

tonium in the administered solution was in the Pu(III) state, the retention (the percentage of the administered dose) in the skeleton and liver after 4 days was 0.006 percent, in the Pu(IV) state 0.001 percent, and in the Pu(VI) state 1.75 percent. After 80 days the retentions were 0.010, 0.001, and 1.57 percent, respectively. Each value is the average for six rats. The results they obtained for Pu(III) and Pu(IV) were in close agreement with those of many other investigators. For those experiments in which the plutonium administered was a mixture of Pu(IV) and Pu(VI), the correlation between the percent Pu(VI) and the percent plutonium absorbed was high.

The authors of the task group's report were aware of the work by Weeks *et al.* (2), as they refer to it in the section on gastrointestinal absorption (7, p. 10). However, the nature of their statement suggests that there was doubt in their minds about the validity of the data: "Although the evidence is meager, Pu(VI) appears to be absorbed more readily than Pu(IV)." As published, the study that Weeks *et al.* carried out appears to be quite definitive.

The gastrointestinal absorptions of Np(VI) by the rat and of U(VI) by man substantiate the absorption of Pu(VI) found by Weeks *et al.* (2). [Both Np(VI) and U(VI) are very close chemical analogs of Pu(VI). The compounds formed when each is precipitated from solution by a particular reagent are isomorphous, they form complexes with the same ligands and to a comparable degree, and they are extremely difficult to separate from each other when they are all in the VI state.] Ballou *et al.* (8) found that the gastrointestinal absorption of Np(VI) by the rat was 2 percent. From measurements of uranium in man and his diet, Hursh and Spoor (9) estimated that the gastrointestinal absorption of U(VI) is between 10 and 30 percent. The absorption of Pu(VI) in man should not differ significantly, that is, by more than a factor of 10, from that of U(VI).

The fact that conditions within the gastrointestinal tract are reducing in nature may lead to the reduction of Pu(VI) to Pu(IV) shortly after water has been consumed. In this case, the gastrointestinal absorption factor for Pu(IV) rather than for Pu(VI) should be used to calculate MPC's. In reviewing the paper of Weeks *et al.* (2) with one of its authors (10), we learned that in their experiments (i) the rats were food-deprived both before and after the administration of the plutonium and (ii) the solutions that contained Pu(VI) were about 0.01M in dichromate. Thus, at the time of administration, the

gastrointestinal tracts of the animals may have been devoid of those constituents that could reduce Pu(VI) or, if these constituents were present, they may have reacted with the dichromate and this forestalled plutonium reduction. At this time we know of no information about the reduction of Pu(VI) to Pu(IV) during the period when digestive processes are occurring.

Our study shows that plutonium in drinking water will be in the Pu(VI) state, but it remains to be shown whether or not Pu(VI) will be reduced to Pu(IV) immediately after ingestion. In establishing this, consideration must be given to the fact that water and food consumption are not necessarily related temporally; Pu(VI) may be rapidly reduced when food is being digested but not when the digestive tract is empty.

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Venus: Further Evidence of Vortex Circulation

Abstract. *A space-time composite of polar stereographic ultraviolet images of Venus from Mariner 10 shows a remarkable circumpolar vortex. The vortex is characterized by a cloud which appears similar to dense terrestrial stratus having an albedo that is 50 percent higher. Spiral streaks converge into it from low latitudes, akin to the spiral bands of a hurricane. The bright visible polar cloud is not axisymmetric but has roughly an elliptical shape. The high brightness of the polar cloud suggests that it has a different origin from the rest of the Venus cloud cover.*

Soon after the Mariner 10 encounter with Venus, the Mariner Venus Mercury-73 imaging team (1) presented a preliminary view of the atmospheric circulation on Venus as revealed by the ultraviolet (UV) markings. In particular, Murray *et al.* made the following comments about the polar region (1, p. 1312): "Our preliminary impression is that the pole of atmospheric rotation is on the terminator. . . . There is an indication of vortex structure in the streaks emanating from the poleward side of the edge of the polar region. Indeed, the entire polar region may be a vortex fed by meridional flow from the equatorial regions." Subsequently Suomi (2) and Suomi *et al.* (3) tracked the motions of UV features of a few Mariner 10 UV frames taken over a small time interval compared to the total Venus encounter. These observations showed highly zonal motion with maximum speeds near $\pm 50^\circ$ latitude suggestive of the conservation of angular momentum in the outer zone of the vortex. We have completed another analysis of Mariner 10 images that covers almost the

entire period of the Venus encounter, about 7 days, using an extension of the basic technique. The new approach has produced striking evidence of a global circumpolar vortex in the stratosphere of Venus.

