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The History and Stability of Atmospheric Oxygen

Several factors regulate the concentration, but the initial rise is unexplained.

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In their well-known theory of the evolution of the earth's atmosphere, Berkner and Marshall (*1*, *2*) envision a gradual increase in the concentration of oxygen in the atmosphere from trace quantities to about the present amount, with major and rapid fluctuations that may have caused the extinctions at the end of the Paleozoic and Mesozoic. They attribute the rise and the fluctuations to similar changes in the rate of photosynthesis. Others (*3*) have applied these conclusions and they seem widely accepted. I believe, however, that the conclusions and the argument leading to them must be modified.

Sources of Oxygen

We start from the fact that, like any unified set of chemical reactions, photosynthesis does not produce a net change in oxidation. Oxygen is produced, except in bacterial photosynthesis, but a stoichiometrically equal quantity of reduced carbon is also produced. Almost all the oxygen is eventually used to oxidize the reduced carbon. Most of this oxidation occurs in respiration—of animals, of decomposers, and of the plants themselves. Some occurs by forest fires and the like. The only net gain in oxygen equals the amount of reduced carbon buried [as peat, black mud, and similar sediments, and smaller concentrations but much larger amounts (*4*) elsewhere] before it is oxidized. Most of this buried carbon is also later oxidized.

Because animals and plants have geologically very short lives, and even plants respire and so oxidize some reduced carbon almost immediately, most individual molecules of carbon will remain reduced only for periods of months or a few years. This parameter (median time between reduction and oxidation) needs to be estimated adequately; trees may extend it somewhat. This is the time interval of any immediate decrease in atmospheric oxygen caused by a decrease in photosynthesis, whatever the cause of the latter decrease. I will show that any such rapid decrease in oxygen must be negligible anyway.

Some reduced carbon is of course incorporated into the bodies of the green plants themselves. In a steady state, however, this is balanced by the loss (to herbivores, parasites, and decomposers) of reduced carbon that had been produced earlier. Unless there is almost always a steady state, even a small excess or deficit will lead to geologically rapid extinction or unlimited increase in plant mass, without a steady state, beyond the mass of the earth. Cycles in the amount of reduced carbon are equivalent to steady states for this purpose.

Other net sources of oxygen, such as nitrogen fixation and the photolysis of water in the upper atmosphere followed by the differential escape of hydrogen, have been thought to be quantitatively unimportant (*2*, *5*). Recently Brinkmann (*6*) has challenged the calculations which led Berkner and Marshall to believe that photodissociation of water vapor in the upper atmosphere was an unimportant source of oxygen. He used a more precise theory and found that this process would produce, over the earth's history (4.5×10^9 years), about seven times the present mass of oxygen in the atmosphere.

However, even Brinkmann had to make three assumptions which may be questionable. One is that the concentration of water vapor in the upper atmosphere has been nearly constant throughout geologic time. To the extent that water vapor above the cold trap in the atmosphere forms by oxidation of methane and other constituents (*7*), some variation over geological time might be expected as the composition of the atmosphere changes. The first assumption is more plausible than the second, which is that half of the hydrogen freed by the photodissociation escapes from the earth's atmosphere. This fraction has a large error of estimation, and even the error can not be usefully approximated yet. The third assumption is of a constant solar flux over geological time, in particular that the present value equals the mean (*8*). The sun's luminosity has, however, increased to several times what its value was when the sun entered the main sequence of the Hertzsprung-Russell diagram, that is, since about the time of the formation of the earth (*9*). The net production of oxygen is directly proportional to the product of the variables in the three approximations.

I have not been able to find an estimate for the net accretion of hydrogen by the earth from the solar wind, but this process qualitatively opposes pho-

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tolysis. The photolysis of methane (*7*) may also be relevant. Therefore, the net production of oxygen by photodissociation of water vapor may well be important, but Brinkmann's estimate may be somewhat too low or, perhaps more likely, too large.

