

was determined from limb geometry, that is, by a method totally independent of photometry (which is to say, of albedo).

There is no obvious stratigraphic relationship between darker and brighter polygons; but their existence, along with systematic patterns of global orientation and the nature of the topography, is consistent with the interpretation that they are relics of tectonic breakup and resurfacing of Umbriel. The tendency for lowest-albedo materials to occur in low-lying terrains is consistent with an internally driven resurfacing event involving darker materials. Such darker materials are known to have been extruded on other uranian satellites, that is, certainly on Miranda and probably on Oberon.

The apparent muting of topographic boundaries between polygons by accumulated impact craters suggests that the proposed resurfacing occurred very early in Umbriel's geological history. Indeed, Strom⁸ has suggested, on the basis of cratering statistics, that Umbriel was resurfaced earlier than other uranian satellites. However, any geological interpretation of the global albedo pattern discovered in our study must be seen in the light

of the very low spatial resolution of the Voyager images of Umbriel. A global quasi-polygonal, low-contrast albedo pattern definitely exists on Umbriel. Limited topographic data suggest that a correlation between albedo and topography exists. The geological interpretation of these patterns is uncertain. □

Received 14 November 1988; accepted 1 February 1989.

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ACKNOWLEDGEMENTS. We thank J. Regester, J. Moersch and B. Boettcher for assistance with figures and M. Roth for help in manuscript preparation.

Influence of long-range transport of combustion emissions on the chemical variability of the background atmosphere

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MAUNA Loa Observatory, located 3,400 m above sea level on the island of Hawaii in the middle of the Pacific Ocean, is a critical site for determining the background chemical reactivity of the unpolluted atmosphere and for monitoring its rate of change on a global scale. However, recent measurements of soluble nitrogen (principally HNO_3) at the observatory find mixing ratios rising from their expected background values of 0.02–0.03 parts per 10^9 by volume (p.p.b.v.) in the winter to 0.07–0.12 p.p.b.v. in late summer with three-hour events as high as 0.25 p.p.b.v. (ref. 1). This raises the specific question of contamination by the long-range transport of pollution¹ and a broader question of the chemical variability of the background atmosphere. Here we show that a general circulation transport model which simulates the global spread and deposition of emissions from fossil-fuel combustion can reproduce the nitrogen measurements at the Mauna Loa Observatory. By isolating individual source regions, we show that US emissions are responsible for the late summer increase and that Asian emissions cause a smaller increase in the spring. These simulations, together with the earlier observations, indicate frequent contamination of the Mauna Loa Observatory by the long-range transport of reactive trace gases, such as HNO_3 , and suggest a highly variable background atmosphere. It is essential that we are aware of such variability in order to discern anthropogenic effects on the atmosphere.

We use a global transport model which has already demonstrated the important role of dry deposition in acid deposition over North America² and the impact of combustion nitrogen on the global nitrogen budget³. The model has 11 altitude levels (31.4, 22.3, 18.8, 15.5, 12.0, 8.7, 5.5, 3.1, 1.5, 0.5 and 0.08 km), a horizontal grid size of ~265 km, and a time step of ~26 min (ref. 4). Using the 6-h time-average winds and precipitation provided by a parent general circulation model^{5,6}, the collection of gaseous and particulate reactive nitrogen compounds that result from the combustion emissions are transported as a single tracer, NO_y . We have already discussed the formulation of tracer transport^{3,4}, the global source of nitrogen resulting from fossil-fuel combustion⁷, the effective dry deposition of NO_y ^{3,7} and the effective removal of NO_y by precipitation^{3,4}.

