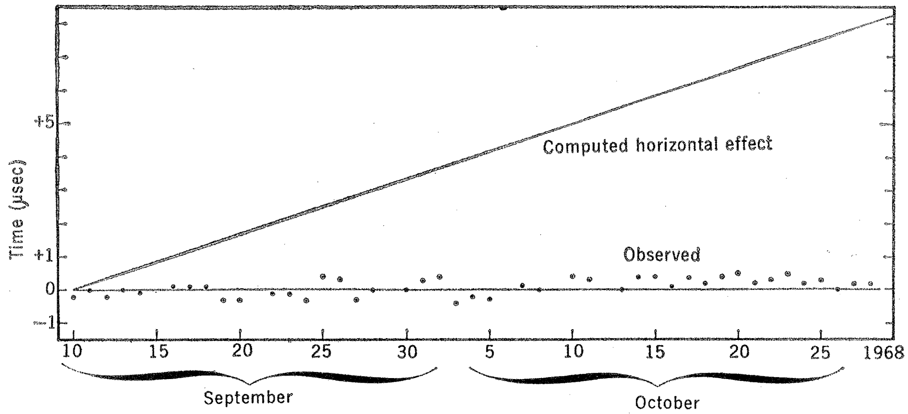

Fig. 2. Difference in times of arrival (K) of cycles from Cape Fear, North Carolina, and Dana, Indiana. The quantity plotted is ($K - 2$) in microseconds. The difference is ($100\,n + K$) μsec, where n is some fixed integer.

used. If the horizontal effect were real, then when the NRL group was at Cape Fear, it should have found that the frequency of Loran C at Nantucket, Massachusetts, was lower than that at Cape Fear by 2 parts in 10^{12}, and that the frequency was higher by 2 parts in 10^{12} when at Nantucket.

A differential experiment can also be performed at a fixed site. Such an experiment was initiated at Marquette on 10 September 1968, monitoring cycles from Dana, Indiana, and Cape Fear, North Carolina. The respective distances from Milwaukee are 350 and 1320 km. If the horizontal effect were real, the Cape Fear value should be lower in frequency by 2 parts in 10^{12}, and a particular cycle from Cape Fear should arrive later each day than the one from Dana by 0.17 μsec.

Loran C is monitored at Marquette by a simple but highly precise visual technique. The incoming carrier waves are amplified and displayed on a dual-trace oscilloscope, which also displays time markers produced by the Marquette clock. The carrier waves from both Cape Fear and Dana are displayed on the same trace (Fig. 1). Coincidence settings of minima with time markers are made to 0.1 μsec with a phase shifter.

Figure 2 shows the difference in times of reception of cycles from Cape Fear and Dana. There is no daily shift, as would be required by the horizontal effect. Hence, the frequency of a radio transmission is not affected by mass (except in accordance with the gravitational red shift of relativity).

In the NRL experiment, the moving clock was checked against a fixed clock at Cape Fear at the beginning and end of the experiment. However, no differential checks were made. In view of the definitive nature of the differential experiment reported here, which is independent of clock rates, it does not appear that a discrepancy exists which contradicts relativity.

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References and Notes

1. D. Sadeh, S. Knowles, B. Au, *Science* **161**, 567 (1968).
2. W. Markowitz, *Advances in Metrology* (Instrument Society of America, Pittsburgh, 1968), vol. 5, paper No. 68-627.
3. To avoid interference, pulse groups are emitted in sequence from the various stations of a chain with a fixed time separation maintained to 0.1 μsec.
4. The Time, Frequency, and Polar Motion Laboratory was established in April 1968 through equipment grants by NSF and the Marquette University Committee on Research. Support provided in part by the Office of Naval Research on behalf of the U.S. Naval Observatory.

