was found to be too low. The average inclination of the magnetization in samples derived from the lava flow drilled at the Mohole test site is 36° ± 1°, which is lower than the present 54° inclination in this area (7). Almost all available data on the direction of magnetization in submarine rocks have been obtained by Vacquier's indirect method of analyses of the associated magnetic anomalies (8). With a few exceptions, the directions that have been obtained have inclinations which are lower than the dip of the present field for the respective sites. Because many of the seamounts are Tertiary or Cretaceous in age, polar or plate movement may account for the differences. The seamounts may have moved since their formation, as has been suggested (9) for the Pacific seamounts. These seamounts should have drifted northward after having acquired their remanent magnetization at lower magnetic latitudes. Because of the young age of our samples from the Reykjanes Ridge, this hypothesis cannot be used to explain the low inclination of D17. The only remaining possibility seems to be that this sample was magnetized during a reversal and thus obtained an intermediate direction of magnetization.

These magnetic measurements indicate that the basalts of the axial zone of the Reykjanes Ridge were magnetized in a field with normal polarity along a direction roughly parallel to that of the present field. The magnetization of the basalt dredged in the area with the negative magnetic anomaly adjacent to the axial positive zone has a reversed polarity. The results support the hypothesis that the magnetic anomalies of the Reykjanes Ridge are caused by basaltic complexes with opposite magnetic polarities probably produced by reversals of the earth's magnetic field.

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References and Notes

1. F. J. Vine and D. H. Matthews, *Nature* **199**, 947 (1963).
2. D. C. Krause and J.-G. Schilling, in preparation.
3. We are preparing a paper which will give the detailed magnetic properties of all samples collected.
4. J. R. Heirtzler, X. LePichon, J. G. Baron, *Deep-Sea Res. Oceanogr. Abstr.* **13**, 427 (1966); E. A. Godby, P. J. Hood, M. E. Bower, *J. Geophys. Res.* **73**, 7637 (1968); unpublished map disclosed by M. Talwani.
5. J. G. Moore, *U.S. Geol. Surv. Prof. Pap. 550-D* (1966), p. 163.
6. R. R. Shrock, *Sequence in Layered Rocks* (McGraw-Hill, New York, 1948).
7. A. Cox and R. R. Doell, *J. Geophys. Res.* **67**, 3997 (1962).
8. V. Vacquier, *Proc. Benedum Earth Mag. Symp.* (1962), p. 121.
9. E. Irving and W. A. Robertson, *J. Geophys. Res.* **74**, 1026 (1969).
10. We thank D. Corrigan for doing some of the measurements and Mrs. D. Kennedy for the drawings. Supported by ONR contract Nonr 396(08).

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Atmospheric Absorption Anomalies in the Ultraviolet near an Altitude of 50 Kilometers

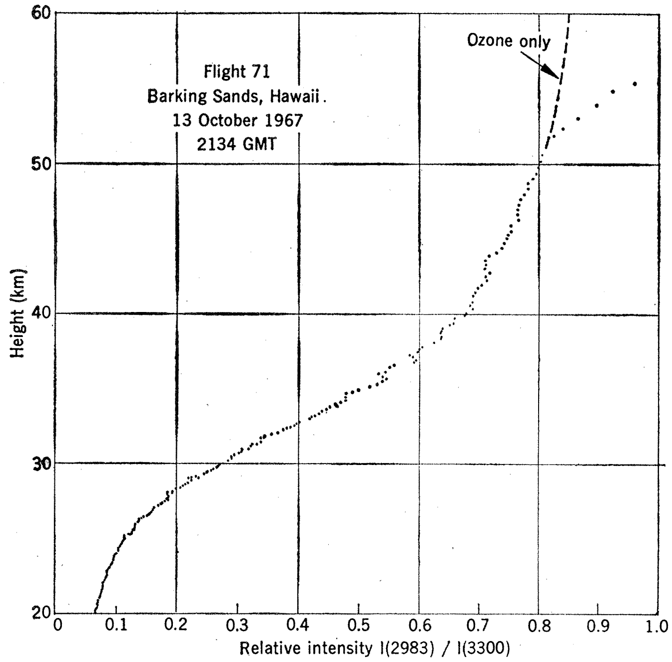
Abstract. *Rocket-borne radiometer determinations of ozone distributions by absorption of ultraviolet sunlight show anomalous effects near 3000 angstroms. The instrument uses four 40-angstrom filters in the spectral region between 2650 and 3300 angstroms. At altitudes below 40 kilometers, signals from filters centered near 3000 angstroms appear reduced at least 25 percent below calculated values. However, at higher altitudes an unpredicted sharp increase in signals is observed. These effects are inconsistent with ozone absorption and cannot be ascribed to instrument characteristics. A previously unobserved absorption band of an atmospheric constituent, possibly the metastable excited states of molecular oxygen* $O_2(^1\Delta_g)$ *or* $O_2(^1\Sigma_g{}^+)$*, can account for the anomalous effects.*

