

where A refers to the measured gas concentration in sea water, normalized to 1 atm partial pressure of the gas, α is the solubility coefficient, and C_{He}^{Air} is the concentration of helium in air. The values of the solubility coefficients were taken for the temperature corresponding to an average temperature based upon the concentration ratios of Ne to Ar and Kr to Ne. The values for the excess helium (Table 1) are plotted in percentages above normal solubility at the corresponding temperature in Fig. 1.

The highest values (around 32 percent) are found in samples taken from depths nearest the bottom. Surface samples gave values close to 8 percent which can be attributed to either incomplete exchange of helium with the atmosphere or systematic error in the solubility data for helium. The two samples (462 and 1039 m) which gave calculated temperatures for the noble gases higher than measured temperatures also show a minimum in the helium excess.

If excess helium found in sea water is attributable to influx of helium from the lithosphere (helium production in the water column itself from dissolved uranium and thorium is negligible), it is possible to consider quantitatively the problem of the helium escape from the upper atmosphere, with the assumption of steady-state conditions. The injection of helium into the water column will occur at the sediment-water interface and the gas will be distributed both horizontally and vertically by convective mixing processes; such a mixing is suggested in Fig. 1. An average value of the excess can be appropriately obtained from the deep water samples (those below the thermocline); after subtraction of the excess found in surface water it is 6.1×10^{-6} cm³/liter or 1.64×10^{11} atom/cm³. Fourteen samples of surface water give an average helium excess of 2.9×10^{-6} cm³/liter. Since the time elapsing between contact of a water mass with the atmosphere and its present location in deep water is of the order of 1000 years (8) on the basis of radiocarbon studies, and with an assumed average depth of 3900 m for the ocean, one can derive a rate of efflux from the lithosphere into the water or an "atmospheric production rate" (9) for helium of $(1.64 \times 10^{11} \times 3.9 \times 10^3)/10^3 = 6.4 \times 10^{13}$ atom cm⁻² year⁻¹. The mean lifetime for a helium atom in the atmosphere is then found to be 1.8×10^6 years, assuming that the

"atmospheric production rate" from the continents is the same as the oceanic value and that the helium content of the atmosphere is 1.13×10^{20} atom/cm³.

Although we agree that more knowledge of the distribution of excess helium in the oceans and of the age of water below the thermocline is desirable, we think that discussion of this novel approach to the helium escape problem in relation to other investigations is justified. The problem of helium escape from the terrestrial atmosphere is considered in two recent papers (9, 10). Nicolet arrives at a figure of $\leq 5.5 \times 10^{13}$ atom cm⁻² year⁻¹, based on observations of the terrestrial heat balance and assuming that the generation rate of helium is essentially equivalent to the "atmospheric production rate."

On the other hand, Wasserburg and co-workers (10) derive an "atmospheric production rate" for helium from observations made on terrestrial natural gases and from certain assumptions on the origin of atmospheric argon. They find a production rate between 4.4×10^{12} and 2.2×10^{14} atom cm⁻² year⁻¹ with 10^{13} atom cm⁻² year⁻¹ as a best estimate. It can be seen that our rate for the atmospheric production of helium, derived from the accumulation of helium during the average time the water

spends below the thermocline, is slightly above Nicolet's upper limit and agrees well with Wasserburg's statement that the true value probably lies closer to the higher production rate.

RUDOLPH BIERI

MINORU KOIDE

EDWARD D. GOLDBERG

Department of Earth Sciences,
University of California at
San Diego, La Jolla

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Solar X-Ray Spectrum below 25 Angstroms

Abstract. Below 25 Å, the solar spectrum consists primarily of the emission lines of Fe XVII, O VIII, O VII, and N VII. The lines of the more highly ionized atoms, Fe XVII and O VIII, originate in localized active regions. Lines of O VII and N VII emanate from the full disk.

On 25 July 1963 spectral measurements of solar x-ray emission were made with a Bragg crystal spectrometer carried in an Aerobee Rocket. The spectrometer consisted of a single crystal of potassium acid phthalate (KAP) as the diffracting element, a Geiger counter detector, and a mechanism to rotate the crystal and detector in a 1:2 ratio. Wavelengths were determined from the Bragg equation:

$$n\lambda = 2d \sin \theta \quad (1)$$

where n is the order of diffraction, λ the wavelength, d the grating constant, and θ the angle of diffraction. The instrument was kept pointed at the sun by a biaxial pointing control. Potassium acid phthalate has a $2d$ spacing of 26.633 Å. The angle θ was varied con-

tinuously during flight to provide one full spectrum scan and a partial repeat. The accuracy of wavelength determination was about ± 0.1 Å and was limited primarily by the precision of mechanical alignment and by pointing excursions. No collimation was used. Consequently the angular width of an observed line was a direct measure of the angular width of the x-ray emitting region.

The observed spectrum was dominated by emission lines which contained at least 85 percent of the integrated flux between 10 Å and 25 Å. No line was detected below 13 Å with an intensity as great as 10^4 photons/cm² per second. All the observed lines are listed in Table 1 together with their respective identifications and in-

Table 1. Solar x-ray spectrum recorded by Bragg spectrometer.

