

KKC Fig 17-13

1991: Mt Pinatubo eruption
1992: Susan Solomon demonstrates vulnerability of global ozone to volcanic eruptions. Involves heterogeneous reactions. (Explain)

- Heterogeneous reactions (on surfaces) convert unreactive Cl to reactive Cl.
- As long as chlorine levels in the stratosphere are elevated, we are vulnerable to adding particulate surface area to the stratosphere.
- When will stratospheric chlorine return to pre-industrial levels?

- Note: One proposed “geoengineering” solution to global warming problem: add particles to stratosphere to reflect sunlight. Do you think this is a good idea?

**Announcements:**
- HW due Monday (at beginning of class)
- late homework: 10% per day

**Today:**
- your feedback
- ozone control (Sci Assessments, Int’l Treaties)
- ozone skeptics
- ozone lessons

**Friday:** math/chem review

**Next week:** Daisyworld and the science of systems (Chapter 2)

**Notes from in-class responses...**

The fundamental theory behind global-warming research is the “energy balance theory of climate change”: \[ \Delta T = \lambda \Delta F \]

Questions: Exactly what is \( \Delta T \)? How is it measured? How well is it known?

**GAAST:** Global-Annual Average Surface Temperature

\( \Delta T \): change in GAAST

Actually, there are two different meanings/roles:

\( \Delta T_{\text{pred}} \) predicted response to a forcing (theory)

\( \Delta T_{\text{meas}} \) measured temperature change (evidence)

**Int’l Treaties and Scientific Assessments**

<table>
<thead>
<tr>
<th>Year</th>
<th>Policy Process</th>
<th>Scientific Assessment</th>
</tr>
</thead>
<tbody>
<tr>
<td>2002</td>
<td></td>
<td></td>
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</tbody>
</table>

**Effect of Int’l Treaties**

**Fron-12**

serious controls begin
### Quotes from 2002 Scientific Assessment

1. "In the troposphere, observations show that the total combined effective abundance of ozone-depleting compounds continues to decline slowly from the peak that occurred in 1992-1994."

2. "Analyses of air trapped in snow since the late 19th century have confirmed that non-industrial sources of the CFCs, halons, and major chlorocarbons were insignificant."

3. "... a future Arctic polar ozone hole similar to that of Antarctica appears unlikely."

4. "Additional measurements continue to confirm that decreases in ozone column amounts lead to increases in UV radiation."

**What scientific question is being addressed by each of these statements? How do those scientific questions relate to policy choices?**

<table>
<thead>
<tr>
<th>Science</th>
<th>Policy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Were these species already present before the modern chemical industry?</td>
<td>Cutting emissions would be a waste of effort if our emissions are not in fact the cause of CFCs and halons in the atmosphere.</td>
</tr>
<tr>
<td>Are humans responsible for the presence of CFCs and halons in the atmosphere?</td>
<td></td>
</tr>
<tr>
<td>Could an &quot;ozone hole&quot; develop in the Arctic? Would it be as dramatic as the one in the Antarctic?</td>
<td></td>
</tr>
<tr>
<td>How serious is this problem? What is the level of danger for the citizens and ecosystems of the far North?</td>
<td></td>
</tr>
</tbody>
</table>

### Typical arguments of the "skeptics"

1. Natural variations are much more important than human impacts.
2. Observed changes may be real, but not due to humans (see 1).
3. Predicted harm based on flawed theoretical models.
4. Regulations designed to reduce human impacts will cause severe economic damage.
“Skeptics” of human-induced ozone depletion

two examples (available for reports):


Dixy Lee Ray:
Ph.D. zoologist, University of Washington
Washington State Governor
Chairman of Atomic Energy Commission

Sallie Baliunas:
Ph.D. Astrophysicist, Harvard-Smithsonian Center for Astrophysics
Deputy Director of Mt. Wilson Institute

Example arguments of a “skeptic”

Dixy Lee Ray:
“Nothing is more obvious than the fact that complex and sophisticated new technology is making our lives better, safer, and more enjoyable than in the years before. Our lives are being saved, our health is being enhanced, our economic well-being is being increased by these new technologies.”