First, all of 22 frames spanning 6.85 days were normalized to a standard scattering geometry. The normalization was performed in order to remove shading due to scattering geometry variation over the planet. The images were normalized to a standard sun-planet-observer geometry as described by Limaye and Suomi (4). Second, the images were remapped into a polar stereographic projection to give a better view of the high-latitude regions of Venus. Third, several separate polar stereographic projections spanning several days were made into a composite for the whole polar region. This procedure simulates the view that would be obtained from a flight over the pole.

The polar projection has the advantage that it is easier to discern motion patterns in the high latitudes than in the

original oblique perspective view. Clearly, the information content of normalized polar stereographic projections is not different from the initial unprocessed oblique perspective view. It is only the ease of interpretation which vastly differs in the two cases.

Our new findings from an analysis of this sequence may be summarized as follows:

1) The polar cloud is about 50 percent brighter than the cloud cover over the rest of the visible southern hemisphere in UV throughout the 7 days.

2) The gross shape of the visible polar cloud is an ellipse, which by its asymmetry causes an illusion of meridional displacements when viewed in an unmapped image sequence. We are unable to discern substantial changes in the area of the polar cloud in the images studied, and the ellipse is suggestive of wavelike

motions at this latitude having planetary wave number 2.

3) This projection allowed us to see more clearly the motions of features within the polar cloud even though much less detail is present there than in equatorial or mid-latitude regions of the planet. Features found at latitudes as high as 60° to 65° still show a dominant solid-like zonal motion.

4) The UV features in these views definitely show differential rotation in mid-to low latitudes, as indicated by Suomi (2) and Suomi *et al.* (3). This is easily confirmed through a simple exercise of constructing a composite hemispheric view. Given the constraint that only a rotation is required about the pole, the continuity of observed UV features across the boundaries can only be preserved if the longitudinal displacement between picture time intervals actually corre-

sponded to the zonal motion for that latitude. The meridional dependence of the zonal component of motion of UV features was obtained from measurements. The space-time composite thus constructed is shown in Fig. 1. The similarity between such a composite view and a satellite view of a tropical cyclone is very striking. Indeed, both are examples of cyclostrophic motion where the pressure gradient is balanced by the horizontal component of the centripetal acceleration. Such a motion was suggested for Venus by Leovy (5) and is evidenced for hurricanes, although on vastly different scales.

5) Despite the very unfavorable viewing geometry, a similar mapping procedure also suggests a vortex on the opposite pole. A time-lapse display of several such frames also suggests a circulation similar to that seen in the southern hemisphere sequence.

Indeed, the polar cloud in both hemispheres and the spiral streaks emanating from low latitudes are compelling suggestions that at least during the 7 days of the Mariner 10 flyby in 1974 the stratospheric circulation was composed of two giant vortices more or less centered on each pole with meridional inflow from low latitudes toward each pole. The vortex seen in the composite view of Venus would be characterized by a region of mass sink in the polar regions in the upper atmosphere and a mass source in the low latitudes, essentially a hemispheric Hadley circulation cell strongly organized by the vortical zonal flow. A meridional flow is implied with such a circulation.

6) The scatter seen in the measured zonal and meridional speeds of the UV features is realistic and not due to navigational errors. The classical Rayleigh criterion for barotropic instability is applicable even to the case of a slowly rotating planet such as Venus, where the Coriolis terms in the equations of motion are quite small and centripetal accelerations dominate. The observed scatter may be indicative of the fact that this criterion, namely, that the vertical components of absolute vorticity must change sign somewhere within the zonal current, may be satisfied in the Venus cloud layer.