Wavelength observed (Å)	Lab. meas. or prediction (Å)	Intensity above atm (10^4 photons $\text{cm}^{-2} \text{sec}^{-1}$)	Element	Transition	Notes
13.7	13.820	1.4	Fe xvii	$2p\ ^1S_0-3p\ ^1P_1$	Possibly also Ne ix. Narrow.
15.0	15.012	11.7	Fe xvii	$2p\ ^1S_0-3d\ ^3D^1$	Narrow.
15.25	15.261	7.2	Fe xvii	$2p\ ^1S_0-3d\ ^1P_1$	Narrow.
16.0	16.006	4.2	O viii	$1s\ ^2S_{1/2}-3p\ ^2P_{3/2, 1/2}$	Lyman β . Narrow.
16.72	16.774	11.1	Fe xvii	$2p\ ^1S_0-3s\ ^1P_1$	Narrow.
{ 17.01 and 17.05	17.051	14.7	Fe xvii	$2p\ ^1S_0-3s\ ^3P_1$	Doubled by excursion of pointing control. Both peaks narrow.
{ 17.65 and 17.72	17.768	21.0	O vii	$1s^2\ ^1S_0-1s4p\ ^1P_1$	Doubled by pointing control excursion.
{ 18.54 and 18.61	18.627	30.0	O vii	$1s^2\ ^1S_0-1s3p\ ^1P_1$	Doubled by pointing control excursion.
{ 18.8 and 18.9	18.969	23.2	O viii	$1s\ ^2S_{1/2}-2p\ ^2P_{3/2, 1/2}$	Lyman α . Doubled. Broad wings.
20.8	20.910		N vii	$1s\ ^2S_{1/2}-3p\ ^2P_{3/2, 1/2}$	Lyman β . Very weak line.
21.55	21.602	461.0	O vii	$1s^2\ ^1S_0-1s2p\ ^1P_1$	Broad.
21.70	21.804	212.0	O vii	$1s^2\ ^1S_0-1s2p\ ^3P_1$	Broad.
23.2		31.2			Broad. Unidentified. Possibly N vi.
24.8	24.781	85.2	N vii	$1s\ ^2S_{1/2}-2p\ ^2P_{3/2, 1/2}$	Lyman α . Broad.

tensities. The intensities are given in numbers of photons per square centimeter per second in each line above the earth's atmosphere.

These intensities have been computed from the observed fluxes and the measured spectrometer efficiency. The estimated accuracy is ± 50 percent. In Table 1, four groups of two lines each are shown bracketed. These are single lines that were doubled by pointing excursions which interrupted the continuity of the spectrometer scan.

The narrow widths of the lines of Fe-xvii, indicate that they originate in active regions of approximately the

same dimensions as plages. The Lyman β line of O viii is also narrow, but the lines of O vii and N vii are as broad as would be expected from a source covering the full disk.

R. L. BLAKE*, T. A. CHUBB
H. FRIEDMAN, A. E. UNZICKER
E. O. Hulburt Center for Space Research†, U.S. Naval Research Laboratory, Washington, D.C.

Notes

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* Present address: Department of Astro-Geophysics, University of Colorado, Boulder.

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Electroconductive Polymers

Abstract. *Polymers of a new type with an unusual combination of properties have been synthesized. They are of high molecular weight, they are soluble in organic solvents, and they can be cast as films. Their electrical conduction is electronic in the solid state and can be controlled up to a conductivity of $10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$.*

That electroconductive organic polymers possessing the mechanical properties of the common insulating plastics have potential value is attested by the numerous reported attempts at synthesis. The work from previous years has been reviewed (1). The more re-

cent contributions (2) deal with the synthesis of conductive polymers by introducing conjugation, free radicals, charge transfer complexes, or metal ions as part of a polymeric structure and, more empirically, by pyrolysis of otherwise nonconductive materials.

The resulting products have been either insoluble, infusible powders or, if soluble, of low molecular weight, low conductivity, or both (3). We now report preliminary studies of a class of electroconductive polymers, of high molecular weight, that can be deposited from solution as homogeneous films suitable for making physical measurements.

Microcrystalline, monomeric salts of the tetracyanoquinodimethane anion (TCNQ^-) and related complex anions—for example, $(\text{TCNQ})_2^-$ —possess conductive properties (4). Our observations are that combinations of these ions with polymeric cations produce polymers that can readily be cast as coherent films and have electric conductivities as high as $10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$ (5).

Poly(2-vinylpyridine), molecular weight 2.2×10^6 , was alkylated with excess dimethylsulfate in alkaline solution. The resulting poly(1-methyl-2-vinylpyridinium methylsulfate) (6) was freed of inorganic salts by dialysis and was shown by titration to be completely *N*-alkylated. A solution of this polymer in 50 percent ethanol, well stirred under nitrogen, was mixed with a solution of the lithium salt of TCNQ in 50 percent ethanol, the amount of TCNQ being sufficient to provide one TCNQ anion for every monomer unit. The precipitate formed was collected, washed with aqueous ethanol, washed repeatedly with ethanol, and dried in a vacuum over phosphorus pentoxide. Films of this material were cast from dimethylformamide or acetonitrile and cut into shapes appropriate for four-point probe measurement of conductivity; silver electrodes were painted on as contacts. Conductivity of these films was markedly dependent on the presence of neutral TCNQ, which was added, in these studies, to the solutions from which the films were cast (Table 1).

A copolymer of styrene and 2-vinylpyridine (molecular weight greater than 5×10^4) containing 45 mole percent vinylpyridine residues was alkylated with *n*-butyl iodide in a mixture of ethyl acetate and nitromethane. Analysis of the ether-precipitated polymer indicated that 80 percent of possible quaternization had occurred. The product was allowed to react with slightly more than the stoichiometric quantity of lithium TCNQ in aqueous ethanol, under nitrogen, and the pr