Table 2. Comparison of data (Å) for bcc silicon and germanium-IV.

	Si		Ge:
hkl	J*	K & R†	this work
200		3.318	3.49
121	2.613	2.709	2.821
123	1.713	1.773	1.853
400		1.659	1.737
a_0	6.40	6.64	6.92

* The a_0 is calculated from the d spacings marked X by Jamieson (*3*) derived from x-ray diffraction at about 120-150 kb. † The *d* spacings are as given by Kasper and Richards (*11*) for the high-pressure silicon x-rayed at atmospheric pressure.

Ge-II⇌Ge-III on release of pressure; it appears instead to be formed by a very slow reconstructive transformation directly from I or II. In any case, it is also certain that even if the III form always results from II, the I→II transition cannot be any higher than about 30 kb at 100°C. The preferred interpretation of these relations is given in Fig. 4.

Examination of x-ray diffraction patterns of samples held at 110 to 130 kb at room temperature for 10 to 40 hours and then quenched disclosed two weak reflections which could not be accounted for. Furthermore, they disappeared at room temperature and pressure within a few hours. More experiments were made in which the samples were cooled to dry-ice temperatures at the end of long runs before release of the pressure. From then on, the samples were stored, ground, and x-rayed at dry-ice temperatures. With such handling, samples from runs at 140 kb and room temperature gave only these two, now very well-resolved reflections: at 31.71° and 49.17°C, 2θ (CuKα); and reflections at 25.5° and 52.7°C, 2θ. The reflections were much better defined than those we had obtained for the bcc high-pressure phase of silicon (*6*); more important, they were indexable on the same bcc cell of proportionately larger dimension. Furthermore, our x-ray data on Ge-IV to some extent are parallel to those of Jamieson on silicon (*3*). He reported two diffraction lines from silicon kept at high pressures for 3 days (and x-rayed at pressure), and these lines persisted at lower pressures. Our calculations show that these two reflections can result from the (121) and (123) planes of the bcc high-pressure phase of silicon, if one allows for a reasonable volume compressibility of about 10 percent owing to the 120- to 150-kb applied pressure. The two strongest lines of Ge-IV may also be indexed as (121) and (123), and the weaker ones as (200) and (400) (Table 2). Taken together, these data are evidence for a new Ge phase, Ge-IV.

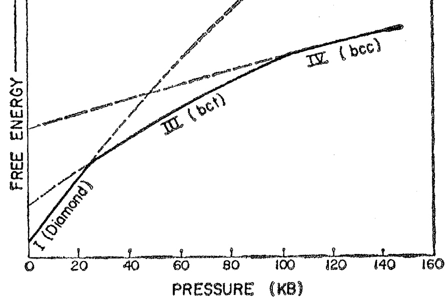

Fig. 4. Schematic free energy–pressure diagram drawn to emphasize qualitative stable and metastable relationships of the four crystalline phases of germanium at about 50° to 100°C.

The a_0 calculated from the (121) and (123) reflections is 6.92±0.01 Å, for which the theoretical density is 5.83 g/cm^3. This value is 9.5 percent greater than that of Ge-I but 1 percent less than that of Ge-III, all at 1 atm.

The Ge-IV may be stored indefinitely at dry-ice temperatures and atmospheric pressure; at 30°C approximately 90 percent disappears in 3 hours with the appearance of some Ge-III. On the other hand, Ge-III will persist at 100°C for several days and at room temperature indefinitely.

We believe our data have bearing on the interpretation of high-pressure work on semiconductor elements, Group III-V, and Group II-VI compounds. Thus, we and most workers in the field have erroneously assumed that phase transitions in semiconductors and metals would be too rapid to quench. We now find that these transitions are in the same general range of activation energy and rate as the sluggish phase transitions in typical oxide systems. It is therefore likely that pressures reported for certain transitions in similar systems are not equilibrium values. Further, the overlap of stable and metastable transitions makes difficult the interpretation of optical and electrical data under pressure in that these measurements are made under what are essentially dynamic conditions.

Our interpretation of the Ge equilibrium phase diagram (Fig. 3) does not show a firm phase boundary for the Ge-III⇌Ge-IV transition. Our data are not sufficient to establish it and an extension of the 1-percent volume differences (observed at 1 bar) to 110 kb is too uncertain to indicate the sign of the slope. Likewise the true slope for the Ge-III⇌liquid transformation is unknown.

