

balance between their formation, transport, and removal, including decomposition. This is best documented in the case of arsenic. The occurrence of monomethylarsonic acid and dimethylarsinic acid is variable and largely limited to the euphotic zone, where they form a significant but not dominant fraction of the total dissolved arsenic<sup>4</sup>. Marine algae in culture produce methylated forms of arsenic from arsenate<sup>5,6</sup>, while bacterial cultures isolated from estuarine waters demethylate dimethylarsinic acid<sup>7</sup>.

The sources of methylgermanium species are not yet known. If they are produced largely on land and carried to the oceans by rivers, the results suggest mean oceanic residence times of about 4 million years for MMGe and half a million years for DMGe, values which are comparable with the residence time of, for example, calcium. On the basis of its close geochemical coherence with silicon, the residence time of inorganic germanium is probably about 10,000 years. The apparent, radiocarbon-based age of 3400 years for total dissolved organic matter in some of the oldest waters in the general oceanic circulation<sup>8</sup>, cannot give unequivocal life-times for particular organic species since dated material is a mixture of compounds that are decomposed or otherwise removed at different rates. Thus the unpredicted existence of very low concentrations of organic species with residence times of about a million years is not necessarily inconsistent with other findings.

The reasons for the stability of MMGe and DMGe remain to be ascertained. The

experiments of Lewis *et al.* on the effects of photo-oxidation with ultraviolet radiation which raise further questions in this respect. They show that methylated germanium species are not decomposed by ultraviolet radiation in natural sea water but are totally decomposed in pure water. In artificial seawater, partial decomposition of DMGe and TMGe to MMGe proceeds more readily than conversion to inorganic germanium. Micro-organisms are often able to carry out reactions that are difficult to achieve by chemical or physical means in the laboratory, and they need to be considered if the reasons for the environmental stability of MMGe and DMGe are to be understood.

In showing distinctive and unexpected biogeochemical behaviour in the marine environment, germanium belies, in certain respects, its old title of ekasilicon. The element is now seen to have an interesting part in the unfolding story of environmental methylation of metals. □

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## Atmospheric chemistry

# Mesospheric ozone variations caused by gravity waves

from Guy Brasseur

FOR about three years, the Solar Mesosphere Explorer satellite has been measuring the key parameters for understanding the budget of ozone in the middle atmosphere (mesosphere). As I have already explained in these columns (*Nature* 305, 15; 1983), in addition to continuous observations of ozone by an ultraviolet and an infrared spectrometer, the satellite provides data on the temperature, the concentration of nitric oxide and nitrogen dioxide, and the strength of the ultraviolet solar irradiance in the mesosphere. A recently published analysis by R.J. Thomas and his collaborators (*Geophys. Res. Lett.* 11, 673; 1984) of the 1982 and 1983 data establishes new and interesting features.

In particular, it has been established that there are large seasonal variations in the ozone density at an altitude of about 80 km and that these variations are highly reproducible from year to year in both hemispheres. At this altitude the ozone concentration exhibits a so-called secondary maxi-

mum as is known both from rocket experiments and from numerical models. This concentration is of the order of  $10^8$  molecules  $\text{cm}^{-3}$ , which is 4 orders of magnitude smaller than the well known maximum at 25 km altitude, and results from complex chemical reactions involving oxygen and hydrogen components, and from dynamical processes which are responsible for the transport of long-lived species such as water vapour or nitric oxide. The detailed analysis of the satellite data on the secondary maximum concentrations show that the peak concentration at the equinoxes is about 2 to 3 times greater than at the solstices. The data at 45°N latitude and 0.01 mbar (about 80 km altitude) show that the maximum concentration occurred in spring on April 22 in both 1982 and 1983 and that in both years there was a smaller peak at the end of September. The southern hemisphere's data show the same pattern but with a time-lag; at 45°S, the large peak is in the middle of October and the small peak

at the end of March.

These seasonal changes cannot be explained solely by photochemical considerations since the solar input, and consequently the ozone production and concentration, exhibit a maximum at the summer solstice and not at the equinox. Thomas and his colleagues suggest that the changes are also related to the variation of the transport strength induced by the dissipation of gravity waves.

Gravity waves, which are perhaps most familiar as the waves that propagate on the surface of water, are also present in a stably-stratified atmosphere, where they propagate both horizontally and vertically. They are produced in the troposphere (the first 12 km or so above the Earth's surface) by a variety of mechanisms including air-flow over surface topographic features. Since, in the absence of dissipation, the kinetic energy density must remain constant, the amplitude of the gravity waves will grow with altitude as the inverse square of the air density. When the density of the temperature wave associated with the density wave becomes large enough to produce a local superadiabatic lapse rate, the wave becomes unstable and dissipates: the breaking of the wave may be an important source of local energy and produces turbulent diffusion. In other words, the process of wave breaking controls part of the transport of chemical constituents in the mesosphere.

The vertical propagation of gravity waves is directly dependent on the zonal wind structure in the atmosphere. In winter, when the zonal winds are westerly, the waves with easterly phase speed reach the 80 km level; in summer, when the mean zonal winds are reversed, it is the westerly phase speed waves that reach the mesosphere. In early spring, however, the winds are westerly in the stratosphere but easterly in the mesosphere and the waves are so rapidly absorbed that no dissipation occurs. Turbulent diffusion in the mesosphere is therefore considerably reduced near the equinoxes. Consequently, the water vapour near 80 km, which is transported from lower levels, is less abundant in spring and autumn than at other periods; since water molecules seem to be the most active agent of ozone destruction in the mesosphere, one should expect slower rates of destruction, and consequently larger ozone concentrations, at the period when the zonal winds reverse. Thomas and his colleagues therefore suggest that variations in the ozone density may provide a sensitive indicator of the effects of gravity waves on the middle atmosphere. Further analysis of the Solar Mesosphere Explorer's ozone measurements, which represent the largest climatological data base of ozone ever compiled, should continue to produce rich rewards. □

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