Those emissions not deposited in the source region become

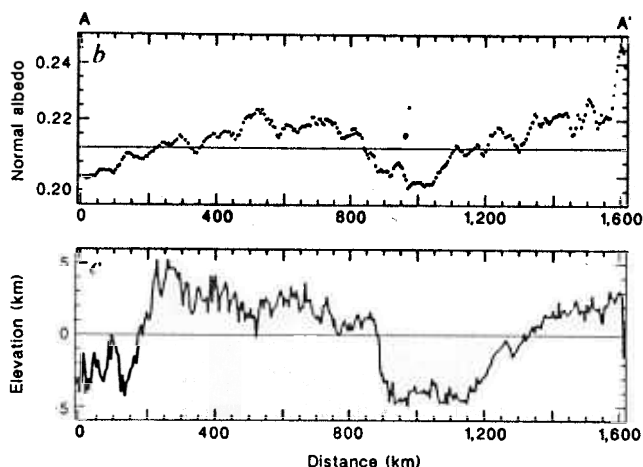
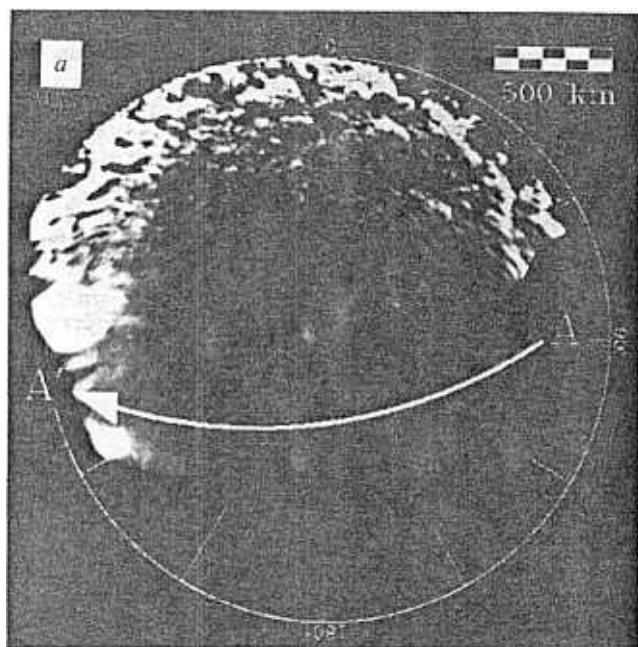


FIG. 2 a Composite polar stereographic projection of four Voyager images of Umbriel. Arrow A–A' identifies the projected location of the limb from image FDS 26840.04 (Fig. 1b). b, Plot of normal albedos from a, along section A–A'. c, Elevation profile along section A–A', corresponding to albedo plot in b.

available for long-range transport. This available NO_y is specified by basing the model's dry deposition and precipitation removal on measurements of nitrogen deposition in precipitation and of surface concentrations of individual nitrogen species. A single linear parameter is adjusted to bring the model's yearly integral of precipitation removal over North America into agreement with observation². This same parameter leads to a good simulation of the yearly wet deposition of nitrogen over the European source region and remote locations in the Northern Hemisphere³. Dry deposition uses effective deposition velocities for NO_y which are based on the surface concentrations of the individual reactive nitrogen species measured over the United States.

The collective transport and parameterized deposition of NO_y precludes the explicit transport of individual nitrogen compounds, particularly insoluble species, such as peroxyacetyl nitrate (PAN) and other organic nitrates. However, we find that much of the transport from Asia and North America to the central Pacific is in stable subsiding air with little precipitation, and that the simulated NO_y deposition and surface concentrations in the central Pacific agree reasonably with observations³. The controlling factor is the model's meteorology—which both lifts the NO_y into the free troposphere (that region of the troposphere that is not directly influenced by boundary-layer mixing) and transports it to Hawaii—and not the detailed chemistry in the source region and along the transport path.

In Fig. 1, we compare the measurements of soluble nitrogen at the Mauna Loa Observatory¹ with the simulated monthly average mixing ratios of NO_y in grid boxes located over Hawaii. The model's simulation of NO_y at 940-mbar level in the atmosphere, ~ 0.5 km above sea level, reproduces both the magnitude and seasonal variation of the observations from the Mauna Loa Observatory. In contrast, the simulated mixing ratios at the 685-mbar level, approximately the height of the Mauna Loa Observatory, agree only with the low winter levels and show no increase in the other seasons. The model does not have sufficient horizontal and vertical resolution to simulate the island of Hawaii, let alone the two mountain peaks and the local complex flow. It simulates long-range transport to grid boxes in the vicinity of Hawaii, and the 685-mbar grid box represents the free troposphere over the Pacific rather than the Mauna Loa Observatory.

