lation changes (*11*) is not matched by my findings in the Arctic. This discrepancy can be explained as follows. During prolonged warm periods, the heat supplied by solar radiation, required to increase surface water temperatures, also enhanced glacial melting. Consequently, as long as continental glaciers existed, seawater at high latitudes did not warm up to the same extent that it did at low latitudes. Alternately, it is conceivable that, owing to the extremely low rates of sedimentation in the investigated region of the Arctic, the resolution is much lower than that obtained by Emiliani in the Carribean (*12*). Emiliani (*10*) suggests the existence of "strong glaciations and warm interglacials" as well as "milder glacials and interglacials." It is quite possible that only during the long warm interglacials did the Arctic become free of permanent pack ice. The Foraminifera-poor beds were deposited in these intervals, whereas the Foraminifera-rich beds were laid down in "mild glacial" times. During the cold minima or "strong glaciations" of the last 0.7 million years, the Arctic surface must have been frozen all year round. Productivity must have been less than at present, and sediments deposited throughout these periods would be limited to clay-sized particles carried in suspension by deep currents. As a result, there would be practically no record of these intervals.

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References and Notes

1. Y. Herman, *Nature* **201**, 386 (1964); *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **5**, 251 (1969).
2. T. L. Ku and W. S. Broecker, *Progr. Oceanogr.* **4**, 105 (1967).
3. B. A. Steuerwald, D. L. Clark, J. A. Andrew, *Earth Planet. Sci. Lett.* **5**, 79 (1968).
4. A. Cox, R. R. Doell, G. B. Dalrymple, *Science* **144**, 1537 (1964).
5. T. I. Linkova, *The Present and Past of the Geomagnetic Field* (Nauka Press, Moscow, 1965), pp. 279–281; T. L. Ku, W. S. Broecker, N. Opdyke, *Earth Planet. Sci. Lett.* **4**, 1 (1968).
6. Y. Herman, C. Vergnaud Grazzini, C. Hooper, in preparation.
7. P. K. Weyl, *Meteorol. Monogr.* **8**(30), 37 (1968).
8. P. E. Damon, *ibid.*, p. 106; R. F. Flint, *Glacial and Pleistocene Geology* (Wiley, New York, 1957); W. Hamilton, *Meteorol. Monogr.* **8**(30), 128 (1968); W. F. Tanner, *ibid.*, p. 126.
9. C. Emiliani and J. Geiss, *Geol. Rundsch.* **46**, 576 (1967); R. Selli, *Progr. Oceanogr.* **4**, 67 (1967); W. A. Berggren, *G. Geol.* **35**(2), 291 (1968).
10. C. Emiliani, *J. Geol.* **74**, 109 (1966).
11. M. Milankovitch, *Handb. Geophys.* **9**, 593 (1938).
12. C. Emiliani, personal communication.
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Hydrogen Bonding in Hydrochloric Acid Solutions

Abstract. *The radial distributions of atom pairs in water and in solutions of hydrochloric acid have been measured by x-ray diffraction. The near-neighbor water correlations are strongly affected by the ions. Part of the experimental distributions is attributed to new oxygen-to-oxygen distances, associated with the presence of excess protons, and these distances become shorter as the concentration of the acid increases.*

Theoretical activity, stemming, in part, from experiments relating to "anomalous water," has developed regarding shorter than normal oxygen-hydrogen-oxygen bond distances in water (*1*). The actuality of "anomalous water" (as a single-phase, pure material) has been challenged (*2*). Nonetheless, the structural calculations, as they relate to the symmetry and length of the O–H bonds and the magnitude of the O–O distances, may be of broader significance. Indeed, those parameters in crystalline materials have been a matter of interest for some years (*3*), and their possible role in solutions has been briefly considered (*4*). We therefore report preliminary results of an x-ray diffraction study of HCl solutions, which may be relevant in a consideration of O–H–O bonding.

A more or less direct reduction of the x-ray intensity scattered by a liquid specimen yields a pair distribution function, $4\pi r^2\rho(r)$. For a pure liquid $4\pi r^2\rho(r)\,dr$ would be the number of atom centers in a spherical shell of radius r and thickness dr, centered on an average atom. For a polyatomic material the function is the sum of partial functions, corresponding to each of the possible pair types, with each partial function weighted on the basis of the relative scattering power of that particular pair (*5*).