Stability

There are several ways in which a net loss of molecular oxygen occurs. Apparently the most important (*5*) is the oxidation of volcanic gases. Ferrous iron, sulfur, sulfide, and manganese are also significant. We should probably include here the oxidation of buried carbon and organic chemicals that become exposed later, and the accretion of hydrogen from the solar wind. These processes are called oxygen sinks.

Estimates of the net gain and net loss (*10*) over geologic time roughly balance, but the error in both is too large to give much confidence in the actual values. This is partly true because the more important estimates that Holland and others use for the relevant parameters have never been adequately derived. Rubey (*11*), the most important single source, has not yet presented the derivations of these estimates. Nevertheless, everyone has taken his estimates as being accurate. They need to be derived again with realistic estimates of error.

Now what can happen if photosynthesis is suddenly and drastically reduced? At the new steady state there will be an equality between production of oxygen and its consumption in the oxidation of carbon. We might think that, before this new steady state occurs, animals and decomposers could use up much of the previously stored carbon in plants, creating a net loss of oxygen. However, even if all the carbon in all organisms now alive were oxidized, this would decrease the atmospheric concentration of oxygen by less than 0.1 percent from its present value (*12*). A larger decrease, but still much less than 1 percent, would occur from the oxidation of all reduced carbon available in soils and the like.

We might alternatively think that animals could maintain their previous abundance and so give a progressive decline in oxygen (*13*). But what material is eaten by animals is unavailable to decomposers, so the oxidation budget is unchanged (*14*).

If the same proportion of reduced carbon is buried at the new steady state (after reduction of photosynthesis) as was the case previously, the net production of oxygen will be lower because less carbon dioxide is being reduced. This will, however, not affect the oxygen sinks, which will continue at their previous rate unless the cause of reduced photosynthesis also affects them. Can the relatively increased sinks cause a moderately rapid reduction in free oxygen?

We can look at this question from three standpoints. Holland (*10*) estimates that, over a minimum period of 10^9 years, about 200×10^{20} grams of oxygen have been used to neutralize inorganic oxygen sinks. This averages to a sixth of the present atmospheric oxygen every 10 million years or probably a longer time, with a reduction of this amount occurring if photosynthesis were completely stopped. Such a decrease is equivalent to an increase in altitude from sea level to less than 1500 meters. Such a reduction is hardly sudden, or even appreciable over a geologically significant time, unless there have been large variations in the emission of volcanic gases, the most important of the inorganic oxygen sinks, or in erosion of previously buried organic carbon (*15*). There are no useful estimates of how variable volcanism has been over geological time (*16*). There are also no adequate estimates on the variation in reduced carbon deposited at different times (*17*). Worldwide variation in erosion has probably occurred, but its amount is controversial (*18*). Any reduction in oxygen will of course be ameliorated by whatever proportion of photosynthesis survives. If only half the photosynthesis of the world is eliminated, a given reduction in oxygen will take twice as long as by the above argument.

A second approach is to see if we can find evidence in the chemistry of ancient rocks that bears on the degree of constancy of atmospheric oxygen concentration during Phanerozoic time. Holland (*19*) thought the approximate constancy of the ratio of ^{13}C to ^{12}C in limestone since the Precambrian indicated a similar constancy in burial of reduced carbon, but all we can really conclude is that the turnover time of the carbon cycle has been relatively low for this interval. The ratio of ^{34}S to ^{32}S is much lower in late Paleozoic rocks than it is in rocks deposited earlier and later (*20*); there is a strong and rather consistent trend that, like any pattern in the natural world, needs an explanation. The explanation that seemed likely in 1966 was that sulfide decreased both absolutely and relative to sulfate as the isotope ratio decreased. This could then be related to the concentration of atmospheric oxygen, which would change in the same direction. It now seems, however, that the sulfur cycle is more complex and that isotope ratios do not give the desired information (*21*).