Furthermore, extremely high-resolution ($10 \text{ km} \times 10 \text{ km}$) simulations of the air flow around Hawaii show that the normal winds at 3,400 m in the free troposphere are greatly modified by the mountainous terrain⁹. Air parcels are carried up from below in direct flow from the windward side of the mountain and also in return flow from eddies that form in the lee of the island. As a result, the air sampled at the Mauna Loa observatory is a complex mixture of normal free-tropospheric air found at 3,400 m, air from stable layers below 3,400 m and above the maritime boundary layer, air from the maritime boundary layer (that is, below the maritime inversion layer and above the sea surface) and air from the island's boundary layer, which is likely to be contaminated by local pollution and natural emissions. Coincident measurements of humidity, wind direction and condensation-nuclei concentration are used to delete soluble nitrogen observations that may be contaminated by local pollution and natural emissions from both the island and the sea¹, but measurements in air from stable layers below 3,400 m are retained. Over the ocean, the model produces a stable layer above a weakly mixed maritime boundary layer that is ~ 1.5 km thick with a well mixed lowest level of ~ 0.2 km. This structure is in qualitative agreement with the observed maritime boundary layer over the eastern tropical Pacific⁸, although the observed thickness increases from ~ 0.5 km near the Baja to 1.5–2.0 km near Hawaii.

By running separate integrations for the global, Asian and US sources, we are able to identify the individual contributions. The observed summer mixing-ratio maximum, which is well

simulated in the model at 940 mbar, results from a sharp increase in transport from the United States to Hawaii that continues through the autumn. During the winter and spring, nitrogen emissions from Asia dominate and produce the spring increase. The low background levels at the 685-mbar level, with a hint of a spring maximum, are completely dominated by emissions from Asia, with little contribution from the United States or the rest of the globe.

A more complete picture of the atmospheric transport is provided by the simulated time series of NO_y at the 940-mbar level over Hawaii in Fig. 2. We see a collection of discrete transport events superimposed, at a frequency of 3–5 days, over a very low background. In particular, we see that the summer maximum is the result of a few large events. The limited observations appear to have a similar character (B. J. Huebert, personal communication). Both this simulation and the observations at Mauna Loa Observatory suggest that the levels of reactive gases in the remote atmosphere may be highly variable.

During the summer, in both the model and the real atmosphere, the time-mean Pacific subtropical high moves from a latitude of $\sim 20^\circ \text{ N}$ off the Baja to a position north of Hawaii at $\sim 35^\circ \text{ N}$ (ref. 10). At times, this produces a subsiding flow in the lower troposphere from the south-west United States and Mexico to Hawaii. When combined with surface transport from the source regions and small-scale vertical mixing over arid land, episodic transport of NO_y to the vicinity of Hawaii occurs in the model. Three-dimensional trajectories and a detailed

