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Paleoclimate: Toward solving the UV puzzle

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face-dwelling marine calcifying organism: the coccolithophores (see the first figure), perhaps the largest contributors to global marine calcium carbonate precipitation. In laboratory experiments, Zondervan *et al.* have shown that the ratio of calcium carbonate to organic matter decreased with increasing CO_2 (3). This is logical: Increased CO_2 is accompanied by decreased CO_3^{2-} . But the implications of this observation are potentially very important, because of the second component of the biological carbon pump in the oceans.

As discussed earlier, the ocean's organic carbon pump provides a sink for CO_2 . The calcium carbonate pump transports inorganic carbon from the surface ocean to the deep-sea floor, but calcification uses carbon dissolved in seawater as HCO_3^- ions. Two moles of HCO_3^- react with 1 mole of Ca^{2+} to precipitate 1 mole of calcium carbonate, releasing the extra mole of carbon as CO_2 . Thus, biogenic calcification is a potential source of CO_2 to the atmosphere, rather than a carbon sink.

This seemingly counterintuitive observation is important for marine calcification. We imagine that the carbonate accu-

mulations that drape the deep-sea floor or form the White Cliffs of Dover provide a sink for CO_2 , which they do—but only on long time scales. The HCO_3^- used in calcification is indeed originally from the atmosphere. But it is delivered to the ocean from the weathering of continents and is buried as carbonates on long time scales, relative to the surface-ocean process that exchanges CO_2 with the atmospheric reservoir on time scales shorter than 1000 years.

The most interesting part of the work by Zondervan *et al.* is that the decrease in calcification associated with increased CO_2 exerts a negative feedback on rising atmospheric CO_2 . Higher CO_2 leads to less calcification and hence less CO_2 release, counteracting the decreased buffer capacity of the anthropogenic carbon world. However, this should not lead to complacency. Decreased calcification might have major effects on ecosystems [calculations (9) and biosphere experiments (10) suggest that corals will be affected]. It may inhibit sinking of organic carbon from surface waters and lower the ocean's ability to take up CO_2 .

To counteract the rising levels of atmospheric CO_2 , the strategy of carbon sequestration, or carbon fixation, is receiving increased attention. The goal is to capture the CO_2 produced by fossil fuel burning and put it out of harm's way. Some are looking at ways to help the oceans sequester more carbon. It is clear that we have a lot to learn about how this process works, even without human enhancement. Certainly, the influence of manmade or glacial-interglacial shifts in atmospheric CO_2 on oceanic carbon sequestration remains unclear.

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PERSPECTIVES: PALEOCLIMATE

Toward Solving the UV Puzzle

Jelte Rozema, Bas van Geel, Lars Olof Björn, Judith Lean, Sasha Madronich

Springtime depletion of the ozone layer above the Antarctic was first observed by ground-based measurements from Halley Bay from 1979 to 1984 (1). Ever since, there has been great concern about ozone depletion and its consequences for the biosphere, because lower ozone concentrations lead to increased exposure to harmful solar ultraviolet radiation from 280 to 315 nm (called UV-B).

Today's ozone depletion and increased UV-B levels are mainly caused by human-made chemicals, especially chlorofluorocarbons (CFCs). But both ozone and UV-B also vary naturally. Knowledge of past stratospheric ozone concentrations and surface UV-B radiation is rudimentary, but

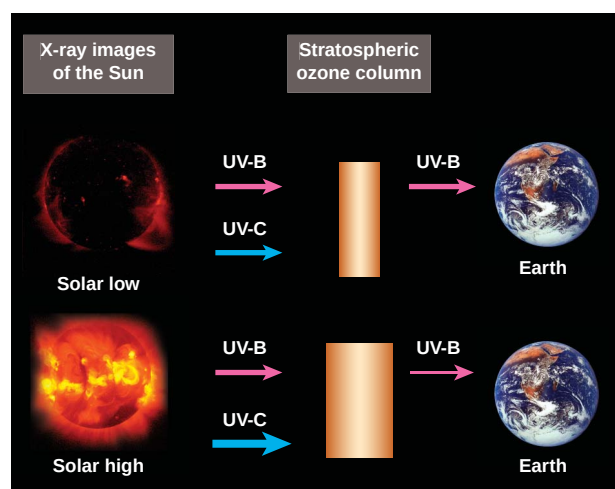
recent research is beginning to shed light on how they have varied on time scales of tens to hundreds of years.