Regulation

The third approach is to note that a continued reduction of oxygen leads to its absence. This is not observed; not all metazoans have become extinct. The rate of possible change is sufficient that random changes in concentration would very likely have either eliminated free oxygen or increased its concentration immensely, or both. An increase by a factor of 1000 would eliminate the water of the oceans; nothing approaching this is possible from the sedimentary record. A large increase would probably have also caused the extinction of terrestrial metazoans much before this point, but because of the adaptability of evolution even the extreme present tolerances do not make a reasonable estimate of past tolerances possible. We therefore need one or more mechanisms of negative feedback. These would be concentration-dependent controls on the oxygen concentration, increasing it when it declines and decreasing it when it rises, and therefore giving a stable equilibrium.

There are only two known inorganic processes that are appreciably dependent on the concentration of oxygen and that would also appreciably affect this concentration (see below). Net photosynthesis, on the other hand, is somewhat inhibited by oxygen (*22*) except at very low concentrations, so this may provide a slight regulation over millions of years. Photosynthesis is, however, rather more dependent on the concentration of carbon dioxide, and it is difficult to predict the effect of a reduction in oxygen or photosynthesis on the concentration of carbon dioxide (*23*) although the two cycles obviously interact. Holland (*24*) believes that the magnesium carbonate buffer system of the oceans has kept the atmospheric concentration of carbon dioxide in the range of one to four times the present value since land plants originated in the Silurian (*25*), but that it may have been as much as 100 times greater earlier. A third or more of the world's photosynthesis now occurs by marine algae (*23, 26*). These would be little affected by changes in carbon dioxide concentration in the atmosphere.

Any regulation of atmospheric oxygen by such concentration-dependent properties of photosynthesis, however, must operate through the slow net increase equivalent to the excess of the burial of reduced carbon over its oxidation during erosion. This increase is roughly a sixth of the present atmospheric oxygen per 10 million years (*5*) for the amount now present, even ignoring all inorganic sinks operating contemporaneously. Considering the latter, the regulation will be much less. Furthermore, plants might respond to an increased partial pressure of oxygen by a higher optimum. However, since the optimum is now markedly below the present partial pressure, this seems unlikely.

By setting the amount of oxidation of solid inorganic substances proportional to the partial pressure of oxygen, Brinkmann (*6*) was able to obtain, for the first time, a regulated system. However, his assumption may be incorrect. Brinkmann ignored the oxidation of volcanic gases, which Holland (*5, 10*), Mason (*27*), and others have considered to be the most important source of reduced material. With a large excess of oxygen, the amount of oxidation is not proportional to the partial pressure of oxygen, since the oxidation will take place soon unless there is very little oxygen available. However, if some hydrogen escapes from the atmosphere, the probability of its not reacting with an oxygen molecule or its dissociation products first should be inversely proportional to the partial pressure of oxygen, so there is a residual effect. The rate of this escape is unknown and should depend partly on the turbulence from occasional but large volcanic explosions, although a large proportion of magmatic gases may escape through fumaroles, hot springs, and less obvious routes. Oxidation of surface materials such as iron, manganese, and sulfur may also not be importantly concentration-dependent in a large excess of oxygen, although some effect is likely.

We have here, however, a second mechanism for regulation of atmospheric oxygen concentration. It can be augmented in three ways. Some of the hydrogen from photolysis of water vapor in the upper atmosphere diffuses down through the atmosphere (*28*). This would also be true for whatever hydrogen is captured from the solar wind. A little hydrogen is also produced by organisms (*23*). Some hydrogen from these sources will escape after reaching the oxidizing region of the atmosphere, but, as with hydrogen from volcanoes, the proportion doing so will be inversely related to the oxygen concentration.

This second mechanism cannot be evaluated qualitatively without more data than are now available. If one uses Holland's figure (*10*) for volcanic hydrogen, however, it is probably no more and perhaps much less important than the weak regulation by photosynthesis. However, a concentration-dependence of some kind seems the only available reason (other than exceptional luck) why atmospheric oxygen has not virtually disappeared at some time in the Phanerozoic. A random walk, which would occur otherwise, is inherently unstable.

