percent found in the preliminary analysis (Table 1) and demonstrates the power of the electron microprobe in making accurate analyses of the abundances of the light elements.

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30 October 1964

Anomalous Abundance of Upper Atmosphere Sodium, 1964

Abstract. *Measurements of atomic sodium in the upper atmosphere by absorption spectroscopy with the Pepsios spectrometer on the Fraunhofer* D_2 *line during February to August 1964 at Madison, Wisconsin, have indicated abundances of about* 10^{10}*/cm*^{2} *for the late winter, about twice the values from a similar method in 1961–62. An abrupt decrease in abundance occurred during March in agreement with established seasonal behavior, but the abundance then increased anomalously in the summer to* 8×10^9*/cm*^{2}*. The summertime increase may be related to observations of increased turbidity of the upper atmosphere, presumably caused by volcanic dust.*

The abundance of atomic sodium in the atmosphere during recent years has been determined spectroscopically from emission measurements on the twilight glow, in dayglow and twilight glow with the Zeeman-effect photometer, in absorption with a sodium scattering cell, and by absorption of direct sunlight with the Hypeac grating-Fabry-Perot spectrometer at high resolution. The complex problem of the annual variation of abundance, with its probable dependence upon geographic location, appears unsolved. Much of the accumulated evidence points to a seasonal variation marked by a late winter maximum and rapid springtime decrease to a summer minimum and slow autumn increase (*1*); but a recent extensive compilation based mainly upon Zeeman-effect photometry points to a summer maximum (*2*).

It is not my purpose in this report to contribute data on the general problem of the annual abundance, but rather to describe a particular anomaly observed at one place in 1964, compare it with the most nearly comparable previous data, and point out a correlation—convincing to me—with an atmospheric disturbance that offers a clue to the origin of at least that sodium which contributes to the anomaly.

The terrestrial absorption associated with the Fraunhofer D_2 line from February to August 1964 at Madison, Wisconsin, was observed with a Pepsios spectrometer (*3*), an instrument particularly suitable for work on this problem because of great luminosity at high resolution in a dense spectrum and the simple interpretability of the output. The observations are compared with those made in a similar manner during 1961–62 by McNutt (*4*) with a Hypeac. Figure 1 is a representative Pepsiogram of the D_2 line. Reduction of the data was accomplished and corrected to vertical abundance (*4*). The method is rather insensitive to the altitude of the layer, here taken to be 85 km.

The 1961–62 and 1964 seasonal variations are shown in Fig. 2. The springtime abundances decrease abruptly during March in both 1962 and 1964, but the 1964 abundance is clearly about twice that of 1962. Systematic errors, especially in determining the no-absorption contour of the line, might have shifted the 1964 abundance points upward, but by not more than about 20 percent.

In recent months visual and photometric observations have been made elsewhere indicating that volcanic dust has been accumulating in the upper atmosphere, reaching the northern hemisphere in the autumn of 1963 (*5*). I suggest that the high 1964 summertime abundance of atomic sodium is a direct consequence of the large amount of volcanic dust, which serves in this instance as the primary source of the increased sodium. The dust layers have been observed to be at 20 km and higher. The spectroscopic observations reported upon here are not sufficiently sensitive to zenith angle to determine the height of the absorbing layer, but consideration of collisional and Doppler broadening and the observed resolution of the 57-mK(millikayser) hyperfine struc-

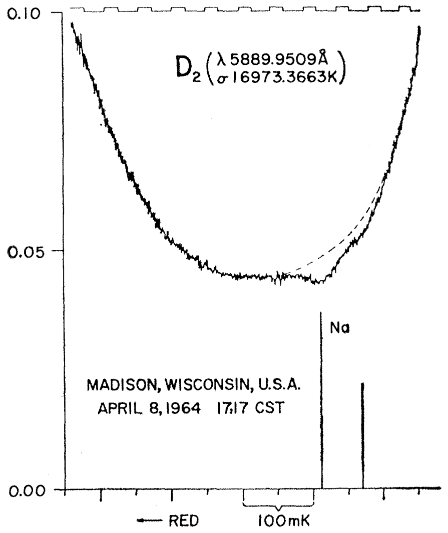

Fig. 1. Pepsiogram of the bottom of the Fraunhofer D_2 absorption line of the solar spectrum. The terrestrial sodium is identified by its position relative to the solar line, which has a gravitational red shift plus a Doppler shift, and by resolution of the two hyperfine structure blends which are observable by virtue of the low pressure and temperature of the upper atmosphere. Ordinate, intensity (continuum ≡ 1.00); abscissa, wave number (50 mK per division).

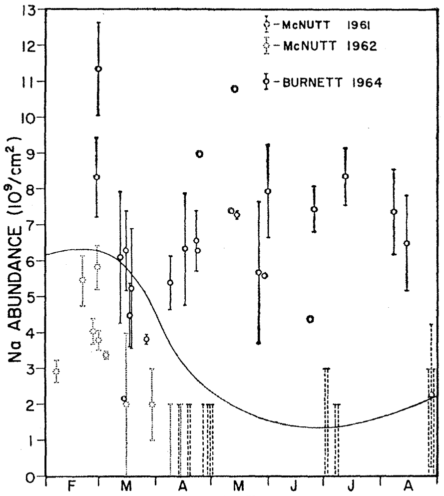

Fig. 2. Abundance of atomic sodium in the atmosphere at Madison, Wisconsin (43° N). Daily averages for 1961–62 and 1964 are shown with vertical lines indicating one standard deviation. Circles without vertical lines are single measurements. The curve is a seasonal curve for Saskatoon, Saskatchewan (52°N).

ture of the terrestrial sodium line indicate that the atomic sodium must be at least as high as 25 km.