The distribution of atmospheric ozone has been measured frequently on balloons (1) and occasionally on rockets (2) by use of the intense Hartley and Huggins absorption bands in the middle ultraviolet. For routine measurements at a height between 20 and 60 km, we have adapted this technique for use on Arcas rockets (3). The ozone concentrations are derived from the height gradient of solar intensity in four wavelength bands between 2650 and 3300 Å, as measured with a filter radiometer. Seventeen flights have been made at nine locations in the last 4 years. Generally, we find that for wavelengths near 3000 Å the intensities below 40 km and the intensity gradients above 50 km depart significantly from those resulting from ozone absorption and Rayleigh scattering. These effects could be explained by an absorber other than ozone existing above 40 km. From the character of the data we can infer certain properties of that absorber. Of the known atmospheric constituents, molecular oxygen in a metastable excited state may account for this anomalous absorption.

The radiometer optical system consists of a transmission integrating sphere, an ultraviolet broad-band filter, narrow-band filters mounted in a wheel, and a photomultiplier (RCA type C70129C). The integrating sphere, with a field of view of 120°, is required because the measurements are taken during descent from apogee on a parachute. The broad-band filter consists of nickel sulfate hexahydrate and filter glass (Corning 9863), which absorb the light at wavelengths outside the region from 2400 to 3300 Å. The individual narrow passbands are formed by multilayer dielectric interference filters (typical half-width of 40 Å) and auxiliary blocking filters (4) in conjunction with the broad-band filter. The filter wheel is rotated at 1 rev/sec and contains an opaque position for dark current determination.

Filter center wavelengths were selected to be near 2750, 2950, 3050, and 3300 Å with a tolerance of ± 50 Å. With these wavelengths the change in ozone absorption coefficient is used to gain dynamic range for the expected thousandfold variation in ozone concentration between 25 and 60 km. The 3300-Å filter, with a low ozone absorption coefficient, is used as a reference. Signals from all filters are telemetered to the ground, where the ratios to the reference signal are calculated. Ideally, the half-widths and peak transmissions of the four filters are adjusted to give extraterrestrial signal ratios near unity. These filter parameters were initially calculated from the solar spectrum (5) and the detector response. From the earliest test flights on balloons, it was found that the signal ratios for filters near 3000 Å were lower than expected at the highest altitudes (near 30 km). This discrepancy in signal ratio does not directly affect the ozone calculation since only the height gradient of the logarithm of signal ratio is required.

As the data quality at the higher rocket altitudes has been improved with design changes, it has become apparent that the anomalous signal ratios may be due to an unexpected absorption. This is illustrated in Fig. 1 where