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5 January 1965

Stratosphere and Troposphere: Transport of Material between Them

Abstract: *Data from two almost simultaneous balloon soundings show that ozone and dust in combination are transported from their stratospheric reservoirs into the troposphere by way of thin laminae measuring about 1 kilometer vertically by at least 480 kilometers horizontally. Transport in this layer occurs across the top of the jet stream in a region of very great vertical wind shear. Stratospheric aerosol may be an important instrument for the destruction of ozone within the stratosphere.*

Recent intensive study of the exchange of material between stratosphere and troposphere has been provoked by the fallout of radioactive debris injected into the stratosphere. The transport processes are undoubtedly important in determining the residence-time of all stratospheric materials: ozone, aerosols, water vapor, and others. All the mechanisms which exchange air parcels between stratosphere and troposphere are not yet clear; some data, however, show the location and structure of the material in transit. Thin ozone-rich laminae with a vertical dimension of the order of 1 km have been detected in the troposphere (*1*). Since the ozone concentration in these layers ("ozone rivers") is characteristic of ozone concentrations in the stratospheric reservoir of ozone, it was proposed that these laminae are in transit between stratosphere and troposphere.

The measurements reported herein show the nature of one of these transport processes. On 18 August 1964, two balloon soundings were made approximately 3 hours apart over New Brighton, Minnesota. On the earlier sounding (flight 719), launched at 0635 C.S.T., a photoelectric particle counter (*2*) measured the aerosol content in the integrated size ranges $D \geqq 0.45\ \mu$ and $D \geqq 0.7\ \mu$, D being diameter of the aerosol particles. At 0930 C.S.T., an ozone sounding (flight 720) by means of a chemiluminescent ozone detector was launched from the same site (Fig. 1).

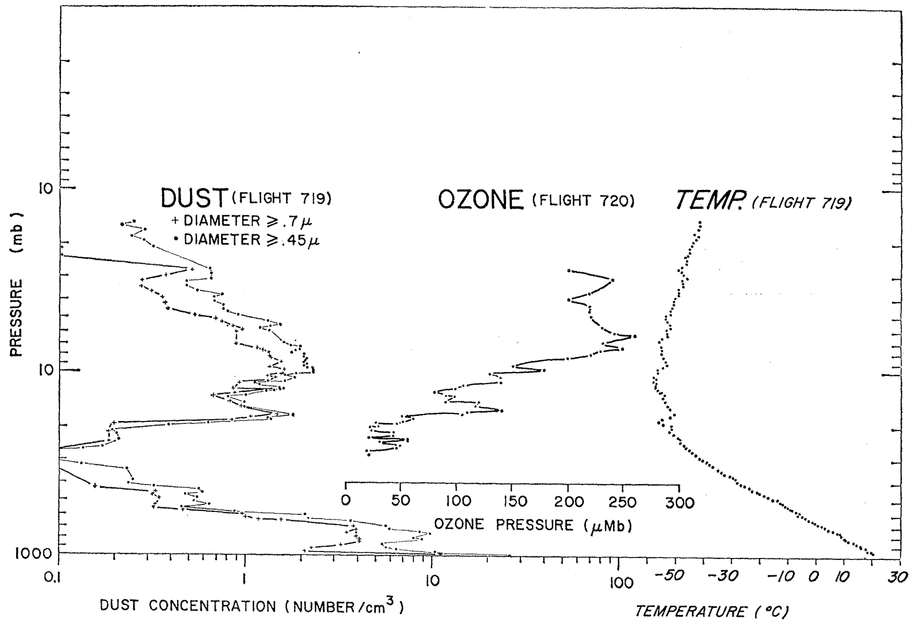

Fig. 1. Dust concentration and air temperature profiles from flight 719 and ozone distribution from flight 720, 18 August 1964.

Of particular interest in these soundings is the layer of the atmosphere between 200 and 130 millibars (mb). At a pressure of 165 mb an ozone river occurs wherein the ozone concentration is about twice that immediately above and below the layer. Since the ozone concentration in this layer is similar to that in the stratospheric reservoir, this layer shows ozone in transport from the stratosphere to the troposphere. In addition to and along with the ozone (Fig. 1), a layer of dust also is in transit. In addition to the ozone river and the dust layer, a strong temperature inversion is a composite part of this layer. To show the detail within the layer more clearly, an exploded view of the region between 300 and 100 mb appears in Figs. 2 and 3; the wind speed appropriate to each atmospheric level is also shown. Wind speeds were determined from the radiosonde azimuth and elevation records for each sounding in conjunction with the time-altitude record for each flight; the two balloon flights yielded separate wind and temperature records. Figures 2 and 3 show that the ozone and dust layers occur in a region of very great vertical wind shear. It cannot be concluded that the material in this layer diffuses downward, since the temperature does not indicate such a transport process and, more importantly, both ozone gradient and dust gradient are such that any mixing that does occur in the vertical must transport ozone and dust out of the layer. Only two alternatives remain: the layer represents either a diffusion transfer in the horizontal direction, with net transport of material from north to south; or inertial instability, in which case one would expect cross-contour flow and descending motion. It should be noted that the transport in this layer occurs across the top of the jet stream in the region of maximum vertical wind shear.