The similarities between the polar stereographic composite view and a vortex such as a hurricane tempt us to speculate about the circulation in the stratosphere of Venus. The inflow at the top of the Venus vortex corresponds to the inflow at the surface of a typical hurricane. If the analogy is valid, then there should be

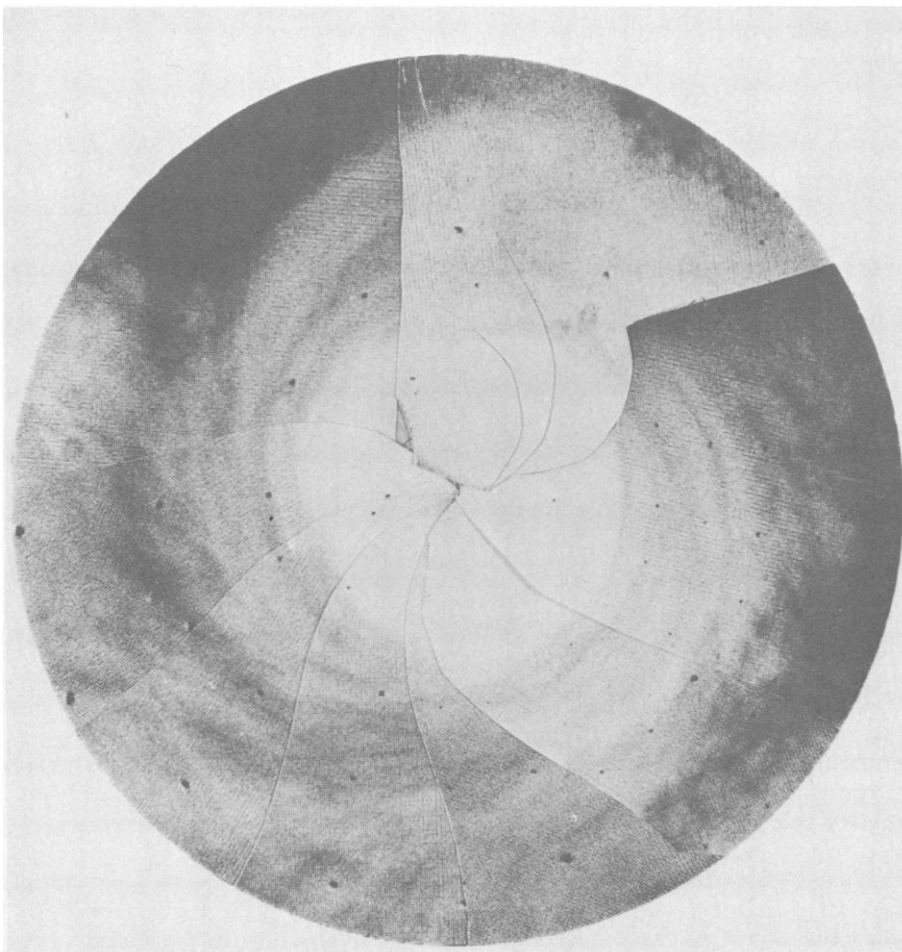


Fig. 1. A space-time composite prepared from several remapped images according to computed match longitudes. The vortex-type organization of the UV features is unmistakable. The center of the vortex, as far as can be discerned, is at the south pole and is in the center of the image. This composite provides a time-lapse view of the southern hemisphere of Venus in a polar stereographic projection. Thus the outer edge of the image is the planet equator, and latitude parallels are a series of concentric circles within. One image was unavailable in photometrically rectified version and appears differently, at the bottom of the picture. There is a time boundary immediately to the left of this image which was shuttered at 10:17:57 Greenwich mean time on day 38 of 1974. Clockwise from this image the images are taken at day 38, 15:32:57; day 39, 08:58:03; day 39, 16:13:26; day 40, 01:43:14; day 40, 10:32:56; day 40, 21:07:50; and day 41, 17:14:49. The southern half of the dark Y-feature is seen in the image in the southeast quadrant. The motion of the features is in the anticlockwise direction.

a corresponding outflow region in the Venus vortex at some lower layer, possibly close to the surface. An inflow region in the upper levels of the atmosphere can easily exist on Venus. The stratosphere (portions of the atmosphere above 38 km) is known to be very stable and stratified (at least in low latitudes). The bulk of the solar energy which maintains the circulation appears to be deposited in this layer (6). There is thus a possibility that an upper boundary layer exists on Venus as suggested by Goody and Robinson (7) but with the return circulation at the poles rather than at the antisolar point.

We have, at present, no evidence that large amounts of latent heat are released in the Venus atmosphere. Hence there is a major difference between the circulation on Venus and that of a tropical cyclone. The tropical cyclone is maintained dominantly by the release of latent heat in the atmosphere; the circumpolar vortex in the stratosphere of Venus is maintained through conversion of solar energy into sensible heat. The bright polar cloud at the center of the global vortex is a puzzle and invites further research.