19 November 1968

Radar Scattering from Venus at Large Angles of Incidence and the Question of Polar Ice Caps

Abstract. *Spectrum analysis of radar waves backscattered from an anulus near the limb of Venus shows that a uniform scattering model applies over regions extending from the equator to within approximately 15 degrees of the poles. These observations indicate that large polar ice caps extending to latitudes as low as 60 degrees are very unlikely.*

A report by Libby (*1*) suggests that the Mariner V and Venera 4 observations of Venus do not discount the possibility of polar ice caps on the surface of this planet. However, a more recent report by Weertman (*2*) shows that if the amount of water present on the earth were locked up as polar ice caps on Venus, the ice caps would have to extend to below 60° latitude. A reply by Libby (*3*) indicates that ice caps extending as low as 45° latitude may not be unreasonable. The data on radar scattering reported here indicates that ice caps at these latitudes are very unlikely.

During the 1967 inferior conjunction of Venus, a number of radar observations were made to study the backscattering properties of Venusian surface at large angles of incidence. Some of these observations were of such quality that acceptable delay-Doppler spectra (maps) could be obtained from the recorded data for incidence angles approaching 80°. Higher quality spectra, of course, can be obtained for smaller incidence angles. However, by choosing the spectra as near the limb of the planet as possible, all latitudes from the equatorial region to the polar region may be observed in a single spectrum, as illustrated in Fig. 1. In such observations, any absorption or ray-bending caused by a uniform atmosphere will be constant over the entire spectrum.

If extensive polar ice caps exist on Venus, what effect might they have on the delay-Doppler spectra? At large incidence angles, the backscattered power is greatly dependent upon the surface roughness. Rough surfaces have a larger number of facets per unit area directed normal to the incident waves, therefore more power is backscattered to the radar. Rocks and other debris that have diameters nearly equal to the radar wavelength contribute extensively to the backscatter, since they scatter roughly isotropically. The backscattered power is also dependent upon the dielectric constant and conductivity of the materials. Materials with high dielectric constants have greater reflection coefficients, which results in greater backscattered power. The conductivity of most natural materials is sufficiently small so that the reflection coefficient is controlled mainly by the dielectric constant. The equatorial region of Venus is known to be very hot (about 600° to 700°K), and the surface material is probably a mixture of granulated solids and rocks of various sizes that have a dielectric constant of 5 over a wide range of radar frequencies. The surface is less rough than that of the moon at centimeter wavelengths, and the average scattering properties are in good agreement with a model by Muhleman (*4*).

The models of the polar ice caps suggested by Weertman (*2*) and Libby (*3*) seem to require continued snowing to remove the atmospheric water vapor that is continually replaced by melting and evaporation of the ice near the rim of the ice cap. Snowing on Venus should be a very gentle process because of the dense atmosphere. Therefore, one might expect loosely packed snow to extend downward for many meters, gradually increasing in density until tight packing or solid ice forms. The dielectric constant of solid ice at a wavelength of 70 cm is about 3.4, and loose to hard-packed snow ranges from 1.2 to 1.5 (considerably less than the equatorial material). Surfaces created by such a process would very likely be smooth, that is, slopes approaching 75° to 90° required for backscattering would be unlikely to be formed; roughness on the scale of a wavelength would be rare. Radar waves impinging upon a surface at oblique incidence would propagate deep into the snow and gradually be absorbed. Waves reflected by whatever transitions that exist in the surface stratification would not be backscattered to the radar but reflected obliquely off into space. The net backscatter from such a region would be exceedingly small.

At the edge of the ice cap, liquid water should exist. Liquid water has a dielectric constant of about 77 at a wavelength of 70 cm. Water in this region would certainly saturate the soil, raising the dielectric constant to perhaps 20 or more depending on the packing factor of the soil. Erosion and debris carried by glaciers could seriously change the roughness of the surface in this region, but the outcome of such a process and how it would affect scattering of radar waves can only be speculated upon. Although it is difficult to predict whether the backscatter would be more or less than that from the dry equatorial regions, it would very likely be different.