At wavelengths shorter than 242 nm, UV

light dissociates molecular oxygen to form oxygen atoms, which combine with additional O_2 to produce ozone. The ozone absorbs solar radiation at UV wavelengths of 200 to 340 nm and in the visible spectrum. This absorption of UV light by ozone is the primary energy input to the stratosphere.

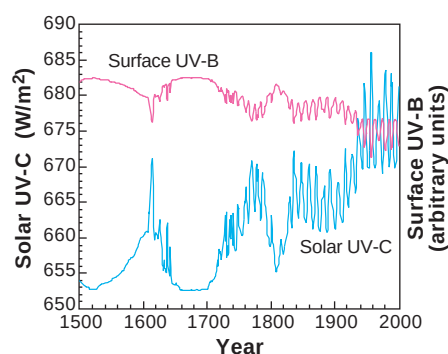
Variations in ozone concentration modulate the stratospheric temperature, leading to changes in atmospheric circulation that may propagate to Earth's surface and influence atmospheric circulation patterns worldwide (2–4). Ozone changes directly alter UV-B received at the surface. However, relating surface UV-B levels to the overhead ozone concentration has proven difficult because ozone variability has multiple causes, the ground-based database is generally poor, and changes in cloud cover and other climate parameters can further alter the surface UV-B.

Systematic instrumental measurements of stratospheric ozone over the Antarctic started only in 1957. Solar UV-B measurements began even later, and systematic ground-



Solar activity, stratospheric ozone, and surface UV-B. At a solar high, solar UV-C is enhanced, leading to a thicker ozone layer and reduced surface UV-B fluxes. Surface UV-B is thus anticorrelated with changes in solar activity (see the second figure). The changing thickness of the stratospheric ozone layer may amplify the changes in solar activity (2) because more ozone means extra absorption of heat, with effects on the stratospheric and atmospheric circulation patterns.

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An anticorrelated past. Reconstruction of annual total solar spectral UV-C irradiance from 1500 to 2000 and predicted (anticorrelated) surface UV-B irradiance. Modified from (22).

based and satellite measurements of total ozone and surface UV-B only exist for the last two decades. Unique measurements of total ozone above Arosa, Switzerland, from 1900 to 2000 indicate a trend of decreasing stratospheric ozone starting between 1975 and 1980, but the strong fluctuations do not allow detection of other patterns in the ozone concentrations (5).

These data sets reveal relations among solar activity, atmospheric ozone concentration, and UV-C radiation (10 to 280 nm). When solar activity is high, so too are solar UV-C radiation and ozone concentrations, which reduce the UV-B radiation that reaches Earth's surface (see the first figure). Irradiance in the UV-C band increased by 2% during recent 11-year solar cycles (6). The corresponding increase in solar (not surface) UV-B irradiance was only 0.4% (7, 8).

Measurements in the tropics suggest a change of ~6% of the total ozone column during the 11-year solar cycle from solar low to solar high (9, 10), whereas estimates from satellite data indicate a column variation of ~2 to 3% (11, 12). Continuous monitoring of spectral UV irradiances at Earth's surface has begun only in the last decade. The collected data are still too noisy to confirm the 11-year variations, but they do show the predicted anticorrelation of UV-B irradiance with ozone column amounts (13, 14).