Figure 1 shows the $4\pi r^2\rho(r)$ functions for pure water and for 2*N*, 4*N*, and 6*N* HCl solutions at 25°C. The average density curves, $4\pi r^2\rho_0$, are also shown. An earlier x-ray study of an HCl solution (*6*) exists but, because of an insufficient range of sin θ/λ, it shows too little resolution in $\rho(r)$ to allow real comparison. In pure water, the most probable near-neighbor O–O distance is about 2.8 Å. As HCl is added, the corresponding peak broadens into a shape which is characteristic of an overlap at a 2*N* concentration and which does become resolved at higher concentrations. It is possible to fit that region of the pair density function with peaks centered at 2.75 and 3.20 Å for 2*N*, 2.68 and 3.25 Å for 4*N*, and 2.56 and 3.20 Å for 6*N* concentrations. A near absence of any pairs at the pure water O–H–O distance of 2.8 Å may be seen directly in the results for the 6*N* solution. An additional peak also develops at about 2.1 Å; because of its position and magnitude we believe it to be due to H–Cl pairs. The peak at 3.2 Å matches expectations for a well-defined O–Cl [or O–H–Cl (*7*)] interaction distance. X-

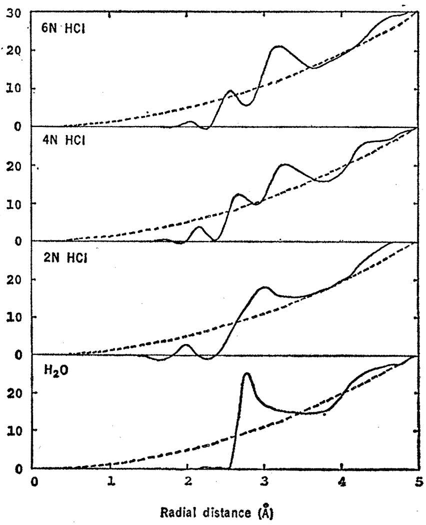

Fig. 1. Distribution of atom pairs in water and HCl solutions. (Solid lines) $4\pi r^2\rho(r)$; (dashed lines) $4\pi r^2\rho_0$.

ray studies of other chloride solutions (*8*) (not HCl) have also shown a strong peak at 3.2 Å, as well as a tendency for the loss of the peak attributable to the O–H–O distance at 2.8 Å. Thus, chloride ions are often ascribed a "structure breaking" attribute (*9*).

We attribute the peaks at 2.56, 2.68, and 2.75 Å in the HCl solutions to strongly bonded oxygen pairs. Since such correlations do not appear in other chloride solutions (*8*), these O–O distances are probably related to the presence of excess protons in the water, and, moreover, appear to be shorter as the concentration of protons increases. Such distances are also suggested by the structures of crystalline di- and trihydrated HCl (*7*).

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References and Notes

1. L. C. Allen and P. A. Kollman, *Science* **167**, 1443 (1970); J. W. Linnett, *ibid*., p. 1719.
2. D. L. Rousseau and S. P. S. Porto, *ibid*., p. 1715; S. L. Kurtin, C. A. Mead, W. A. Mueller, B. C. Kurtin, E. D. Wolf, *ibid*., p. 1720.
3. See, for example, the review and analysis by R. E. Rundle, *J. Phys. Paris* **25**, 187 (1964).
4. A. F. Beecham, A. C. Hurley, M. F. Mackay, V. W. Maslen, A. McL. Mathieson, *J. Chem. Phys.* **49**, 3312 (1968).
5. R. Kaplow, S. L. Strong, B. L. Averbach, in *Metallurgical Society Conferences*, vol. 36, *Local Atomic Arrangements Studied by X-Ray Diffraction*, J. B. Cohen and J. E. Hilliard, Eds. (Gordon & Breach, New York, 1965), p. 159.
6. O. Bastiansen and C. Finbak, *Tidsskr. Kjemi Bergvesen Met.* **3**, No. 8, 98 (1943).
7. J.-O. Lundgren and I. Olovsson, *Acta Crystallogr.* **23**, 966 (1967); *ibid*., p. 971.
8. R. M. Lawrence and R. F. Kruh, *J. Chem. Phys.* **47**, 4758 (1967); G. W. Brady and J. T. Krause, *ibid.* **27**, 304 (1957); G. W. Brady, *ibid.* **28**, 464 (1958); *ibid.* **29**, 1371 (1958); *ibid.* **33**, 1079 (1960).
9. J. L. Kavanau, *Water and Solute-Water Interactions* (Holden-Day, San Francisco, 1964), p. 59.
10. We thank A. McL. Mathieson for suggesting this problem to us and for providing helpful comments. Supported under NSF grant No. GK 1947.