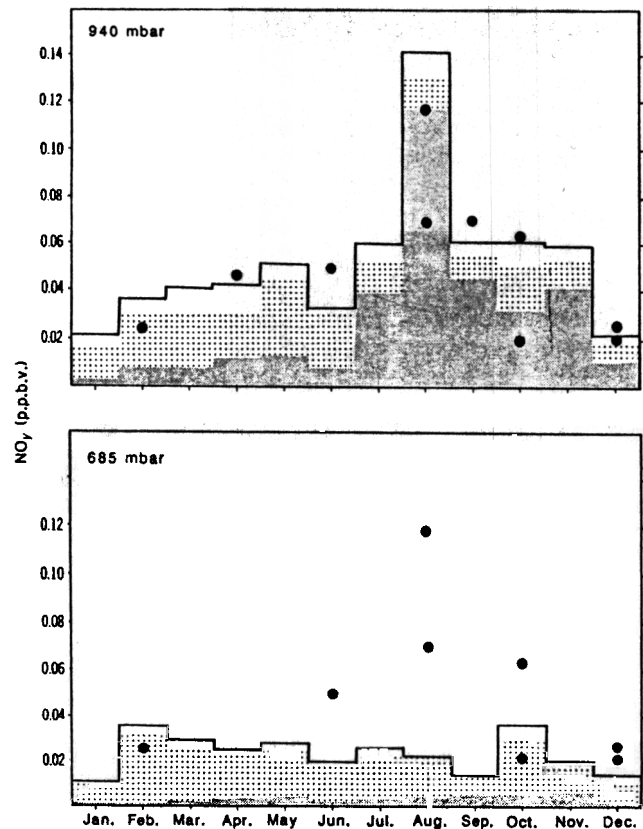


FIG. 1 Ten-day averages of soluble-nitrogen measurements at Mauna Loa Observatory compared with simulated monthly average mixing ratios of NO_y in the 940-mbar and 685-mbar grid boxes located over Hawaii. The dark shaded portion represents the simulated contribution of the US source, and the lighter shading represents the contribution from Asia (in our model a source region bounded on the south by the Equator, on the north by 60° N latitude, on the west by 50° E longitude and on the east by 150° E longitude) and the white area under the solid line represents the contribution from the rest of the globe, principally Mexico, Central America and Europe. The observations are represented by large black dots.

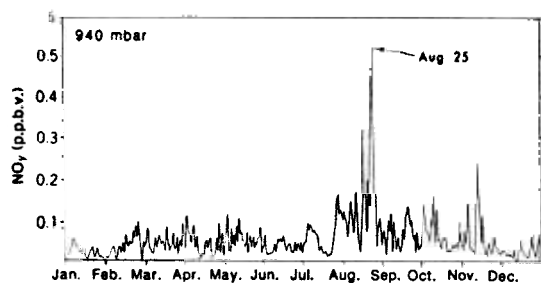


FIG. 2 The NO_x time series at the 940-mbar level in the vicinity of Hawaii constructed with instantaneous values taken every six hours from the simulation for a global source of combustion nitrogen.

synoptic analysis were used to identify this complex transport process (W.J.M., manuscript in preparation).

When using observed wind data, vertical velocity is not available and one must approximate atmospheric motion by assuming that either pressure or potential temperature remains constant. Such approaches can be misleading. Robinson and Harris¹¹ use observed winds to calculate approximate trajectories on constant-pressure surfaces for a number of actual transport events at Mauna Loa Observatory in August. Finding that none of the 700-mbar back-trajectories from Hawaii returned to the United States and none of the 850-mbar trajectories from the United States approached Hawaii, they conclude that US emissions are not involved¹¹. We believe that the actual summertime transport events are as complex as those simulated by the model and cannot be represented by trajectories on constant-pressure surfaces.

The transport of NO_x from Asia is composed of a large number of relatively small (~ 0.1 p.p.b.v.) events. Asian dust, which also has surface sources and is removed by precipitation, may serve as a surrogate for Asian emissions. The dust has been observed throughout the central Pacific, including Mauna Loa, and has a spring maximum^{12,13}. Nitrogen emissions from Asia are expected to follow a similar transport path. To reach Hawaii in the subtropics, the Asian emissions must first be lifted into the free troposphere by storms and carried eastward and north-eastward over the central Pacific. Then the NO_x must be caught in descending air, transported anticyclonically (clockwise) towards the Equator and carried far enough south to be caught in the low-level easterly flow. Such paths have been determined for actual springtime Asian dust events¹⁴ and for our simulated springtime transport of Asian NO_x . Both the lifting over Asia and the descent over the Pacific occur at a range of levels in the troposphere. As a result, the model's Asian emissions are dispersed throughout the lower troposphere. In contrast, the transport from North America is descending all the way to Hawaii in the stable flow of the Pacific subtropical high and should arrive just above the maritime boundary layer.

