

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.

C. R. BURNETT\*

Department of Physics,  
University of Wisconsin, Madison

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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.
- \* On leave of absence from Pennsylvania State University, 1963-64; present address: Department of Chemical and Physical Sciences, Florida Atlantic University, Boca Raton, Florida.

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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<sup>20</sup> and Ne<sup>22</sup> (the detection limit under dynamic operation was ~ 3 × 10<sup>-9</sup> cm<sup>3</sup> 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<sup>20</sup> to Ne<sup>22</sup> in the jacket was 9.76. The fractionations (that is, the ratio of Ne<sup>20</sup> to Ne<sup>22</sup> of the permeated sample divided by the ratio of Ne<sup>20</sup> to Ne<sup>22</sup> 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<sup>22</sup> in this sample was very low (~10<sup>-7</sup> cm<sup>3</sup>). 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

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

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

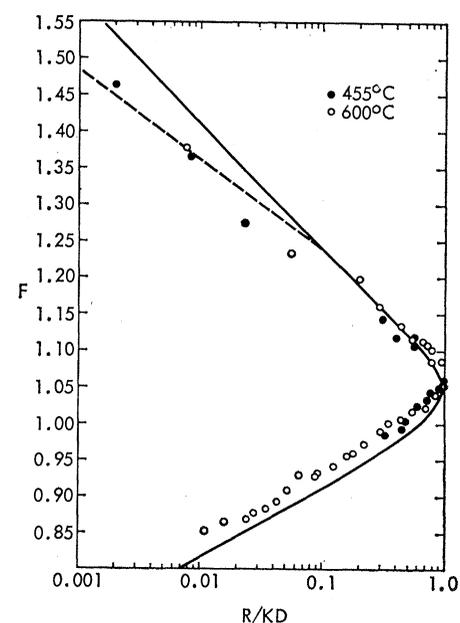


Fig. 1. Fractionation of neon isotopes during transient permeation. Small circles are experimental points; the curves are theoretical.

will gradually decrease with time as given by

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

The fractionation in the sample permeating at time  $t$  is given by

$$F_t = \frac{D_{20}}{D_{22}} \frac{1 + 2 \sum_{n=1}^{\infty} (-1)^n \exp\left(\frac{-n^2 \pi^2 D_{20}t}{F^2}\right)}{1 + 2 \sum_{n=1}^{\infty} (-1)^n \exp\left(\frac{-n^2 \pi^2 D_{22}t}{F^2}\right)}$$

An expression for the fractionation for the decay can be similarly written. If it is assumed that the diffusion coefficients for the two isotopes are in the ratio of the inverses of the square roots of their respective masses, for which there is evidence both from our experiment and the experiment of Frank, Swets, and Lee (2), the fractionation factors are calculated using  $D_{20} = 1.05 D_{22}$ .

From the foregoing equations, one can obtain  $F_t$  as a function of  $R_t/KD$  (the ratio of the permeation rate at time  $t$  to the permeation rate at steady state). This function depends only on the ratio  $D_{20}/D_{22}$ , and is shown by the solid curve in Fig. 1. This relation, however, is applicable only to instantaneous values of  $F_t$  and  $R_t/KD$ , while the experimental data are obtained over an interval of  $R_{t1}/KD$  to  $R_{t2}/KD$ . Therefore, in order to compare the experimental data with theory, an average value of  $F$  was calculated by integrating Eq. 1 for proper intervals of  $R_t/KD$ . These values of  $F$  differ significantly from the instantaneous ones only in the early stages when the permeation rate is changing very rapidly. They are shown by the broken curve. The experimental data are shown by small circles. The fit of the experimental data to the theoretical curve is considered very good at both temperatures; the small apparent departures are not beyond the systematic and random errors in the measurement of  $F$  and  $R/KD$ .

Fractionations may occur in nature by similar processes. These might be partly responsible for some of the isotopic anomalies observed, for example, in the meteorites.