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Retinal Tapetum Lucidum: A Novel Reflecting System in the Eye of Teleosts

Abstract. *A new type of tapetum lucidum has been found in eyes of bony fishes (teleosts). It is retinal, lying in the processes of the pigment epithelial cells; it has a white appearance and reflects light diffusely. The cell processes are loaded with highly refractile lipid particles; as examined by electron microscopy these are about 400 nanometers in diameter, spherical, and homogeneous. This tapetum lucidum has been found in seven families of teleost fishes occurring in inshore waters and rivers of South Texas, all of which have high turbidity; the correlation indicates a role in dim-light vision.*

A reflecting layer, or tapetum lucidum, occurs in the eyes of many different kinds of animals and is generally regarded as an adaptation to dim-light vision. Several types of tapeta have been recognized in vertebrates (*1, 2*), and in fishes two types have been described. Both of these, an oriented reflecting layer in the chorioid of elasmobranchs and some primitive bony fishes (*3*) and a retinal reflector in pigment epithelial cells of teleosts (*1, 4*), contain guanine crystals. While investigating the eyes of fishes living in very turbid inshore waters of the Gulf of Mexico, we have encountered another type of tapetum lucidum having unusual properties.

The tapetum lucidum which we briefly describe is an integral part of the pigment epithelium and forms a diffusely reflecting white layer of a lipid nature. Fishes in which it occurs show eye-shine after dark-adaptation and, when the eye is opened and the retina has bleached, the fundus exhibits a whitish hue. The reflecting layer can be exposed by removal of the retina. Examination of this layer microscopically with light from above reveals a sheet of white tufts, each tuft representing a columnar epithelial cell (Fig. 1). Cells of this sort are shown in longitudinal section in Fig. 2.

Our first encounter with this tapetum was in the speckled sea trout *Cynoscion nebulosus*. Seeking to document its occurrence, we have examined many other species (63 species of 39 families) of the inshore waters and rivers of South Texas; among them a lipid tapetum occurs in seven families (Table 1). Further searching will probably reveal this kind of lipid tapetum in other families. Its appearance is generally the same except in the cusk eel *Otophidium* and the spadefish *Chaetodipterus*, where it has a bluish tint. Fishes of two families examined, namely Elopidae and Clupeidae, have a retinal tapetum lucidum of another kind, generally regarded as containing guanine particles (*1*), which is also a diffuse white reflector.

Table 1. Families of fishes containing retinal tapeta lucida.

Family	Representatives
Ariidae	Marine catfishes
Ictaluridae	River catfish
Polynemidae	Threadfins
Sciaenidae	Croakers or weakfishes, *Menticirrhus, Cynoscion, Micropogon, Leiostomus, Bairdiella, Pogonias, Sciaenops*
Haemulidae	Grunts
Ophidiidae	Cusk eels
Ephippidae	Spadefishes

Attention has been focused on the sea trouts *Cynoscion nebulosus* and *C. arenarius*. The lipid material of the tapetum is contained in the processes of the pigment epithelial cells, which appear white in reflected light, brown in transmitted light. The pigment epithelial cells are easily ruptured, whereupon a dense cloud of minute whitish particles streams forth, gleaming brightly under superior illumination. The reflecting component is eliminated by some organic solvents (chloroform, methanol), exposing the dark retinal pigment beneath. Measurements of reflectance of fresh tapeta show that they reflect about equally well across the visible spectrum; reflectivity is about 45 percent.

The components of the eye execute normal retinomotor movements, the rods, cones, and pigment becoming radially displaced in light and darkness. In the light, the pigment granules migrate inward, partially obscuring the reflecting material, and the fundus becomes dull gray. In the dark-adapted state, the rod outer segments, lying inside the reflector, are in a position to receive diffuse light from the latter.

The lipid material is lost in the usual techniques employed in making histological preparations. It was possible to examine the lipid in the light microscope after Flemming fixation, or in frozen sections. The lipid nature of the reflecting material is suggested by solubility in fat solvents and by osmophilia. Although the material is sudanophilic, it is a negative to the acid hematin test and Nile blue sulfate test for phospholipids and to the Liebermann-Burchard test for cholesterol and its esters. The reflecting material has been extracted by chloroform and methanol (2 : 1 by volume). It is saponifiable; cholesterol and cholesteryl esters are counter-indicated by gas and thin-layer chromatography. A diffusely reflecting retinal tapetum containing cholesterol occurs in the opossum (*5*).

When viewed in the electron microscope, the tapetum granules are seen