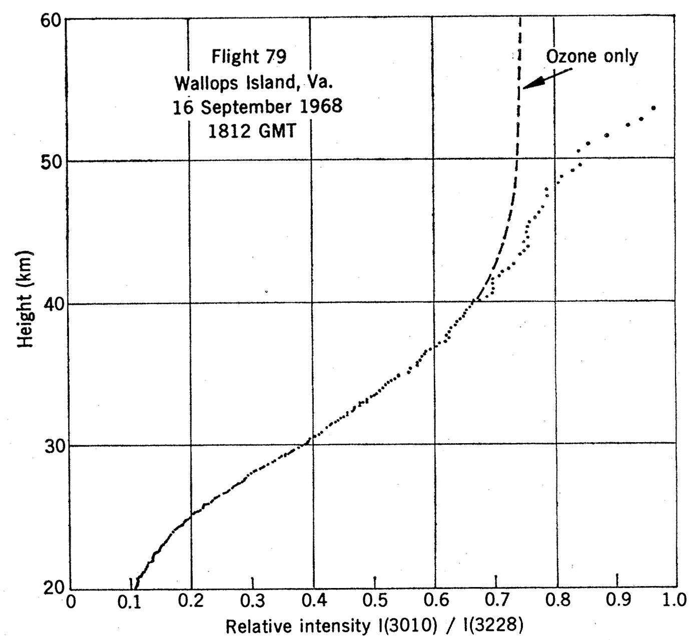


Fig. 1 (left). Height distribution of the solar light intensity observed at Barking Sands, Hawaii, with a 40-Å half-width filter centered at 2983 Å relative to the light intensity observed with a similar filter centered at 3300 Å. The flight data are smoothed and shown as points. The solid dashed line is an extrapolation of the ratio from the observed value at 35 km to the zero ozone value. Fig. 2 (right). Same as Fig. 1 except for Wallops Island, Virginia, with filters centered at 3010 and 3228 Å.

relative intensity data at 2980 Å are given for a flight from Barking Sands, Kauai, Hawaii, in October 1967. The points shown are edited and smoothed flight data. Above 50 km the observed intensity gradients are inconsistent with those due only to ozone, as shown by a dashed line. At those altitudes the ozone concentrations are independently derived from data at 2750 Å and are in general agreement with theoretical estimates (*6*) and some prior rocket data (*7*). This characteristic deviation from an ozone absorption profile has been found in a number of flights; all flights have resulted in anomalous data in this region.

Furthermore, ozone concentrations calculated from 3070-Å filter signals in the region below 35 km are improbably low and, when integrated over the atmospheric column, do not result in agreement with simultaneous Dobson spectrophotometer measurements of the total ozone amount. Redundant data from the 2980-Å filter, however, give quite reasonable concentrations and the correct total amount. The difficulty with the 3070-Å filter signals could be caused by an incorrect effective absorption coefficient. These coefficients are derived by integration of the solar spectrum, weighted by ozone absorption and Rayleigh scattering, across the filter transmission curve. An error in the weighted spectrum due to a missing absorber with a steep gradient in absorption coefficient could produce the observed discrepancy.

To check this possibility, a sounding from Wallops Island, Virginia, during September 1968, was made with a different set of filters with center wavelengths at 2630, 2875, 3010, and 3230 Å. The concentrations derived from the 2875- and 3010-Å filters now agree within 10 percent when the computed effective absorption coefficients are used, and the total ozone amount is within 3 percent of the Dobson value (*8*). However, the intensity gradient anomaly remains in the data from 3010 Å (Fig. 2). The reference signal at 3230 Å is essentially constant.

We have critically reviewed both the instrument and flight characteristics in an attempt to explain the anomalous data. Any instrumental effects would most likely arise from changes in the optical components, since the electronic system is common to all optical channels. Our first opportunity to determine such changes was the Wallops Island flight when the payload was recovered in an air retrieval with no damage to the instrument. Both preflight and postflight calibrations of the optical components were made with a spectrophotometer (Cary model 14R) with a digital output. For the 3010- and 3230-Å filters, the calculated extraterrestrial signal ratio changed from 1.018 to 0.993. The 3 percent difference, which is within the calibration error, indicates that no significant permanent change occurred in these filters. Either value is inconsistent with the extrapolated extraterrestrial signal ratio, 0.73, based on the observed ratio at 35 km and the independently determined ozone amount above that altitude. It is also unlikely that temporary changes in the optical components, which could account for the anomalous data, occurred during flight. The integrating spheres are sealed to avoid any effects due to air density changes, and development of an absorption band due to ultraviolet exposure or temperature changes has not been substantiated in laboratory testing. The filters, likewise, do not seem to respond differentially to environmental changes, although air density effects cannot be completely ruled out. The influence would have to be primarily on filters near 3000 Å, an unlikely situation.