Sallie Baliunas:
“Given the overall scientific consensus on the importance of chlorofluorocarbons (CFCs) and similar chemicals in destroying the ozone layer, a competent and forthright refutation of their role has to be given serious consideration. However, at present, the case against the connection between CFCs and the destruction of the ozone layer is weak.”

Summary of consensus science is presented as an allegation

Author claims to speak for “science” human cause is disputed; changes are natural

Proposed protections are the real danger

Example arguments of a “skeptic”

Dixy’s advice...

from Environmental Overkill (1993) by Dixy Lee Ray:

“Although the presence of chloride appears to be directly involved in ozone breakdown, the origin of that chloride is open to question.” [p.34]

1. World production of CFCs is ~750,000 tons of Cl per year, but...
   1a. seawater evaporation puts ~600,000,000 tons of Cl into the atmosphere per year, and
   1b. volcanic eruptions put millions of tons of Cl into the atmosphere.

2. Besides, there are some “obvious” problems with the theory of CFCs being responsible for Cl in the stratosphere. “How does CFC rise when its molecules are four to eight times heavier than air?” [p.35]

Question: Which of these three points (1a, 1b, or 2) has merit? Why?

Answers: 1a: Neither particulate NaCl nor gaseous HCl mix into the upper troposphere much less the stratosphere, in significant amounts.

2: Turbulent motions mix all gases throughout the atmosphere regardless of molecular weight. Heavy gases have no tendency to “fall out.”

Question: Why are 1a and 1c absurd?

Answers: 1a: Neither particulate NaCl nor gaseous HCl mix into the upper troposphere much less the stratosphere, in significant amounts.

2: Turbulent motions mix all gases throughout the atmosphere regardless of molecular weight. Heavy gases have no tendency to “fall out.”

WMO: global ozone changes are small

measurements showing change in global ozone

replotted to reveal small magnitude of change

Figure source: http://www.ciasc.noaa.gov/OV/WWW/0330pub/Assessment93FAQs.html
correlation of ozone changes with the solar changes (implying cause is natural)

Predicted increase in UVB is not supported by the data, which actually shows a decrease in UVB at all stations.

Note: Report date is 1995 but data only runs to 1985 (?).

Are these stations correctly located to see the predicted UVB increase? (Did ozone actually thin over these locations?)

Ozone absorbs UV-B radiation, thereby - warming the upper atmosphere and creating a stable layer known as the "stratosphere" - shielding the surface from UV-B and making terrestrial life possible

Ozone exists in a state of "dynamic equilibrium", a balance between the production and destruction of "odd-oxygen". Since the production rate is essentially fixed, the destruction rate controls the concentration.

Chlorine and other compounds catalyze the destruction of odd-oxygen and thus the depletion of stratospheric ozone.
Stratospheric ozone recap

CFCs accumulate in the troposphere (long atmospheric lifetimes) and undergo photolysis in the stratosphere to release chlorine atoms. This has already caused a modest (few percent) decrease in global-mean ozone column amount.

Most chlorine from CFCs is locked up in unreactive forms that do not threaten ozone.

BUT heterogeneous reactions on PSC's (and volcanic particles) can sequester the compounds that normally bond to Cl and, thereby, release it to the active, ozone-destroying form. This process caused an "ozone-hole" to develop over Antarctica in the springtime starting about 1980 and growing worse through the 1990's.

Global ozone depletion has been modest (a few percent). The expected increase in UV-B radiation at the surface has been detected. Both these measurements are difficult because the changes are small with respect to natural variability.

The Montreal Protocol (1987) and subsequent amendments have put the world on a course to eliminating CFCs (and halons) from the atmosphere, thereby protecting the ozone layer. This will take 50-100 years.

Meanwhile, high chlorine levels make stratospheric ozone vulnerable to volcanic eruptions or other sources of particulate matter.

Due to international regulation, stratospheric chlorine has probably peaked and will decline over the coming decades. Without these treaties (assuming business as usual), it would have reached levels 5-10 times higher during this century.

A lucky escape?

We have seen that both chlorine, Cl (from CFCs) and bromine, Br (from halons) can catalytically destroy ozone.

CFCs are far more common, largely due to their use as refrigerants and blowing agents.

In fact, halons also make great refrigerants and blowing agents. But Br is 10 times more efficient than Cl at destroying ozone.

It just happens that freons are cheaper and easier to manufacture.