

scanned in a 4π paper scanner (Fig. 1).

Immediately after infusion there was high radioactivity in kidneys, adrenal glands, and uterus; the radioactive substance had the electrophoretic mobility of angiotensin. Thirty minutes after the end of the infusion, the radioactivity of the brain had increased significantly, but high levels remained in the kidneys and adrenals. However, the mobility of these radioactive products was different from that of angiotensin (Table 1).

Because of the close physiological association of angiotensin with the kidneys and adrenal glands (11), it is significant that high levels of angiotensin accumulate initially in these organs. Within 30 minutes angiotensin can no longer be recovered. Hence its half-life is similar to the half-life of vasopressin, oxytocin, and bradykinin (3), but not to the half-life obtained when I^{131} is used as tracer (2).

Incubation of tritiated angiotensin with undiluted human plasma containing heparin for 6 hours showed only slight destruction of pressor activity, or none at all, and no change in electrophoretic or chromatographic mobilities. Plasma diluted 1:10 with phosphate buffer (pH 7.4) or saline destroyed 70 percent of the pressor activity in 10 to 20 minutes. A new peak appeared in the chromatogram with an R_F of 0.15 to 0.20. Incubating angiotensin with hemolyzed red blood cells destroyed pressor activity completely in 60 to 90 minutes; at the same time a new peak with an R_F of 0.71 to 0.76 appeared.

We assume, therefore, that two different "angiotensinases" exist, one in red blood cells and the other in plasma (12).

P. A. KHAIRALLAH, IRVINE H. PAGE,
F. M. BUMPUS, R. R. SMEBY
Research Division, Cleveland Clinic
Foundation, Cleveland, Ohio

References and Notes

1. R. L. Wolf, M. Mendlowitz, S. E. Gitlow, N. Naftchi, *Circulation* **23**, 754 (1961); R. L. Wolf, M. Mendlowitz, J. Pick, S. E. Gitlow, N. Naftchi, *Proc. Soc. Exptl. Biol. Med.* **109**, 308 (1962).
2. M. Mendlowitz, R. L. Wolf, S. E. Gitlow, N. Naftchi, *Circulation* **25**, 231 (1962).
3. H. A. Miller, *Oxytocin*, R. Caldeyro-Barcia and H. Heller, Eds. (Pergamon, New York, 1961), pp. 137-57; L. Silver, I. L. Schwartz, C. T. O. Fong, A. F. Delons, L. K. Dahl, *J. Appl. Physiol.* **16**, 1097 (1961); K. Saameli and T. K. A. B. Eskes, *Am. J. Physiol.*, in press.
4. V. du Vigneaud, C. H. Schneider, J. E. Stouffer, V. V. S. Murti, J. P. Aroskar, G. Winestock, *J. Am. Chem. Soc.* **84**, 409 (1962).
5. C. T. O. Fong, L. Silver, D. R. Christman, I. L. Schwartz, *Proc. Natl. Acad. Sci. U.S.A.* **46**, 1273 (1960).
6. Kindly supplied by Dr. R. Schwyzler of Ciba, Ltd., Basel.
7. For the pressor assay and unitage, see F. M. Bumpus, P. A. Khairallah, K. Arakawa, I. H. Page, R. R. Smeby, *Biochim. Biophys. Acta* **46**, 38 (1961).
8. The tritiation was conducted at Tracerlab, Inc., Waltham, Mass.; for further details of the procedure see F. L. Jackson, G. W. Kittinger, F. P. Krause, *Nucleonics* **18**, 102 (1960).
9. J. H. Seu, R. R. Smeby, F. M. Bumpus, *J. Am. Chem. Soc.*, in press.
10. C. Neuberg, E. Strauss, L. E. Lipkin, *Arch. Biochem.* **4**, 101 (1944).
11. I. H. Page and F. M. Bumpus, *Physiol. Rev.* **41**, 331 (1961).
12. This work was supported in part by U.S. Public Health Service grant H-96 and by a grant from the American Heart Association. Dr. Frank Jackson and Frank Krause, Procter and Gamble Research Center, Cincinnati, Ohio, gave us invaluable assistance with tritiation experiments. One of us (P.A.K.) is an established investigator of the American Heart Association.

24 September 1962

Relation of Infrared Spectra to Coordination in Quartz and Two High-Pressure Polymorphs of SiO_2

Abstract. Infrared spectra of the four-coordinated quartz and coesite polymorphs of SiO_2 , the rutile six-coordinated (stishovite) polymorph of SiO_2 , and the quartz and rutile polymorphs of GeO_2 show that a change from tetrahedral to octahedral cation coordination results in (i) a 23-percent increase in the wavelength of the main absorption band for both the SiO_2 and GeO_2 polymorphs and (ii) a significant increase in the force constant of the same magnitude for the SiO_2 and GeO_2 polymorphs. The quartz and the rutile isostructural pairs for SiO_2 and GeO_2 show that the effect of increasing mass is to increase proportionally the wavelength of the respective main absorption bands. The infrared data for the rutile form of SiO_2 fit the empirical equation of Dacheville and Roy relating cation coordination, mass, atomic number, valence, and main absorption wavelength.