The measurements reported here and previous measurements of dust (*2*) and of ozone (*1*) lead one to speculate on the effect of stratospheric aerosol on the ozone concentration. Until now, it has generally been thought that ozone was a conservative atmospheric constituent between the ozone sink at ground level and the level at which photochemical time constants become comparable to the residence-time at approximately 35 km. However, it now appears possible that stratospheric aerosol provides an additional important sink for the decomposition of ozone. It is instructive to compare the strength of the aerosol sink with the sink at the

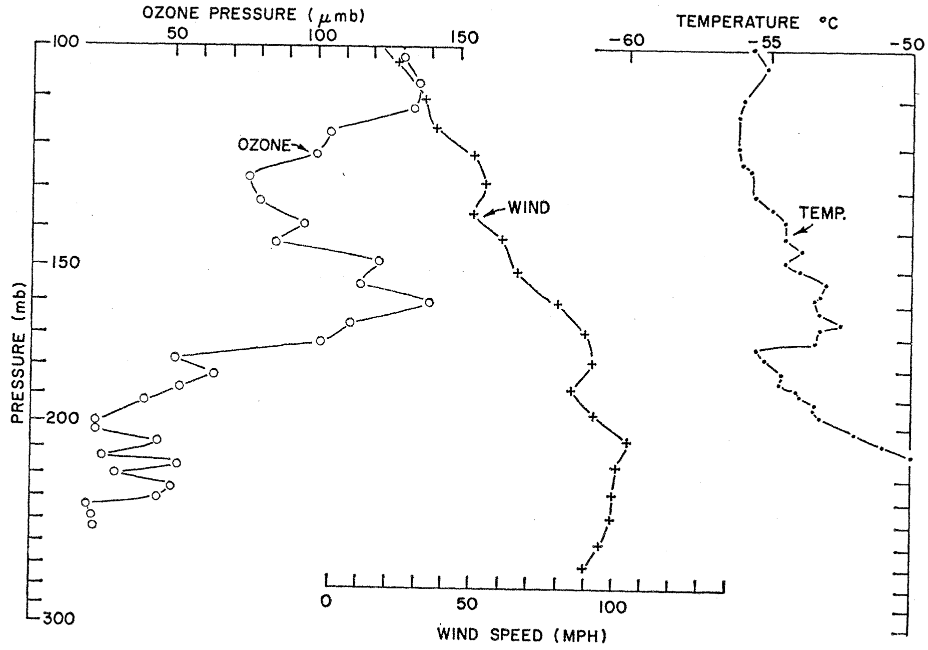

Fig. 2. Fine structure of the ozone, wind, and air temperature obtained between 300 and 100 mb on flight 720, 18 August 1964.

