Analysis of earth's upper stratosphere reveals unusual ozone chemistry

November 9, 1995

Hold for SCIENCE Embargo: 2 p.m., Pacific Time, Thursday, November 9, 1995, Media Contact: Warren R. Froelich, (619) 534-8564

ANALYSIS OF EARTH'S UPPER STRATOSPHERE REVEALS UNUSUAL OZONE CHEMISTRY

The first analysis of air brought back from the Earth's upper stratosphere and beyond has revealed that atmospheric ozone briefly merges with carbon dioxide and oxygen, transferring a significant amount of energy in the process.

Until these findings, atmospheric chemists did not know that ozone reacted at these heights, roughly 27 miles above the Earth's surface, with anything other than manmade chemicals and light.

The results, published in the current issue of the journal Science, suggest that current computer models about ozone depletion over the planet lack a significant component.

"It's not that they are incorrect," said Mark Thiemens, a UCSD professor of chemistry and biochemistry who designed the study. "They are correct based on everything that was known. But until this gets calculated you don't know for sure what the impact of this chemistry will be until further observations are made and models are constructed which incorporate this additional chemistry."

Also participating in the study were Teresa Jackson, a staff research associate in chemistry and biochemistry at UCSD; and Edward Zipf, Peter Erdman and Cornet van Egmond, all from the department of physics and astronomy at the University of Pittsburgh.

The new findings stem from a series of small rocket launches in 1992 from White Sands, New Mexico, during which a specially designed instrument called a Cryogenic Whole Air Sampler (CWAS) grabbed samples of frozen air some 60 kilometers (about 27 miles) above the Earth's surface. That's half-way through the stratosphere and into the next higher region, the mesosphere. Prior to these flights, scientists relied on balloon flights that traveled only as high as 40 kilometers (about 18 miles).

The CWAS consisted of three gold-plated chambers frozen in liquid helium at temperatures 3 degrees above absolute zero. At these intensely cold temperatures, everything freezes except nitrogen and oxygen. Once launched, valves on each chamber were systematically opened at predetermined times and heights. The frozen atmosphere of the chambers created a supervacuum that sucked in all the air that would fit. Once filled, the valve closed, the rocket and instrumentation returned to the Earth's surface, and the chambers sent back to UCSD for analysis.

Led by Thiemens, the scientists focused on a peculiar isotope "signature" that he previously determined by laboratory tests to be characteristic of oxygen found in ozone, a heavyweight cousin of oxygen. (Isotopes of atoms of the same element with a different number of neutrons). For ozone, the proportion of oxygen 16 is significantly larger than oxygen 17 and oxygen 18, when compared to other oxygen-related materials.

By following the trail of this unique chemical signature, the scientists were able to see an unusual chemical reaction involving stratospheric ozone.

"When you break apart stratospheric ozone it makes a product, another oxygen atom," Thiemens explained. "This oxygen, in turn, interacts with carbon dioxide, giving off some of its energy.

"In fact, when you look at these isotope ratios in the carbon dioxide associated with ozone, you can see a real significant chunk of ozone energetics goes through this process. And no one has ever considered this before."

The scientists found that samples of atmospheric oxygen--ordinary oxygen that we breathe--also exhibited this unique isotopic signature, the likely result of brief interactions with oxygen atoms released from ozone brought down from the mesosphere into the stratosphere.

"No one has ever seen a change in air oxygen in its composition or its isotopes before," said Thiemens. "This is the first time anyone has seen this. If the second-most abundant molecule in the atmosphere (oxygen) is changed, it takes a big process to do this."

Thiemens stressed that no one knows how these new findings might affect the life cycle of ozone, or other chemical processes in the atmosphere. Questions about the variability of global measurements for this effect, in terms of location and time of year, also need to be answered.

"You want to know what it is doing seasonally, over time, around the globe," said Thiemens.

Funding for the study was provided by the National Science Foundation and the National Astronautical and Space Administration (NASA).

(November 9, 1995)