Based on these results, other model studies⁹, observations^{12,13} and actual climatology¹⁰, we conclude that the maximum in soluble nitrogen observed at Mauna Loa Observatory in the summer and autumn is a result of US fossil-fuel combustion. It travels to Hawaii in stable descending air and is carried up to the observatory by the complex flow associated with the mountain orography. Springtime measurements in the vicinity of Hawaii, but away from the influence of the island's orography, should find episodes of elevated NO_x (mainly from Asia) up into the middle troposphere, while summertime measurements should find episodes of elevated NO_x concentrated in shallow layers just above the maritime boundary layer. □

Received 19 December 1988; accepted 14 February 1989.

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ACKNOWLEDGEMENTS: We thank B. J. Huebert for providing unpublished data and acknowledge the helpful comments of S. Manabe, J. D. Mahman, K. Hamilton and J. R. Toggweiler.

Synthesis of bulk superconducting $\text{YBa}_2\text{Cu}_4\text{O}_8$ at one atmosphere oxygen pressure

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THE well-known 90-K superconductor $\text{YBa}_2\text{Cu}_3\text{O}_7$ ('123') is the first ($n=0$) member of a homologous series of compounds with the general formula $\text{Y}_2\text{Ba}_4\text{Cu}_{6+n}\text{O}_{14+n}$. These compounds combine layers of copper–oxygen pyramids with single and/or double copper–oxygen chains. The $n=2$ member, $\text{YBa}_2\text{Cu}_4\text{O}_8$ ('124'), with double Cu–O chains, and the $n=1$ ytterbium analogue, $\text{Yb}_2\text{Ba}_4\text{Cu}_7\text{O}_{15}$ ('247'), which mixes single and double chains, were first observed as intergrowths in bulk 123 by electron microscopy^{1,11}. The 124 phase was then synthesized as a majority phase in thin films^{2,3,12}, and its crystal structure was determined⁴ and found to be in agreement with the model proposed from microscopy. An important advance in the synthesis of bulk materials, the result of extensive pressure–temperature phase equilibria studies, was the isolation of 124 and 247 at oxygen pressures of >200 atm, and detailed determinations of their crystal structures (see, for example, refs 5–9). High-pressure studies have also shown that the 124 phase could be made with many rare-earth elements¹³. Here we report the synthesis of the 124 phase in pure bulk form by a novel synthetic route in a flowing oxygen stream at 1 atm pressure. This technique allows $\text{YBa}_2\text{Cu}_4\text{O}_8$ to be synthesized without specialized equipment, will make it generally available for study of its normal and superconducting properties, and will make possible more extensive comparisons with $\text{YBa}_2\text{Cu}_3\text{O}_7$ and other high- T_c superconductors. Our results suggest that 124 is the thermodynamically stable phase at low temperatures and 1 atm pressure, under oxidizing conditions; the usual inability to synthesize it in these conditions is probably due to the limitations of reaction kinetics.

The synthesis is a two-step process. In the first step, starting materials are mixed in the correct stoichiometric proportion and heated very slowly to 750 °C in dense, oversized Al_2O_3 crucibles. They are then allowed to react for 16–24 h. All heating, soaking and cooling is carried out in flowing O_2 . Best results are obtained when an intermediate mixing-and-grinding step is performed after the first few hours of reaction at 750 °C. Different combinations of starting materials yield slightly different results. We investigated three different sets of starting materials: (1) $\text{Y}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$, $\text{Ba}(\text{NO}_3)_2$ and $\text{Cu}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$; (2) $\text{Y}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$, $\text{Ba}(\text{NO}_3)_2$ and CuO ; and (3) Y_2O_3 , $\text{Ba}(\text{NO}_3)_2$ and CuO . The first of these, with all materials present as nitrates, always yielded the most phase-pure materials, although 124 did occur as the major phase for all three sets of starting materials. As it was necessary to use hydrated nitrates, the amount of water in the starting materials was determined directly by weight loss on decomposition to the simple oxides, which indicated that