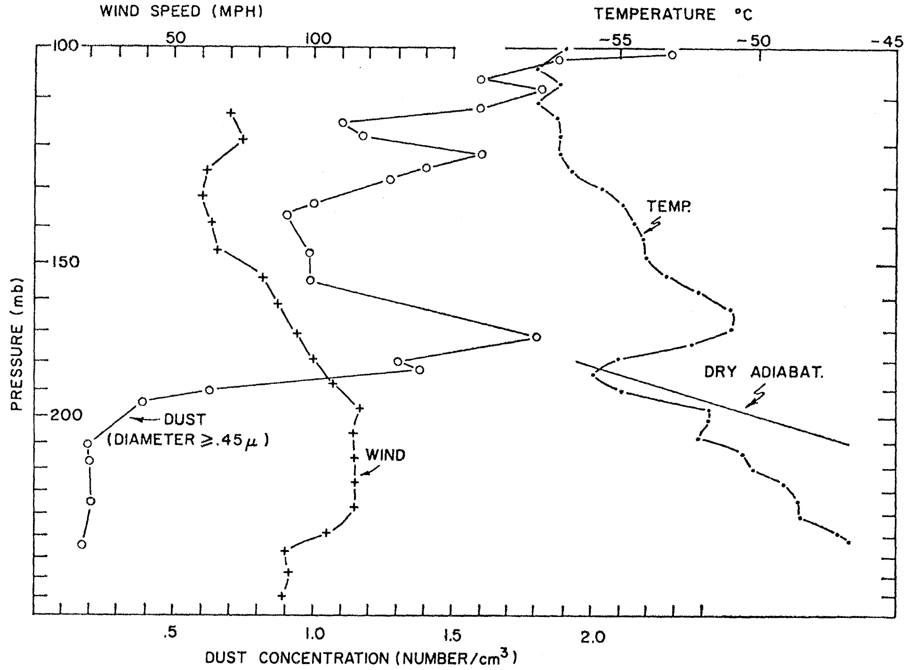

Fig. 3. Fine structure of the dust, wind, and air temperature obtained between 300 and 100 mb on flight 719, 18 August 1964.

earth's surface. The total aerosol area A in a 1-cm^2 column of stratosphere is given by:

$$A = N\,4\pi R^2 H$$

where N is the number density of aerosol particles at the base of the stratosphere, R is the mean particle radius, and H is the atmospheric scale height. If $N \simeq 3$ per cm^3, $R \simeq 0.5\ \mu$, and $H \simeq 7 \times 10^5$ cm, then $A \simeq 0.1$ cm^2.

Thus it seems not unreasonable to expect that the surface area of aerosols in the stratosphere may be as much as one-tenth of the earth's surface area. However, the diffusion of ozone to the aerosol particles does not impede the ozone decomposition process as it does at the earth's surface. Furthermore, the aerosol is strategically located in the stratosphere where the ozone concentration is five to ten times higher than the concentration near the earth's surface.

Thus, unless an activation energy or adsorption energy of ozone on the aerosol is important, it appears that the stratospheric aerosol may be an important sink for ozone. Decomposition must be catalytic, since the ozone concentration exceeds the aerosol concentration by a weight factor of ~ 100.

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Entrainment of a Tidal Rhythm

Abstract. *The endogenous tidal rhythm of locomotor activity of the sandbeach isopod,* Excirolana chiltoni, *has been entrained in the laboratory by a device designed to simulate wave action on a beach. The essential component of the treatment appears to be mechanical stimulation by a water current.*

Endogenous tidal rhythms—behavioral and physiological oscillations which are synchronized with the tides under field conditions and which persist in the animals for several cycles in a constant laboratory environment—were first described more than 50 years ago (*1*). The occurrence of these rhythms, particularly in intertidal crustaceans of several orders, has been thoroughly documented in recent publications (*2, 3*). The nature of the environmental stimuli which synchronize tidal rhythms on the shore, however, has remained an open question (*4*); hypotheses have ranged from mechanical or chemical stimulation (*3*) to the actions of subtle geophysical influences linked directly with lunar gravitation (*5*).

Experiments have now been conducted, in which synchronization of the activity rhythm of an intertidal isopod was achieved by means of water movements, which suggest that mechanical stimuli arising from wave action on a beach may be the normal synchronizing factor for the tidal rhythm of these crustaceans. This is apparently the first experimental demonstration that ecological factors other than cycles of light and temperature can act to synchronize an endogenous rhythm (*6, 7*).

Cirolanid isopods, *Excirolana chiltoni* (Richardson, 1905), were collected on 5 October 1964 from the mid-intertidal zone of the sand beach which fronts the Scripps Institution of Oceanography, La Jolla, California. This species, when freshly collected and placed in seawater in a laboratory aquarium, shows an activity rhythm similar to that described for *Synchelidium* sp. (*3*): if sand is provided, the animals remain buried except during a 4- to 6-hour interval shortly after tide crest on the beach of collection; during this interval, a large percentage of the animals can be seen swimming in the water of the aquarium.

For the first 7 days after collection, the animals were used in a number of preliminary experiments. On 13 October about 200 of the survivors were thoroughly mixed and then divided at random into three approximately equal groups. Those in groups A and B were subjected to intermittent swirling with water and sand, 15 seconds out of every minute, for a period of 6 hours, and were then left for 6 hours without movement. This 12-hour cycle of swirling water as opposed to quiet water, simulating the tidal pattern, was repeated for five cycles (2½ days). Groups A and B received entrainment regimes which differed by 6 hours in timing: group A was swirled from 4 to 10 p.m. and from 4 to 10 a.m.; group B was swirled from 10 p.m. to 4 a.m. and from 10 a.m. to 4 p.m. The third group, C, was not swirled, and thus served as a control group.