microgram quantities of substances. But the challenges awaiting organic synthesis are unlimited as ever more complex biological structures are discovered.

In this context, Hirama *et al.*'s synthesis of ciguatoxin CTX3C **1** (see the figure), which is reported on page 1904, is a formidable achievement (*9*). Ciguatoxin CTX3C, a highly potent marine toxin produced by the dinoflagellate *Gambierdiscus toxicus*, belongs to the ciguatera family of neurotoxins, which are causative agents of seafood poisoning in subtropical and tropical regions. These neurotoxins, which are far more dangerous than the related red-tide toxins, the brevetoxins (*10*), can be carried by more than 400 species of fish and are responsible for poisoning more than 20,000 people annually. The content of ciguatoxins in fish is so low that it has hampered their isolation, studies of their biological activity, and, most importantly, the preparation of antibodies to ciguatoxin that would be of enormous help in detecting their presence in contaminated seafood.

The synthetic challenge in building up ciguatoxin CTX3C **1** is reflected in its uniquely complex, ladderlike structure, which contains 13 rings with 5 to 9 members. Twelve of the rings are trans-fused and one belongs to a spiroketal function. In addition, 30 stereogenic centers are disseminated throughout the backbone of the molecule, which does not contain any other elements than carbon, hydrogen, and oxygen.

Hirama's synthesis of **1** hinges upon the union of the two halves **2** and **3** by a remarkably selective acetalization reaction, followed by a challenging metathesis reaction to install the final C–C double bond and, at the same time, complete the construction of the whole skeleton of ciguatoxin CTX3C. It is a clear testimony to the power and selectivity of modern synthetic reagents that this metathesis proceeds, on such a complex structure, with a yield of 77%.

The beauty of Hirama's approach lies not only in the ultimate preparation of the natural product itself and in the demonstration of the ability of organic chemists to assemble such fascinating and complex structures but also in his elegant and highly convergent strategy. The latter should eventually lead to the synthesis of congeners of **1** and to the establishment of antibodies to ciguatoxin for the detection of contaminated seafood.

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PERSPECTIVES: PLANETARY SCIENCE

Clues to the Martian Atmosphere

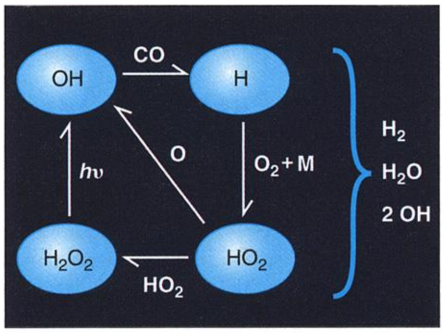
Donald M. Hunten

On page 1914 of this issue, Krasnopolsky and Feldman (*1*) report the detection of molecular hydrogen in the upper atmosphere of Mars. Its presence was predicted almost 30 years ago, but detection proved difficult. The new results furnish strong support for the photochemical models developed (*2*, *3*) to explain the scarcity of CO and O_2 in the martian lower atmosphere. These gases are the photodissociation products of the principal gas, CO_2, in the martian atmosphere and would therefore be expected to be abundant. It took several years to work out why they are not.

The fact that the main constituent (95%) of the martian atmosphere is CO_2 was established almost simultaneously in 1965 by the radio occultation experiment on Mariner 5 (*4*) and by ground-based spectroscopy (*5*). Further ground-based observations detected trace amounts (~0.1%) of CO (*6*) and O_2 (*7*). Earlier work had already established that O_2 was rare. An early attempt to explain this observation (*8*) postulated the formation of a CO_3 molecule that could rapidly react with CO, but this idea was soon refuted by laboratory measurements. A more successful suggestion was that species such as OH and HO_2, produced from water vapor, could be responsible. Water vapor was detected in 1970 (*9*) and has been extensively studied by further ground-based spectroscopy and from the Viking orbiters (*10*, *11*). It shows strong seasonal variations at high latitudes, with maxima in summer and minima in winter.

Attempts to rationalize these observations are based on the concept of "odd hydrogen" (*2*, *3*). Photolysis of H_2O yields H and OH, which engage in catalytic oxidation of CO. Odd hydrogen consists of H, OH, and HO_2. These species rapidly interconvert but only slowly recombine back to "even hydrogen" (H_2O and H_2) (see the figure). The catalytic cycle OH–H–HO_2 is traversed several times per minute under typical daytime conditions near the surface. Each traversal combines one CO molecule and one O atom into a CO_2 molecule, thereby preventing the buildup of CO and O.

However, there is considerable production of O_2 by reactions not shown. Furthermore, the cycle just mentioned requires atomic O. Two solutions for this problem have been offered. Parkinson and Hunten (*2*) invoke the production and photolysis of H_2O_2, whereas McElroy and Donahue (*3*) inhibit the production of O_2 by mixing O atoms down from the upper atmosphere so rapidly that they do not have enough time to react. A number of models published in recent years use better measurements of reaction rates and of the vertical distribution of water vapor in the Mars atmosphere, but the underlying ideas are the same.



Flow chart for the odd-hydrogen system. M is a third body and *hν* represents a solar ultraviolet photon. H_2O_2 appears in the odd-hydrogen box because photolysis rapidly converts it to a pair of OH radicals.

In the present context, the interesting issue is the production of H_2. The reaction of H and HO_2 produces H_2, H_2O, and OH (see the figure). H_2 is nearly inert until it is mixed up to the ionosphere, where reactions with positive ions convert part of it to H atoms. H atoms were first observed by the ultraviolet spectrometers aboard Mariners 6 and 7 (*12*). The detection of H_2 requires much better spectral resolution and has only just been achieved (*1*). It confirms the body of theory that was first worked out to explain the stability of CO_2.