Broecker (*29*) has recently proposed a third kind of regulation. An increase in atmospheric oxygen would probably cause a decrease in the proportion of water that is anaerobic. This would then increase the proportion of organic carbon that is oxidized before burial and so permit the inorganic oxygen sinks to decrease the free oxygen. A decrease in atmospheric oxygen would have the reverse effect. The effect of this mechanism depends on what proportion of buried reduced carbon is buried under anaerobic conditions. I know of no estimate of this parameter. Because terrestrial sediments often persist for long periods, they are as relevant here as elsewhere.

Like my first regulating mechanism, Broecker's depends on the burial of reduced carbon and so may be slow even geologically. Any large and rapid effect would require the net burial of an amount of reduced carbon an order of magnitude or two greater than all the known coal of the Carboniferous.

Within a large sampling error, the mean rates of production of oxygen and of its loss have been equal for the last 10^9 or so years. In fact this must be approximately true, because the amount of oxygen used to neutralize sinks has been one to three orders of magnitude larger than the amount that is now in the atmosphere. This near equality is puzzling. The oxygen sinks are largely independent of the concentration of oxygen, and they may well have varied somewhat over geologic time. Other factors than the weak dependence on oxygen concentration may well have been much more important in determining the world rate of photosynthesis. Some of these factors are carbon dioxide concentration; temperature (perhaps related); proportion of land, shallow sea, and deep sea; oceanic currents; the composition of seawater; and actions of animals and plant parasites on green plants. Furthermore, the feedback response in the atmosphere, caused by photosynthesis, to change in oxygen concentration is slow even on a geologic scale. Broecker's mechanism or some similar process may be more powerful, but this is now unclear. The relative constancy of the concentration in the face of perturbations itself argues for a more powerful regulation, possibly involving carbon dioxide. It would nevertheless not be surprising if gradual and moderate changes in concentration have occurred.

Early History

A major contribution of Berkner and Marshall was to emphasize the significance of the Pasteur point, the concentration (more strictly partial pressure) of oxygen at which respiration becomes more efficient than fermentation. It is about a hundredth of the present concentration, although it varies for different organisms. Before this time there may not have been a balance between the oxygen production by photosynthesis and oxidation of the reduced carbon. The oxygen excreted by plants would be used in large part for the reduction of more reactive inorganic oxygen sinks. Because this oxygen could not be used simultaneously to reoxidize the carbon reduced in photosynthesis, there would be an accumulation of a relatively large part of the reduced carbon then present in organisms unless, as Macgregor (*30*), Rubey (*31*), Fischer (*25*), and Cloud (*32*) have proposed, there were major heterogeneities in the ocean. Because even bacteria respire, with virtually the same enzymes as does a tree or a mammal, at least local and temporary advantages for respiration presumably preceded the origin of eukaryotes.

To reach and pass the Pasteur point requires, by most current theory, the oxidation of a reducing atmosphere. How much of the atmosphere was of reducing gases is disputed to orders of magnitude (*5, 23*), but this may be of relatively minor importance (*33*). In one alternative, among organisms there was a large net excess of oxidation over reduction, because of a low rate of respiration. An increase in world photosynthesis would oxidize the atmosphere and keep pace with the continuous inorganic sinks in a very short time geologically at a rate of photosynthesis much below the present. This time and rate of course depend on each other and on the values chosen for the other variables. The rate-limiting factor might be the carbonate dissolved in water. The increase would probably stop only when balanced by respiration. There seems to be no way to predict within more than an order of magnitude the concentration at which such a balance would occur; it might be more than, or much less than, the present value. However, at this time there would be a very large amount of reduced carbon more or less available for decomposers, so the oxygen concentration would decrease somewhat. This decrease would not be a large proportion of the present mass of atmospheric oxygen because of the calculations given above, but it might have been a significant part of the atmospheric oxygen at that time. This alternative implies, however, that there would be an enormous volume of reduced carbon buried [far more than the reserves of coal and oil (*34*) now known] in a geologically negligible time. Such deposits have not been found.

In the other alternative (and intermediate situations are possible) there is a near balance between organic oxidation and reduction for, say 10^9 years before the Pasteur point as well as later. A mechanism for such a balance is not apparent before the Pasteur point, but we should examine the consequences of such an assumption because the first alternative gave an unverified prediction.