The observations during the Mariner 10 flyby lasted only 8 days, and we must not draw too general conclusions from this very limited data set, particularly since ground-based observations show that the bright cloud appears and disappears occasionally in the polar regions. The cause of such long-term in-

stabilities is still a mystery. Nevertheless, polar cloud or no polar cloud, the atmospheric circulation in polar and high latitudes is different from that at other latitudes and is important for a deeper understanding of the Venus atmosphere and its circulation.

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Isoleucine Epimerization in Peptides and Proteins: Kinetic Factors and Application to Fossil Proteins

Abstract. *The observed rate of isoleucine epimerization in peptides and proteins is dependent on (in addition to time and temperature) (i) the position of isoleucine in the peptide chain, (ii) the nature of adjacent amino acids, and (iii) the stability of the isoleucine peptide bonds. The relative rate is: NH_2 -terminal $>$ $COOH$ -terminal \gg interior \geq free amino acid. The gradual hydrolysis of peptides and proteins to the more slowly epimerizing free amino acid causes a decrease in the apparent first-order rate constant with time. These results explain the isoleucine kinetics observed in fossil shells.*

Amino acid racemization-epimerization reactions are being used increasingly as a geochronological tool to date fossil bones, shells, and deep-sea foraminiferal deposits (1). Efforts to develop an accurate dating technique based on the kinetics of amino acid racemization-epimerization have been somewhat more successful with bone than with carbonate shell. In bone, diagenetic racemization reactions apparently follow reversible first-order kinetics approximate-

ly to equilibrium (2), while nonlinear kinetics prevail for the racemization-epimerization reactions in mollusk shells and foraminifera (3-5). The nonlinear kinetics in carbonates may be a result of the different racemization-epimerization rates experienced by amino acids in various fractions (free amino acids, small and large peptides, and proteins) formed by slow hydrolysis of the original skeletal protein over geologic time. If diagenetic racemization-epimerization reac-

tions are ever to be useful in dating carbonate fossils, however, a better understanding of the factors responsible for the nonlinear kinetics is necessary. In our experiments we focused attention on the interconversion of L-isoleucine and D-alloisoleucine (alle), an epimerization reaction which has been studied in fossils (1).

Generally, isoleucine is epimerized to different degrees in the various amino acid fractions of fossil shells and foraminifera, with free isoleucine being more extensively epimerized than the protein- or peptide-bound isoleucine (4-6). These relations in specimens of modern *Merccenaria*, heated to simulate geologic aging, are illustrated in Fig. 1. The conclusion usually drawn from these observations is that, in fossils, isoleucine epimerizes faster in the free state than in the bound state. The greater degree of epimerization of free isoleucine in foraminifera and other carbonate fossils has been attributed to a concerted process of hydrolysis and epimerization (4) or to catalysis by metal ions (5). We now present evidence that the extensive epimerization of isoleucine does not occur in the free state. Instead, isoleucine preferentially epimerizes at the terminal position of a peptide or protein chain, with a markedly lower rate of epimerization occurring at both interior and free positions. Subsequent hydrolysis of the terminal, more extensively epimerized, isoleucine leads to an enrichment of alloisoleucine relative to isoleucine in the free fraction. We suggest that this mechanism offers a better explanation both for the observed epimerization relationships in fossils and for the nonlinear kinetics.

To investigate the kinetics of isoleucine epimerization we have conducted, at elevated temperatures, kinetic studies of various dipeptides, tripeptides, and proteins containing isoleucine. Samples (1 ml) of 0.1 percent aqueous solutions (pH = 8.0) were sealed under nitrogen in Pyrex tubes and heated at 152°C in a sand bath. At the end of the heating period, a portion of the samples was hydrolyzed (6N HCl at 105°C for 24 hours). During the heating some hydrolysis occurred. The ratios of alloisoleucine to isoleucine of both the free fraction and the total hydrolyzed (free plus bound) fraction were measured on an automated amino acid analyzer.

Initial epimerization rates of isoleucine are different for each dipeptide and tripeptide and are up to an order of magnitude greater than the epimerization rate of free isoleucine in aqueous solution; but they are about the same as ini-