The solid curve in Fig. 2 shows a theoretical delay-Doppler spectrum based on a homogeneous scattering model by Muhleman (*4*). The procedure for computing theoretical radar spectra, based on various scattering models when convolved with the radar ambiguity or resolution function, has been given by Shapiro (*5*) and Jurgens (*6*). Theoretical spectra were computed for two values of the roughness parameters, α, in Muhleman's scattering model and for one value of the roughness parameter in a model by Hagfors (*7*) in order to be sure the spectra were not sensitive to either the model used or the roughness parameter. The differences in the computed spectra were slight and would not be visible when plotted in the scale of Fig. 2. The peak at the spectrum is caused by a larger effective area contributing power at that Doppler frequency. It can be seen from Fig. 1 that the power contributing to the peak comes from the equatorial region while the power at the center of the spectra comes from the polar regions. If the polar regions were less effective in backscattering power than the equatorial region, the observed ratio of the power at the peak to the power at the center of the spectrum would be larger than indicated by the spectrum.

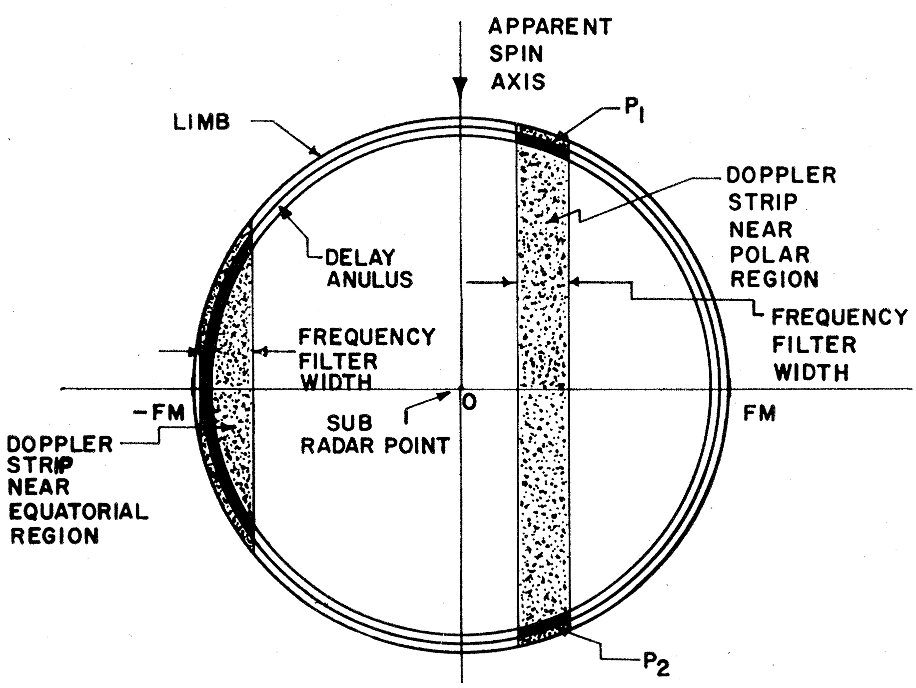

Fig. 1. Delay-Doppler resolution of Venus. Note that all latitudes from the equator to the pole may be observed in a single spectrum if the delay anulus is placed on the limb. *FM* is one-half of the limb-to-limb Doppler shift; P_1 and P_2 indicate two regions having the same delay and Doppler frequencies.

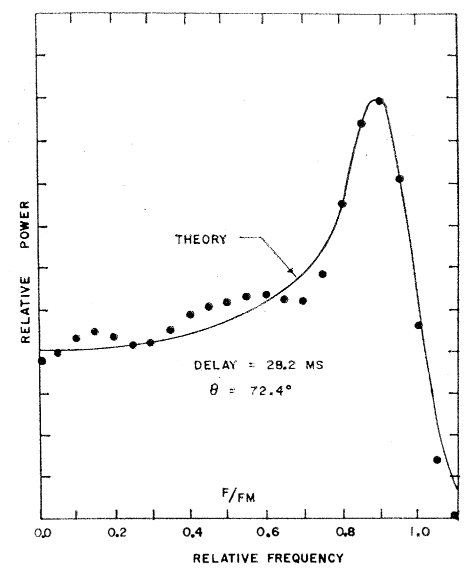

Fig. 2. An averaged spectrum at an incidence angle of 72.4°. The spectrum was folded about the zero-frequency axis to increase the number of independent regions contributing to the spectrum. The observations used were made on 4, 22, and 29 September 1967. Also shown is the least-squares fit of the theoretical spectrum to the observed spectrum points. MS, millisecond.