Certain external effects have also been considered. Immediately after ejection from the rocket, the payload-parachute system pendulates at high angles, which allows backscattered light from the lower atmosphere to enter the radiometer. The spectrum of this light is, however, strongly weighted toward the longer, unabsorbed wavelengths (*9*). Any influence should lead to the reverse of the observed effect. Light reflected from the parachute, which is made of partially metallized silk or Mylar, could also contribute, but our tests on the silk material indicate a very low reflectivity in the ultraviolet. Other potential problems, such as optical absorption in the expulsion charge gas cloud, should not lead to consistent results. Therefore, we have found it increasingly difficult to account for the anomalous results in terms of an instrumental problem.

If a real atmospheric effect is present, certain optical characteristics can be specified. They are (i) maximum extinction between 2950 and 3000 Å, (ii) steep gradient between 3000 and 3100 Å, (iii) decreasing extinction below 2900 Å, and (iv) total attenuation at 3010 Å near 25 percent (*10*) for the Wallops Island flight. The bandwidth would suggest an absorber rather than a scatterer.

The absorption spectra of many of the atmospheric constituents have been measured. None of these spectra appear to have the required characteristics. Of the constituents with unknown absorption spectra, most can be ruled out on the basis that a realistic cross section would require a minimum concentration of $\sim 10^9$ molecules per cubic centimeter to produce the observed intensity gradient. Two possibilities that remain are the metastable excited states of molecular oxygen, $b^1\Sigma_g{}^+$ and $a^1\Delta_g{}^+$ (*11*), which have been observed in the red and infrared airglow. A theoretical estimate (*12*) gives $O_2(^1\Sigma_g{}^+)$ concentrations barely above the acceptable limit. In the case of $O_2(^1\Delta_g)$, the distribution has been measured with a rocket flight from White Sands Missile Range (*13*). A sharply peaked distribution, with a maximum concentration of 3.6×10^{10} molecules per cubic centimeter at 49.5 km, was found. Use of this concentration with the 3010-Å intensity gradient at 52 km from the Wallops Island flight results in an absorption cross section of 9×10^{-18} cm^2, which is reasonable for an allowed transition. The total amount of $O_2(^1\Delta_g)$, based on this cross section, would be 4×10^{16} molecules per square centimeter, which is in substantial agreement with the White Sands total amount.

Although the ultraviolet spectra of these metastable states of oxygen apparently have not been determined, allowed transitions should exist from either state to a $^1\Pi_u$ state. The potential energy curve for this state is not known but is expected to be repulsive (*14*). The minimum photodissociation energy from the $^1\Delta_g$ state is 4.08 ev, corresponding to 3037 Å. The values for the $^1\Sigma_g{}^+$ state are 3.51 ev and 3531 Å, respectively. Until the character of the Π state is known or the absorption spectra are measured, it may be concluded only that one of the two transitions could have the correct energy and bandwidth for the anomalous absorption.

An explanation of the observed effects is of considerable importance to our work. At this time absorption by a metastable state of oxygen appears to provide a solution. The presence of such an absorber at 50 km will also affect other measuring techniques. A satellite method, using backscattered ultraviolet light from the atmosphere to determine the ozone distribution (*15*) requires precise information on all high-altitude absorbers in the spectral region from 2500 to 3400 Å. Neglect of a 3000-Å band absorber, above the ozone layer, would result in erroneously high ozone concentrations derived for the 30- to 40-km region. Standard measurements of total columnar ozone could be affected if this absorption were present beyond 3055 Å, the shortest wavelengths used in the Dobson spectrophotometer. In addition to effects on measurements, if the suggested excited oxygen absorption exists, an additional source of atomic oxygen would have to be considered in photochemical calculations of the composition of the stratosphere and mesosphere.

