function at a single promoter. Together with biochemical studies of other *ets* proteins, the GABP structure suggests that autoinhibition, conformational change and allosteric effects are potent strategies for modulating the affinity and specificity of DNA-protein interactions and derepressing autoinhibition. Just as transcription is controlled both by positive- and negative-acting proteins, transcription factors can be themselves regulated by opposing pathways.

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ATMOSPHERIC CHEMISTRY

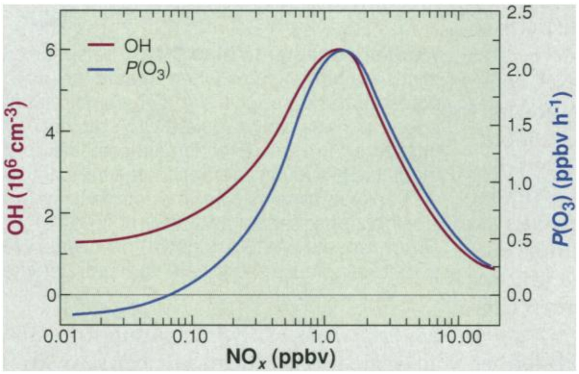
Radical Ideas

Dieter H. Ehhalt

In a recent research article in *Science*, Wennberg *et al.* (*1*) derived the production rate of ozone (O_3) in the middle and upper troposphere from measured concentrations of the hydrogen peroxy radical (HO_2), the hydroxyl radical (OH), and nitrogen oxide (NO). They were able to do so because of the unique and central role OH plays in tropospheric chemistry: OH is the main oxidizing agent in the troposphere, reacting with most trace gases, in many instances as the first and rate-determining step in a chain of reactions. Thus, OH controls the removal and, therefore, the concentrations of many manmade gaseous pollutants as well as natural trace gases. For example, of the 2800 million tons of carbon monoxide (CO) that are turned over annually in the atmosphere, 85% is removed by the reaction with OH to form carbon dioxide (CO_2) (*2*).

The hydroxyl radical is ubiquitous. It is formed primarily in the reaction of water vapor with excited oxygen atoms from the photolysis of O_3 by solar ultraviolet radiation. The required wavelength range below 320 nm nearly coincides with that causing sunburn. We should expect OH formation because O_3 is found virtually everywhere as part of a natural cycle, which in mixing, pushes it down from the stratosphere.

The reaction of OH with molecules, such as CO or hydrocarbons, returns another radical, HO_2 [see reactions 1, 2, 9, and 10 in (*1*)], which eventually is recycled to OH. Thus, the oxidation by OH is catalytic: one OH can destroy several molecules. The rate of HO_2 recycling, and therefore the OH concentration, is greatly enhanced by the presence of NO. At the same time, the other nitrogen radical, NO_2, which is always present along with NO, reacts with OH to form nitric acid (HNO_3), removing OH from the atmosphere. The opposing actions of both processes lead to a highly nonlinear dependence of the OH concentration on $NO_x = NO + NO_2$ (see figure).



Nonlinear chemistry. OH concentration and net O_3 production rate *P* as a function of NO_x concentration, calculated for a clean rural site (ppbv, parts per billion by volume per hour). All other parameters were held constant at the values observed at noon in Mankmoos, eastern Germany (53.8°N, 11.7°E) on 16 August 1994 (summertime). The exact position of the maximum in OH and $P(O_3)$ depends on the choice of the other parameters. In the upper troposphere, its position is shifted to considerably lower NO_x concentrations (*1, 5*).

The nitrogen oxides NO_x have another important role. The reaction recycling HO_2 oxidizes NO to NO_2. Similar reactions take place with organic peroxy radicals formed in the oxidation of hydrocarbons. The resulting NO_2 is rapidly photolyzed in the sunlit atmosphere to produce NO and an oxygen atom that quickly recombines with molecular oxygen to form O_3. This reaction chain is the sole process of O_3 production in the troposphere. In combination with anthropogenic emission of NO, it is the cause of the regional episodes of O_3 pollution as well as of the general increase in the background O_3 concentrations at northern mid-latitudes during this century (*3*). The emission of NO into the upper troposphere by aircraft are another, relatively recently identified element of man's impact on the tropospheric NO_x and O_3 budget (*4, 5*). Without NO, the chemical processes of trace-gas removal induced by OH lead to a destruction of O_3, a phenomenon that has been observed in pristine background air.

Therefore, NO_x not only influences the rate at which HO_x (= OH + HO_2) is cycled between OH and HO_2, it also controls how much O_3 is produced during each cycle. The resulting net production rate of O_3 depends on NO_x concentration in a highly nonlinear fashion, quite similar to the one found for the OH concentration (see figure).

This nonlinear dependence makes model predictions about changes, even the sign of the change, in local OH concentration and net O_3 production induced by the additional input of NO_x dependent on the preexisting levels of NO_x. As in the case of the upper troposphere, these concentrations are often not known. It also causes problems in the design of O_3 abatement strategies, because the lowering of NO_x emissions in areas with a large NO_x burden can lead to local increases in O_3 concentrations, at least temporarily.

Given its role as a driver of tropospheric chemistry, the measurement of OH provides a crucial test of our understanding of atmospheric chemistry. In the case of the upper troposphere, the measured OH concentrations exceed those predicted by models by up to a factor of 5 (*1*). This discrepancy requires the consideration of additional sources of HO_x. Besides the photolysis of acetone, the photolysis of hydrogen peroxide and methyl hydrogen peroxide have been put forward as plausible explanations (*1*).

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This explanation requires a correction of the model processes that transport trace constituents into the upper troposphere from lower altitudes where they are abundant. Such a correction will have a strong impact on the prediction of the photochemical O_3 production in the upper troposphere (*1*).