In order to obtain a good indication of the average scattering properties of Venus, a number of spectra must be averaged over an extended period of time to reduce the effect of anomalous scattering regions. Such scattering anomalies are known to be associated with various distinct surface features. Because the planet rotates as it is viewed from various aspect angles from the earth, anomalies at a given delay and frequency are caused by independent surface areas. If a number of spectra are averaged over a period of several weeks, the effect of the distinct surface features is smoothed out, but the poles always remain near the center of the spectra and the equatorial region remains near the edge. Thus, any latitude-dependent scattering anomaly would be observed in the averaged spectrum. Figure 2 also shows the resulting averaged spectrum at a delay af 28.2 msec which corresponds to incidence angle 72.4°. The procedure used to average the spectra has been discussed by Jurgens (*6*) in an earlier study of the average scattering properties of Venus for incidence angles less than 45°. The averaged spectrum shown is in remarkably good agreement with the theoretical spectrum.

The results of this study and the previous study by Jurgens (*6*) clearly indicate that a homogeneous scattering model can represent the average scattering properties of Venus over a range of incidence at least as large as 75°, and that no latitude dependence is observable. Therefore, ice caps do not exist on Venus unless the very unlikely situation has occurred and their radar-scattering properties at large incidence angles are not significantly different from those of the equatorial region. Large fields of broken ice slabs could duplicate the radar-scattering behavior of the equatorial region at large angles of incidence if the surface roughness were just slightly greater than the roughness of the equatorial material, but snow is excluded by these radar observations.

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References and Notes

1. W. F. Libby, *Science* **159**, 1097 (1968).
2. J. Weertman, *ibid.* **160**, 1473 (1968).
3. W. F. Libby, *ibid.*, p. 1474.
4. D. O. Muhleman, *Space Sci. Rev.* **6**, 341 (1966).
5. I. I. Shapiro, *Astron. J.* **72**, 1309 (1967).
6. R. F. Jurgens *CRSR Report*, No. 297 (Center for Radiophysics and Space Research, Cornell University, 1968).
7. T. Hagfors, *J. Geophys. Res.* **69**, 3779 (1964).
8. I thank R. B. Dyce and F. D. Drake for helpful suggestions and R. B. Dyce, D. B. Campbell, and T. W. Thompson for assistance in observations.
9. The Arecibo Ionospheric Observatory is operated by Cornell University with the support of the Advanced Research Projects Agency under a research contract with the Air Force Office of Scientific Research.

31 July 1968

Kaolinite Layer Structure: Relaxation by Dehydroxylation

Abstract. *Single-crystal electron-diffraction data reveal features of metakaolin. The basal plane parameters increase 2.2 percent in formation of metakaolin produced by heating kaolinite in air at 700°C for 12 hours. This increase results from removal of the distortion of sheet structure (relaxation).*

Although the sequence of thermal reactions by which kaolinite (a triclinic, 1 : 1 layer silicate) passes through a poorly crystallized, and more or less anhydride phase (metakaolin), then through a spinel-type cubic phase to yield finally a chain silicate (mullite) plus excess silica (appearing finally as cristobalite) was shown by Brindley and Nakahira (*1*) to be a structure-controlled process, the specific nature of metakaolin remains very difficult to evaluate. New single-crystal electron diffraction data, showing an expansion of the layer parameters, *a* and *b*, in the formation of metakaolin, provide some valuable additional information.