The existence of continuous inorganic oxygen sinks is a formidable problem. The net production of oxygen even today, and throughout Phanerozoic time, is about equal to that absorbed by the sinks, as noted above. Where then is the oxygen to come from that would not only oxidize these sinks at a time of presumably much less photosynthesis than now but would also oxidize a reducing atmosphere? We may postulate that the sinks were much lower than in the Phanerozoic even though less degassed crust was being recycled (*35*). We may postulate that net photodissociation of water vapor was much greater. We may postulate a very large amount of photosynthesis (*36*). We may postulate much burial of organic carbon. We may postulate the former absence of an unknown major regulator of Phanerozoic oxygen. We may postulate, with Davidson (*37*) and Brinkmann (*6*), an early oxidizing atmosphere. None of these partly interdependent postulates seems particularly plausible, but I do not see any alternatives except the temporary imbalance rejected above. The problem is in an unsatisfactory state, but we may at least recognize that there is a problem.

Summary

There are three processes weakly concentration-dependent that keep changes in concentration of atmospheric pressure from being a random walk—inhibition of net photosynthesis by oxygen, the passage of hydrogen through the oxidizing part of the atmosphere before it escapes from the earth, and burial of reduced carbon in anaerobic water. A stronger regulator seems desirable but remains to be found. The cause of the initial rise in oxygen concentration presents a serious and unresolved quantitative problem.

References and Notes

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2. ———, *J. Atmos. Sci.* **22**, 225 (1965).
3. P. E. Cloud, Jr., in *Evolution and Environment*, E. T. Drake, Ed. (Yale Univ. Press, New Haven, Conn., 1968), pp. 1–72; H. Tappan, *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **4**, 187 (1968); M. G. Rutten, *ibid.* **2**, 47 (1966); → A. L. McAlester, *J. Paleontol.* **44**, 405 (1970).
4. About 1000 times as much reduced carbon occurs dispersed in sediments, as in coal, oil, and the like [H. Borchert, *Geochim. Cosmochim. Acta* **2**, 62 (1951) and (*11*)].
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12. This result was suggested by an analogous calculation of D. L. Gilbert [in *Handbook of Physiology*, W. O. Fenn and H. Rahn, Section Eds. (American Physiological Society, Washington, D.C., 1964), vol. 1, section 3, pp. 153–176] and E. K. Peterson [*Environ. Sci. Technol.* **3**, 1162 (1969)]. Others [W. S. Broecker, *Science* **168**, 1537 (1970); J. H. Ryther, *Nature* **227**, 374 (1970); L. Macheta and E. Hughes, *Science* **168**, 1582 (1970)] have recently come to the same conclusion. Estimates of the amount of carbon in living organisms vary from 1.8×10^{15} to 70×10^{15} grams [A. Poldervaart, in *Crust of the Earth*, A. Poldervaart, Ed. (Geological Society of America, New York, 1955), pp. 631–650; his table 7 is too high by an order of magnitude by comparison with his sources]. There are about 12×10^{20} grams of oxygen in the atmosphere, and 2.7 grams of oxygen oxidize 1 gram of carbon. Some carbon in organisms is already partly or completely oxidized. Peterson [cited above; *Environment* **12(3)**, 32 (1970)] and others [Broecker and Ryther, cited above; (*29*)] have come to a similar conclusion for possible increase in magnitude of all present human technological effects. In fact, Peterson's conclusion led to my investigation of the problem. Moreover, if synthetic foods are ever developed and become widespread, there can be a geologically rather rapid depletion of atmospheric oxygen, but a rough calculation, based on average use of 100 grams of oxygen per day per person [S. Brody, *Bioenergetics and Growth* (Reinhold, New York, 1945)] indicates several million years for the present population to use all the oxygen now available.
13. The decomposers get some reduced carbon back from dead animals, but the latter have already oxidized some when alive.
14. This argument, together with the relatively small amount of reduced carbon deposited in sediments [0.1 percent according to W. S. Broecker (*29*)] is strong evidence that the joint density of herbivores, decomposers, predators, and parasites is regulated in the long run by the availability of reduced carbon in plants [L. G. Hairston, F. E. Smith, L. B. Slobodkin, *Amer. Natur.* **94**, 421 (1960)]. I will present elsewhere quite different evidence that gives the same conclusion for herbivores alone. The details of the flow of reduced carbon is the basis for what ecologists call "energy"; the latter concept, however, includes trophically irrelevant energy sources. Some carbon is incorporated into heterotrophs from the reduction of carbon dioxide [H. G. Wood and M. F. Utter, in *Essays in Biochemistry*, P. N. Campbell and G. D. Panville, Eds. (Academic Press, New York, 1965), vol. 1, p. 1], but its amount is small and is balanced by corresponding oxidations.
15. H. D. Holland (personal communication) has revised estimates which considerably decrease the minimum time for an appreciable effect to occur.
16. A. M. Ziegler, personal communication. A. B. Ronov [*Geokhimiya* **1959**, 397 (1959) (translated in *Geochemistry* (*USSR*) **1959**, 493 (1959)] has given a graph of some variations in volcanism but without estimating errors or converting volume to rate of production. Seafloor spreading, a concept popularized after 1959, also affects the estimates.
17. Ronov [see (*16*)] has given estimates of proportion of reduced carbon in sediments of different ages, but the comments on this paper [see (*16*)] also apply here. Rate of sedimentation also needs to be incorporated for carbon. This approach is nevertheless potentially critical to the extent that the areas sampled can be taken as random for the purpose of variation in deposition of reduced carbon over geological time.
18. A. B. Ronov [*Sedimentology* **10**, 25 (1968)], like most previous authors, believes the present rate of erosion is several times larger than the average over the last 10^9 years. Others [J. Gilluly, J. C. Reed, W. M. Cady, *Bull. Geol. Soc. Amer.* **81**, 353 (1970)] believe the present rate is probably not more than twice the mean Phanerozoic rate. B. Gregor [*Nature* **228**, 273 (1970)] has a partly intermediate conclusion. Ronov's paper, like others on the subject, ignores possible regeneration of crust, which would reduce the difference between estimates of present and past rates, but man seems to have increased the mean rate significantly (see B. Gregor, cited above).