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References and Notes

1. W. Kulcke and H. K. Paetzold, *Ann. Meteorol.* **8**, 47 (1957); A. Vassy, *J. Sci. Meteorol.* **10**, 63 (1958). A comprehensive description of balloon techniques is given by H. K. Paetzold, in *Handbuch der Aerologie*, W. Hesse, Ed. (Akademische Verlagsgesellschaft, Leipzig, 1961).
2. Most of the early rocket results may be found in R. Tousey, in *The Middle Ultraviolet: Its Science and Technology*, A. E. S. Green, Ed. (Wiley, New York, 1966), chap. 1, p. 35. More recent results are given by J. P. Bancarel and A. Vassy, *C. R. Hebd. Seances Acad. Sci. Paris* **263B**, 845 (1966) and A. J. Krueger, *Ann. Geophys.* **25**, 307 (1969).
3. The original design is described in A. J. Krueger and W. R. McBride, *Nav. Weapons Center Tech. Publ. 4512* (1968). Design improvements and recent data are reported by A. J. Krueger and W. R. McBride, *Nav. Weapons Center Tech. Publ. 4667* (1968).
4. The optical filters were characterized and calibrated under the guidance of Dr. W. R. McBride.
5. The original high resolution solar spectrum was derived from data furnished by Dr. J. D. Purcell. Recent calculations use 1-A averages computed by Dr. C. L. Mateer from P. M. Furukawa, P. L. Haagenson, M. J. Scharberg, *Nat. Center Atmos. Res. Tech. Note No. 26* (1967).
6. E. Hesstvedt, *Geofys. Publikasjoner* **27**, No. 5 (1968); J. London, in *Space Research 7* (North-Holland, Amsterdam, 1966); B. G. Hunt, *J. Geophys. Res.* **71**, 1385 (1966).
7. The data of F. S. Johnson, J. D. Purcell, R. Tousey, K. Watanabe [*J. Geophys. Res.* **57**, 157 (1952)], when corrected for improved ozone absorption coefficients, are generally accepted.
8. This flight was made by comparison with a rocket ozonesonde devised by E. Hilsenrath, which uses the chemiluminescent technique for ozone measurement. At heights below 52 km, where data are available from both instruments, the agreement in ozone concentration is within 10 percent.
9. J. V. Dave and P. M. Furukawa, *Meteorol. Monogr. 7* (1966).
10. At the ground the anomalous absorption would be largely masked by ozone. A 5 percent increase over ozone absorption is calculated for the Wallops Island case.
11. A further possibility is absorption by vibrationally excited ground state O_2. A transition from the $v'' = 10$, 11, or 12 levels of the $X^3\Sigma_g{}^-$ ground state to the $v' = 0$ or 1 levels of the $B^3\Sigma_u{}^-$ state could have the correct energy. These electronic states produce the well-known Schuman-Runge bands in the case where $v'' = 0$. Population of the higher vibrational levels at 50 km could come from the reaction of O_3 with O.
12. B. G. Hunt, *J. Atmos. Sci.* **23**, 88 (1966).
13. W. F. J. Evans, D. M. Hunten, E. J. Llewellyn, A. Vallance Jones, *J. Geophys. Res.* **73**, 2885 (1968).
14. F. R. Gilmore, *Rand Corp. Memo RM-4034-PR* (1964).
15. S. F. Singer and R. C. Wentworth, *J. Geophys. Res.* **62**, 299 (1957); S. Twomey, *ibid.* **66**, 2153 (1961); L. D. Kaplan, *Int. Union Geod. Geophys. Monogr. 19* (1961), p. 30; Z. Sekera and J. V. Dave, *Planet. Space Sci.* **5**, 122 (1961).
16. I thank Dr. C. A. Barth for suggesting $O_2(^1\Delta_g)$ and Drs. W. R. McBride, C. L. Mateer, J. London, J. B. Pearce, and D. F. Heath for discussions and suggestions. The rocket data were obtained with the assistance of W. L. Burson. Supported by Independent Research funds, Director of Naval Laboratory Programs.
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Structure of "Polywater"

Abstract. *A structure for "polywater" is proposed. It consists of hydrogen-bonded clusters of water molecules lying at the vertices of rhombic dodecahedra. This structure contains features which are less unattractive than those which are part of several earlier models.*

There have been recent speculations (*1–3*) concerning the structure of "polywater." Models proposed include: (i) tetrahedral clusters (*1*) of $(H_2O)_4$; (ii) square tetramers (*2*) of $(H_2O)_4$; (iii) planar hexagonal sheets (*3*); and (iv) (apparently) planar, highly branched polymer chains (*3*). Unsymmetrical O–H · · · O bonds were postulated in models (i) and (ii) (*1, 2*), with O · · · HOH · · · O angles of 60° and 90°, respectively. Symmetrical O · · H · · O bonds were postulated in models (iii)