S. N. I. RAMA\*

S. R. HART

Department of Terrestrial Magnetism,  
Carnegie Institution of Washington,  
Washington, D.C.

#### References and Notes

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- \* Present address: Tata Institute of Fundamental Research, Bombay, India.
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#### Nuclear Magnetic Resonance Studies of Living Muscle

**Abstract.** *Measurements of nuclear magnetic relaxation times for protons of water in living skeletal frog muscle show the transverse relaxation time,  $T_2$ , increases when a muscle contracts isometrically. This result and other experimental data suggest that a fraction of the intracellular water molecules have restricted rotational freedom and that this fraction decreases when contraction occurs.*

Nuclear magnetic resonance studies of protons in living muscle point to a correlation or binding or immobilization of some of the water molecules relative to the structure of the muscle cell. Part of the bound water appears to be freed reversibly during isometric contraction and irreversibly in death.

The tissues used were the skeletal muscles of the frog *Rana pipiens*. Most of the experiments were performed on the gastrocnemius muscle, but a few were performed on the semitendinosus and sartorius muscles. Within the limits of error the results were the same. A copper-wire radio-frequency coil was wound on a pyrex tube (inside diameter, 8 mm), and a muscle was suspended within the tube. Tension was continuously recorded from a resistance strain gauge attached to one end of the muscle. Electrical stimulation was delivered through attached platinum electrodes. The complete assembly was centered in the gap between the pole faces of a Varian V-4012A electromagnet equipped with a Varian VK-3519 homogeneity control unit capable of maintaining fields varying less than 5 mgauss over the sample volume.

The preliminary studies were made with slow sweep techniques at a Larmor frequency of 24 Mc/sec. The steady-state response of the protons was ob-

tained by phase-sensitive detection of the first sidebands caused by 1 kc/sec modulation of the main magnetic field. A single, well-defined proton line several milligauss in width was observed, but no broad, superimposed line was detected. From the strength and definition of the line we conclude that this signal came from the protons of water which constitutes approximately 80 percent of the total weight of a muscle. By comparison with proton standards of known line widths and chemical splittings, the width of the line was judged to originate from relaxation processes and not from inhomogeneities of the field alone. When the muscle was stimulated to undergo tetanic isometric contraction, the proton signal was distinctly narrowed by approximately 20 percent. Repeated sweeps confirmed the effect as  $20 \pm 5$  percent.

An increase in line width of the proton signals from water in which various substances have been dissolved or suspended is not unprecedented. Notable examples of organic solutes for which the effect has been observed are DNA (1) and agar (2). Proton-line broadening has also been observed in samples of human tissues and cells (3). Several possible causes are (4, 5) paramagnetic impurities, chemical exchange, anisotropy of the local static magnetic fields, and adsorption processes.

To ascertain the cause in our experiment and to eliminate interfering static-field inhomogeneities, the transverse relaxation time,  $T_2$ , was measured directly by the Hahn spin echo technique (6) which makes use of pairs of pulses of  $90^\circ$  and  $180^\circ$ . The decay in amplitude of repeated spin echoes followed a simple exponential curve and showed thereby the relative unimportance of diffusion effects. The relaxation time,  $T_2$ , was also measured by the Carr-Purcell modification (7) of the spin echo method (with results that agreed with those obtained by the Hahn method), which has the advantage that a single measurement requires less time—approximately 0.1 second compared to about 1 minute for the Hahn method.

The longitudinal relaxation time,  $T_1$ , was also measured with a pulse technique (7). The measurements of  $T_1$  and  $T_2$  were made at two field strengths corresponding to Larmor frequencies of 24.0 and 4.30 Mc/sec. The longitudinal relaxation time,  $T_1$ , was found to be 400 msec at the higher field strength and 250 msec at the lower field strength. Within experimental error  $T_1$  did not change with changes in the state of a