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29. W. S. Broecker, *J. Geophys. Res.* **75**, 3553 (1970).
30. A. M. Macgregor, *S. African J. Sci.* **24**, 155 (1927).
31. W. W. Rubey, in *Crust of the Earth*, A. Poldervaart, Ed. (Geological Society of America, New York, 1955), pp. 631–650.
32. P. E. Cloud, Jr., *Science* **148**, 27 (1965).
33. Among other curious conclusions, M. G. Rutten [*Space Life Sci.* **2**, 5 (1970)] maintains that there was a regulation of oxygen concentration at the Pasteur point, because with a greater concentration respiration would increase and use the oxygen, whereas with a lower concentration fermentation would increase and oxygen would accumulate. However, both respiration and fermentation are oxidative processes (see arguments elsewhere in this article for additional points).
34. M. K. Hubbert, in *Resources and Man*, Committee on Resources and Man of the National Academy of Sciences, Eds. (Freeman, San Francisco, 1969), pp. 157–242.
35. A. B. Ronov [*Geokhimiya* **8**, 175 (1964); translated in *Geochem. Int.* (1964), p. 713] believes there was an immense outgassing about 2.6 × 10^9 years ago in conjunction with the implacement of half or more of the earth's plutons, but if this event is real it may be related to the closest approach of the moon [J. A. Cooper, J. R. Richards, F. D. Stacey, *Nature* **215**, 1256 (1957)], which would undoubtedly affect the atmosphere also. The "anorthosite event" and other later phenomena [N. Herz, *Science* **164**, 944 (196 → P. E. Cloud, Jr., *ibid.* **160**, 729 (1968)] have also been related to the moon's approach.
36. It is not impossible that world photosynthesis was then much more than it is today. I will present elsewhere a mechanism for controlling the ratio of nitrogen to phosphorus in the ocean; the mechanism implies that nitrogen is not, and that phosphorus may be, the major limiting factor for total marine photosynthesis. The mechanism requires the presence of nitrogen-fixing blue-green algae. The similarity of *Gunflintia* to the nitrogen-fixer *Anabaena* in morphology, as suggested by G. E. Hutchinson (personal communication), makes plausible a physiological similiarity. If more phosphorus was present than there is now, and Hutchinson suggests this might have been the case because of the prevalence of ferrous rather than ferric iron, then the rate of photosynthesis may also have been larger.
→ C. F. Davidson, *Proc. Nat. Acad. Sci. U.S.* **53**, 1194 (1965).
38. I am an ecologist, not a geochemist, and the viewpoint of this article comes readily from familiarity with the formally similar problem of regulation of population density of organisms. In fact, the question as to the cause of regulation of oxygen seemed so obvious that I assumed the answer was well known until I asked what it was. Several areas of science relate to the subject of this article, and I am grateful to the following people for information, comments, or reading of the manuscript: R. G. Alderfer, A. T. Anderson, Jr., W. S. Broecker, S. Chandrasekhar, R. N. Clayton, P. E. Cloud, Jr., H. D. Holland, J. D. Hudson, G. E. Hutchinson, D. A. Janzen, J. P. Lodge, B. Mason, P. Meyer, E. K. Peterson, T. J. M. Schopf, J. M. Witting, and A. M. Ziegler. Partly supported by a research career development award from PHS.