The layer structure of kaolinite consists of a Si–O tetrahedral sheet linked with an Al–O,OH octahedral sheet; the OH ions are coordinated only with Al ions and not with Si ions. Dehydroxylation causes a major alteration of the Al–O,OH sheets, with the Al ions taking up fourfold, in place of their original sixfold, coordination as shown by x-ray fluorescence analysis (*2*), and also by infrared spectroscopic data (*3*, *4*). The basal spacing of metakaolin is not directly observable by x-ray diffraction, and possibly is variable from crystal to crystal, and within crystals. An estimated average value based on density data (*1*) is about 6.3 Å, while electron diffraction results (*5*) on single crystals turned edgewise to the electron beam have given values in the range 6.8 to 5.6 Å, with an average of 6.2 Å. From a detailed infrared analysis, Pampuch (*4*) recently has concluded that the Si–O sheets take up a higher symmetry after dehydroxylation, becoming hexagonal instead of ditrigonal, and that the Al–O,OH sheets break down into an arrangement of corner- and edge-shared AlO_4 tetrahedra forming chains.

Further structural information has now been obtained from electron diffraction measurements of single crystals with the use of an aluminum shadowing technique to provide accurate calibration rings on the diffraction spot patterns (*6*). Measurements have been made of the basal plane parameters of exceptionally well-crystallized kaolinite taken from geodes which occur near Keokuk, Iowa (*7*), and of the metakaolin produced by heating this kaolinite in air at 700°C for periods of 12 hours or longer to give 13.88 percent weight loss, that is, corresponding to essentially complete dehydroxylation. The *b*-parameter measurements, made on many crystals, have given the following results:

Initial kaolinite	$b = 8.95 \pm 0.03$ Å
Metakaolin (700°C)	$b = 9.145 \pm 0.035$ Å

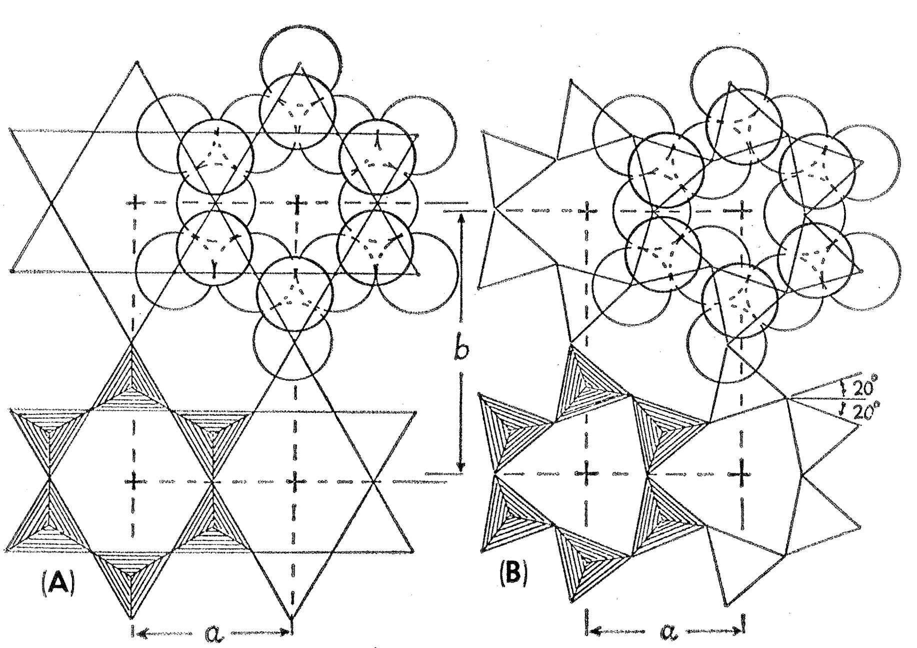

Fig. 1. Arrangement of silicon–oxygen, SiO_4, tetrahedral groups in (A) ideal hexagonal sheet structure, (B) ditrigonal sheet structure, with tetrahedra rotated alternately +20° and −20° with respect to ideal positions. The *b* parameter arising from the rotations is reduced. The upper part of each diagram shows the oxygen atoms in tetrahedral groups; the silicon atoms at centers of tetrahedra are hidden. The lower part of each diagram indicates the tetrahedral faces connecting centers of oxygen atoms.