In contrast, the ground-based measurement of OH in remote or rural areas shows better agreement with the model-predicted values. There is, however, a consistent overprediction by the models of about 30% (*2*, *6*). Because the difference is much smaller and the chemical system much more complex than those in the upper troposphere, there are many possible explanations for the difference, few of which can be excluded at present. On the other hand, the approximate agreement that holds for a broad range of environments, including NO_x levels of a few parts per billion, indicates that our basic understanding of the processes controlling OH is correct. Still, there is much to do. Only a few of the atmospheric chemical regimes have been tested by OH measurements. In particular, the more polluted environments have hardly been investigated. The few older measurements that exist indicate larger discrepancies and poor correlation between measured and modeled OH concentrations (*2*). Only recently have accurate and fast measurements of OH and HO_2 in the troposphere been possible, and only by a few groups worldwide. Moreover, proper interpretation requires a large number of support measurements to determine the various parameters that control OH, which in turn demands large field campaigns. Such work is in progress, hopefully at an accelerated pace as more groups join the field.

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CLIMATE

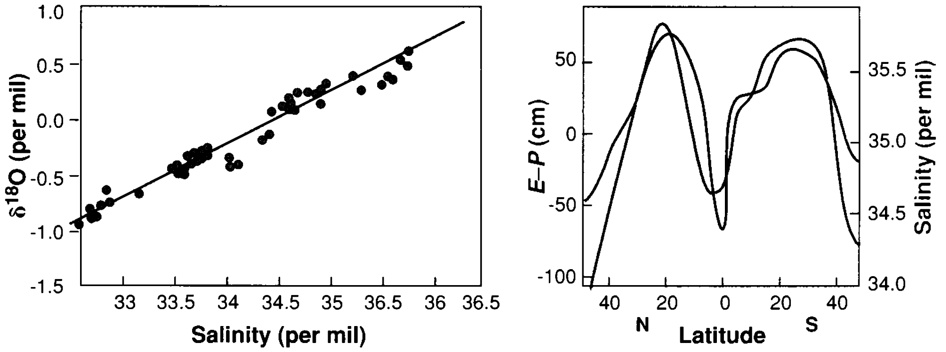
Warmer and Wetter 6000 Years Ago?

Warren Beck

Since the first quantitative measurements of ice-age temperatures (*1*) in the early 1950s, there has been controversy over the use of oxygen isotopes of marine carbonates in reconstructing past climate. Originally viewed as the Rosetta Stone for unlocking the mysterious causes of climate change, measurements of past temperatures based on oxygen isotope data have never quite lived up to expectations. The main defect of this technique has been that there are too many variables and not enough equations. More particularly, the $^{18}O/^{16}O$ ratio of marine carbonates varies as a function of temperature and the $^{18}O/^{16}O$ ratio of seawater. The latter ratio is not constant, however, changing substantially on glacial to interglacial time scales because of fluctuations in the volume of the polar ice caps. This variability results from fractional distillation of ^{18}O from ^{16}O during the formation of vapor and precipitation as water is transferred between the oceans and ice caps (*2*). Various clever strategies (*3*) have been employed as means of placing bounds on this ocean water $^{18}O/^{16}O$ variability, but these methods have not been entirely successful, particularly for sea-surface temperature (SST) reconstructions. High spatial and temporal variability in ocean surface water $^{18}O/^{16}O$ has hampered such efforts. This variability is linked to changes in the salinity of the sea surface, which is caused by fluctuations in the patterns of rainfall, evaporation, and water mass transport fields (*4*). Altogether, these salinity-related effects can have an impact on the $^{18}O/^{16}O$ ratio of marine carbonates formed at the ocean surface that is as large or larger than the impact of temperature variations.

As reported on page 1014 of this issue, Gagan *et al.* turn this defect in the oxygen isotope thermometer into a strength through use of coupled $^{18}O/^{16}O$ and Sr/Ca concentration measurements in corals (*5*). Because coral Sr/Ca ratios also vary as a function of SST (*6*), the use of both tracers in parallel apparently allows for simultaneous solution of SST and ocean surface $^{18}O/^{16}O$ ratios. The latter can tell us a great deal about the patterns of evaporation, precipitation, and ocean surface salinity over the ocean basins (see figure). Gagan and colleagues have used this technique on a ~6000-year-old coral (*5*) from the Great Barrier Reef, Australia, to show that mean SST was then 1.2°C warmer than present, and that the sea surface in this region was enriched in ^{18}O by a substantial 0.5 per mil (1 per mil = 0.1%) relative to modern seawater. These authors suggest that these two observations may be coupled, that is, increased tropical SST may have enhanced evaporation from the tropical Pacific, causing ^{18}O enrichment of the residual sea surface.

To sustain this ^{18}O enrichment, the additional water vapor distilled from the tropical oceans, they argue, must also have been exported to higher latitudes. If Gagan and colleagues are correct, then the extratropics should have experienced wetter conditions at this time as a result of intensified Hadley circulation. This is, in fact, a result predicted by some general circulation models as a consequence of increased tropical temperatures (*7*). Secondary effects of this moisture redistribution may have included changes in the high-latitude surface ocean salinity field, which might have triggered



How rainy was it? The salinity of ocean surface waters (*9*) covaries with $^{18}O/^{16}O$ (as $\delta^{18}O$) (**left**). This covariance is linked to the difference between precipitation to evaporation (*9*) occurring over the ocean surface (**right**). These linkages allow us to recover information about the variations in past rainfall and atmospheric moisture transport from paleorecords of ocean surface $^{18}O/^{16}O$.

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