Historical reconstructions of solar spectral irradiance based on analyses of solar cycles (7) suggest that long-term UV-C variations exceed the 11-year solar cycle amplitudes by a factor of ~2 (see the second figure). During the 17th-century Maunder Minimum (1645 to 1715), UV-C irradiance may have been 3 to 4% lower than today (7). Reduced solar UV-C radiation during the Maunder Minimum epoch of low solar activity suggests that ozone concentrations may also have been lower and surface UV-B radiation higher.

Since the Maunder Minimum, ozone thickness may thus have increased by double the amount of solar cycle variations. On the basis of the ~2 to 6% changes of total ozone and a radiation amplification factor (indicating the increase of radiation damage with 1% ozone depletion) of 2.1 for DNA damage (15), the dose of surface UV-B should be ~4 to 13% lower at maxima of the 11-year solar cycle (16), and surface UV-B should have changed by ~9 to 27% from the Maunder Minimum to today. These changes are comparable to and may even exceed those caused by CFCs.

Biological proxies—indirect records of past changes of UV-B radiation (and hence stratospheric ozone)—can be used to reconstruct historical levels of UV-B on Earth. Recent research (17, 18) shows that plants exposed to elevated UV-B radiation levels, simulating 10 to 50% ozone depletion, generally develop UV-B-protective pigments. These UV-B-absorbing compounds often consist of simple phenolic acids (such as ferulic and coumaric acid), or more complex (poly)phenolic compounds such as flavonoids. They are chemically relatively stable and are preserved well under special environmental conditions (frost, waterlogging, high acidity). Soil cores and lake sediments in the Arctic and Antarctic therefore represent unique archives of past UV climates.

Evidence for increased UV-B radiation during an epoch of reduced solar activity comes from a recent analysis of UV-B-absorbing pigments (scytonemin) of cyanobacteria in shallow Antarctic lake sediments (14, 19). Similarly, flavonoid levels of leaves of the terrestrial moss *Bryum argenteum* collected between 1957 and 1989 from the Ross Sea area of continental Antarctica (20) show that when Antarctic stratospheric ozone concentrations decreased from 1971 to 1980, both UV-B absorbance and relative flavonoid levels increased.

UV-B-induced aromatic groups such as (soluble) flavonoids in pollen and coumaric acid in sporopollenin are particularly promising candidates for reconstructing historic solar UV-B levels. The UV-B-absorbing compound *p*-coumaric acid was found to be a monomeric building block of the highly bioresistant sporopollenin (21), the part of pollen grains that is particularly well preserved in the fossil record.

Reconstructions of past UV-B radiation should be based on the dose-response relation between solar UV-B and the content of UV-B-absorbing compounds in plants. The *p*-coumaric acid content of pollen grains of plants exposed to UV-B levels simulating 15% and 30% ozone depletion has been found to increase substantially (17, 18).

Highly sensitive pyrolysis gas chro-

matography-mass spectrometry allows the quantitative analysis of *p*-coumaric acid content of small numbers of pollen grains or spores (17, 18). This offers the possibility of tracking changes in surface UV-B during 11-year cycles as well as periods characterized by a longer term decline of solar activity. Frozen moss peat banks in the Antarctic, radiocarbon-dated to be 3000 to 5000 years old, are a particularly well-preserved archive. Dry-stored and dated pollen grains from old herbarium specimens may also be analyzed for their flavonoid and coumaric acid content.

The use of biological proxies to reconstruct UV-B on Earth and infer stratospheric ozone variations may help to test and validate relations among solar irradiance, ozone, and climate change during past centuries. The anticorrelation between surface UV-B and solar activity may amplify or mitigate the human impact on climate change. For example, an increase of total ozone caused by increased solar UV-C may counteract CFC-related ozone depletion, whereas a decrease of total ozone caused by lower solar UV-C may exacerbate it. Better knowledge of long-term solar radiation-ozone relations may help to elucidate the resulting climate change processes (2).

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