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The models also predict the presence of the powerful oxidants OH and H_2O_2, which would be expected to be present in the soil as well as the atmosphere. The Viking landers performed soil analyses to test for metabolic activity, but it is generally thought that they detected oxidants such as those mentioned above instead. Another experiment looked for organic molecules in the martian atmosphere but found none, a result explained as owing to their destruction by OH. The Mariner 6 and 7 orbiters observed small amounts of ozone in the winter hemisphere but not in warmer regions (*13*), where the odd-hydrogen oxidants would destroy it.

The early work described above was carried out just a few years before the chemistry of Earth's stratosphere suddenly aroused wide attention because of concerns about loss of ozone caused by aircraft exhausts and chlorofluorocarbons. This chemistry had been of interest since Chapman's work in 1930 on the presence of ozone, but the numerical methods were greatly refined by the work on Mars (and Venus). The same reaction set that is important for Mars also plays a key role in Earth's mesosphere (the region just above the stratosphere), except that there is no need to invoke the photolysis of H_2O_2 because O atoms are much more abundant than they are on Mars.

Despite its scarcity on present-day Mars, water carries great interest in a variety of fields (*14*). The presence of eroded channels and other erosion features requires the liquid to have been important earlier in the planet's history. Water is also a component of the polar caps. It must be considered in any scenario for the formation of the solar system. If life ever existed on Mars, liquid water must have been present. And the traces of water vapor in the atmosphere have the profound effects discussed above.

The odd-hydrogen reactions summarized in the figure are responsible for the stability of CO_2, the principal constituent of the martian atmosphere, and the absence of even traces of organic gases. The molecular hydrogen reported in (*1*) is another sign of the presence of odd hydrogen and its photochemical activity.

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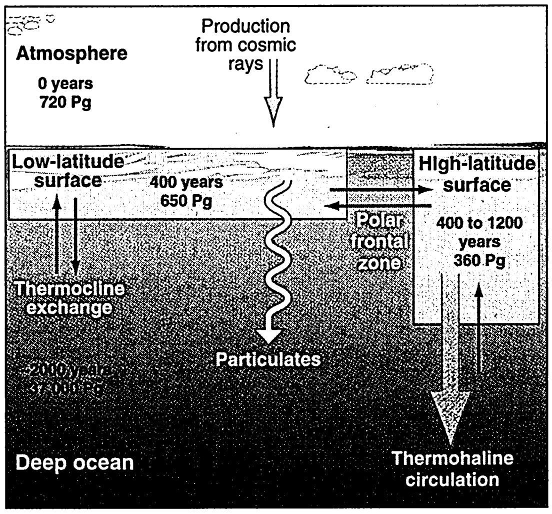
PERSPECTIVES: PALEOCLIMATE

Dating—Vive la Différence

Jess Adkins

Radiocarbon (^{14}C) is a potentially powerful chronometer in paleoclimate studies. Its half-life of 5730 years is well suited to date events from the modern to beyond the Last Glacial Maximum (about 20,000 years ago). However, realizing this potential has proven to be difficult. To know the true age of a carbon-containing sample, one must know the initial amount of ^{14}C at time zero. Because ^{14}C atoms are created in the atmosphere by cosmic rays and are exchanged among active carbon reservoirs on many time scales, this initial value is quite variable.

On page 1917 of this issue, Siani *et al.* (*1*) report a creative approach to circumventing these problems in dating marine sediment cores. The authors use volcanic ash layers to mark synchronous deposition of charcoal and planktonic foraminifera. The difference between radiocarbon dates from the charcoal (which reflects the ^{14}C content of the atmosphere) and the foraminifera (which reflect surface ocean conditions) from the same core is the "reservoir" age of the surface ocean. Using the contemporaneous charcoals to adjust for variability in initial ^{14}C, the planktonic ^{14}C dates can be placed on an absolute age scale, provided the charcoals have not been altered. Marine sediments are among the most important archives of past climate, and the ability to constrain the phasing between them and other records (such as ice cores and terrestrial data) is therefore of fundamental importance.



The ocean/atmosphere radiocarbon system. Today, surface waters between ~40°N and ~40°S have a uniform radiocarbon age of 400 years (the "reservoir age"). A leak of older waters from below pulls them away from the atmospheric value. Modern high-latitude surface waters are older and more variable. The exception is the North Atlantic, where ages remain at 400 years. This feature is the result of the position of the polar front close to the east coast of Greenland. In the past, the position of this front, and therefore the location of old reservoir ages to the north of it, have moved far to the south. Ages are for the inorganic carbon in the reservoir (organic carbon in the ocean is a small fraction of the total) and sizes are in petagrams (10^{15} grams).

To better understand Siani *et al.*'s approach, we need to know how radiocarbon is distributed among its various reservoirs in the ocean/atmosphere system (see the figure). ^{14}C data are reported as $\Delta^{14}C$, a normalized deviation from a standard, in units of per mil (‰) (*2*). New ^{14}C atoms are produced by cosmic rays in the upper atmosphere at a rate of about 2 atoms cm^{-2} s^{-1}. This radiocarbon is quickly oxidized to CO_2 and exchanges with the high- and low-latitude oceans. At high latitudes where new deep waters are formed, ^{14}C is carried to the abyss as dissolved inorganic carbon. Low-latitude surface waters exchange carbon by mixing across the thermocline (*3*), thus increasing the reservoir age away from the atmospheric value. Surface waters also export carbon as organic and $CaCO_3$ detritus, but this has a small effect on the oceanic ^{14}C budget.

Because the bulk of the radiocarbon is contained in dissolved

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