Various origins of the sodium in the upper atmosphere have been considered; these sources include sea salt, volcanic dust, and extraterrestrial sources, with the terrestrial origins being largely discounted (*6*). Turbidity measurements by Goody and Volz (*7*) in 1959 and 1960 demonstrated that atmospheric dust then present had a seasonal abundance closely paralleling the established seasonal abundance of atomic sodium. Although it is possible that the dust and the atomic sodium might have been of either extraterrestrial or terrestrial origin at that time, it seems highly probable that the increased 1964 sodium is related to the increased dust of volcanic origin. A seasonal pattern of upper atmosphere circulation might produce the springtime decrease of the upper atmosphere dust as well as the related springtime fallout of radioactive debris (*8*). Thus, the atomic sodium may follow this same seasonal variation because it depends on the dust layers as the source of sodium.

On the basis of this spectroscopic study of the constituents of the upper atmosphere, similar observations with the Pepsios spectrometer on relative abundances of other elements may be possible, giving additional information on the source of these elements in the upper atmosphere.

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9. The laboratory facilities and the encouragement and advice of Prof. J. E. Mack are gratefully acknowledged. Considerable technical support was given to this study by the entire spectroscopy staff. F. E. Barmore operated the spectrometer during July and August. Partly supported by the research committee of the Graduate School from funds of the Wisconsin Alumni Research Foundation and partly by the National Science Foundation.

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Neon Isotope Fractionation During Transient Permeation

Abstract. *Fractionation of neon-20 with respect to neon-22 during a single-stage transient permeation process results in as much as 45-percent enrichment of neon-20. The observed fractionations agree with those calculated from simple diffusion theory.*

The measurement of isotopic fractionation of a gas at the extremities of transient states of permeation provides a sensitive and convenient means to check on the mechanisms taking part in the permeation process. Such measurements for the isotopes of neon in samples permeated through a vycor membrane are reported here, and the results are compared with those expected from a theory of transient permeation based on a simple diffusion mechanism.

In our experiment, the membrane consisted of a vycor tube (22 mm outside diameter, 1.25 mm thick, 28 cm long) which could be alternately evacuated from inside or connected to the gas inlet system of a mass spectrometer. The membrane was surrounded by a jacket into which neon could be introduced from a reservoir or withdrawn by applying high vacuum.

The membrane was first outgassed at 800°C by applying high vacuum on both sides. The temperature was then brought down to a steady desired value, and high purity neon was introduced into the jacket at a pressure of ~ 700 mm-Hg. The permeated gas samples were collected for intervals of some minutes and transferred to a reservoir from which they were introduced into the mass spectrometer for measurement of Ne^{20} and Ne^{22} (the detection limit under dynamic operation was $\sim 3 \times 10^{-9}$ cm^3 for either isotope). The experimental data have been deposited with American Documentation Institute (*1*).

The uncertainty in the temperature measurement is approximately ± 10°C. The diffusion coefficients and the permeation constants obtained from the data are in good agreement with those reported (*2, 3*).

The ratio of Ne^{20} to Ne^{22} in the jacket was 9.76. The fractionations (that is, the ratio of Ne^{20} to Ne^{22} of the permeated sample divided by the ratio of Ne^{20} to Ne^{22} in the jacket) observed at different stages of transient permeation are shown in Fig. 1. The measurement of fractionation factors are believed to be accurate to ~ 1 percent, except for the earliest one which may be uncertain by ~ 5 percent since the amount of Ne^{22} in this sample was very low ($\sim 10^{-7}$ cm^3). The uncertainty in the individual measurement of permeation rates is about 10 percent.

The observed fractionations may now be compared with those expected from theory if it is assumed that the permeation process may be characterized by simple empirical diffusion laws. The permeation rate as a function of time can be obtained by solving the diffusion equation with proper boundary conditions.

The solutions (*4*) which are readily usable in the present case give the permeation rate R at time t after the gas is let into the jacket as

$$R_t = KD \times \left[1 + 2\sum_{n=1}^{\infty} (-1)^n \exp\left(\frac{-n^2\pi^2 Dt}{l^2}\right) \right]$$

where K is a constant depending on the size and shape of the membrane and the pressure of the gas in the jacket, l is the thickness of the membrane, and D is the diffusion coefficient.

The permeation rate increases with time until, at large values of t, a steady flow of gas across the membrane is established and the permeation rate attains a constant value equal to KD. If the gas is now suddenly withdrawn from the jacket, the permeation rate

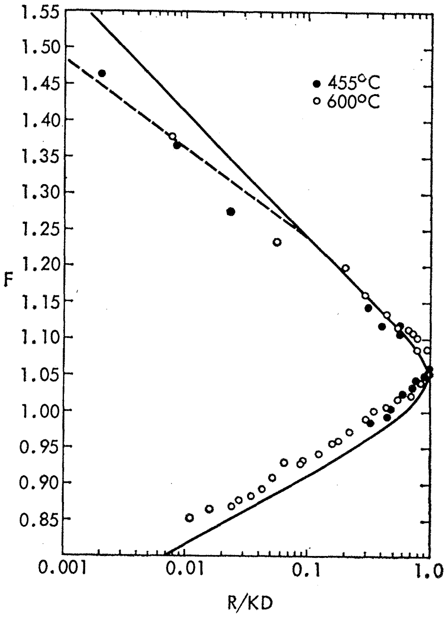

Fig. 1. Fractionation of neon isotopes during transient permeation. Small circles are experimental points; the curves are theoretical.