Mammalian Scent Marking

Mammals mark when dominant to and intolerant of others, not just when they possess a territory.

Katherine Ralls

Most mammals have a highly developed olfactory sense which they employ in social communication, using chemical signals originating in urine, feces, or cutaneous scent glands (*1*). Many use specialized motor patterns to deposit the chemical signals on environmental objects or other animals of the same species; such behavior is referred to as scent marking or marking (*2*). Very little is known about the chemical nature of these signals although the composition of some scent gland secretions has been studied by perfume chemists (*3*). One of the major components of the secretion of the tarsal gland of male black-tailed deer, *Odocoileus hemionus columbianus*, has recently been identified (*4*).

Although marking has long been recognized as an important form of communication in mammals, our understanding of the messages communicated by the marks has remained vague due to lack of information on the stimulus situations which elicit marking and the reactions of other animals to the marks.

Several general kinds of marking can be distinguished on the basis of the functions which the marks seem to serve. For example, marks or scents may be used primarily for laying trails, as in the slow loris, *Nycticebus coucang* (*5*); for alarm signals, as in mice (*6*) and probably rats (*7*); for individual recognition, as in mice and deer (*8*); for group recognition, as in the sugar glider, *Petaurus breviceps* (*9*); for species or subspecies recognition, as in voles and mice (*10*); for sexual attraction, as in many estrous female mammals (*11*); and as primer pheromones influencing reproductive processes, as in mice (*12*). One secretion may serve a number of these functions (*9*).

A very common kind of marking is that which, since the classic paper by Hediger in 1949 (*13*), has been characterized as "territorial marking." This terminology implies that the marks serve to identify a territory, that is, a fixed area of land which the marking individual will defend against rivals of the same species. Such an interpretation is no doubt correct for some species, but it should not be assumed that all marking is territorial.

Among Hediger's examples of "territorial marking" were the ritualized urination and defecation of the black rhinoceros, *Diceros bicornis* (*14*), and the marking with the retrocornal gland shown by the chamois, *Rupicapra rupicapra* (*13*). Recently, both of these species have been studied in the field. Schenkel (*15, 16*) reports that the black rhinoceros is not territorial; Krämer (*17*) finds that the marking of the chamois is not associated with the possession of a territory. In both cases, it must be some factor other than the possession of a territory which stimulates the animals to mark. Several experimental studies of this kind of scent marking carried out within the last 5 years (*9, 18–32*), have provided a closer look at the stimulus situations which elicit marking. The species which have been studied experimentally tend to mark frequently in any situation where

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