The infrared spectra of four polymorphs of SiO_2 and two polymorphs of GeO_2 were investigated independently by Lippincott *et al.* (1) and Dacheville and Roy (2). The SiO_2 polymorphs included quartz, tridymite, and cristobalite, all of which have silicon in four-fold coordination, and coesite, a high-pressure polymorph of SiO_2 whose coordination scheme was not known at that time. The GeO_2 polymorphs were the hexagonal four-coordinated quartz form and the tetragonal six-coordinated rutile form (3). Both groups of investigators showed that the main Si-O stretching frequency is the same for all the SiO_2 polymorphs and concluded that coesite had fourfold coordination,

a conclusion since confirmed by the single-crystal x-ray study of Zoltai and Buerger (4). They also found that the main Ge-O stretching frequency for the quartz form of GeO_2 is about 23 percent greater than that for the rutile form, and they ascribed this shift to the difference in primary coordination of the cation. Before the latter relationship can be used as a general indicator of coordination in simple compounds, additional pairs of polymorphs related by reconstructive transformation must be examined. With the exception of GeO_2 , however, no other pairs of suit-

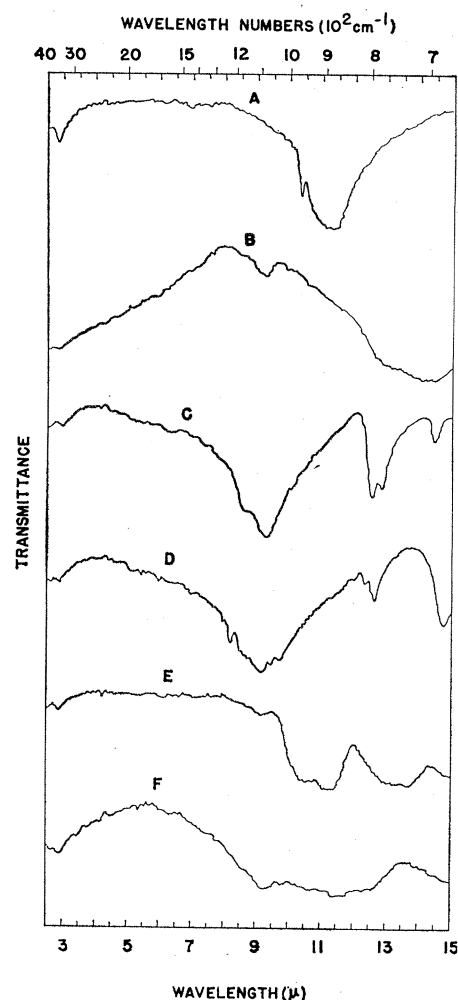


Fig. 1. Infrared absorption spectra of GeO_2 and SiO_2 polymorphs. (A) GeO_2 (quartz form), Fisher reagent; (B) GeO_2 (rutile form), prepared at 50 kb and 1000°C from the quartz form in a belt-type apparatus (7); (C) Quartz, high-purity single crystal from Hendersonville, North Carolina; (D) Coesite, prepared at 50 kb and 800°C from hydrated silica gel in a belt-type apparatus; (E) Stishovite from Meteor Crater, Arizona (8); (F) Mixture of stishovite and coesite prepared at 120 kb and $>1000^\circ\text{C}$ from hydrated silica gel in a girdle-type apparatus (7).

Table 1. Calculated values of K for SiO_2 and GeO_2 polymorphs.

Main absorption band, λ in microns			Calculated K		
Lippincott <i>et al.</i>	Dachille and Roy	This paper	Lippincott <i>et al.</i>	Dachille and Roy	This paper
11.30	11.5	11.35	<i>GeO₂ quartz</i>		
			0.176	0.170	0.174
13.89	14.0	14.10	<i>GeO₂ rutile</i>		
			0.174	0.172	0.169
9.24	9.15	9.22	<i>SiO₂ quartz</i>		
			0.167	0.171	0.168
9.11	9.2	9.15	<i>SiO₂ coesite</i>		
			0.172	0.169	0.171
		11.25	<i>SiO₂ rutile</i>		
					0.169
			Average: 0.172	0.171	0.170

ably related polymorphs were known which could be studied at ambient temperatures.

Stishov and Popova (5) recently synthesized a very high-pressure polymorph of SiO_2 with a rutile structure in which the silicon is in octahedral coordination. Chao *et al.* (6) discovered this new polymorph of SiO_2 in the coesite-bearing Coconino sandstone from Meteor Crater, Arizona, and named it stishovite. We have recently synthesized stishovite at pressures between 75 and 120 kb and temperatures greater than 800°C (7). Stishovite and either coesite, quartz, tridymite, or cristobalite thus constitute a pair of polymorphs related by reconstructive transformation.

Infrared spectra of quartz and rutile forms of GeO_2 , quartz, synthetic coesite, natural stishovite from Meteor Crater, and an experimental product composed of a mixture of coesite and stishovite are shown in Fig. 1. All the samples were prepared by the KBr pressed-pellet technique; approximately 1 mg of sample and 300 mg of KBr were used. The spectra were obtained with a Perkin-Elmer "Infracord" recording spectrophotometer. The curves for the GeO_2 polymorphs and for quartz and coesite are in close accord with those previously published (1, 2). The spectra show that the effect of increasing the primary coordination of germanium in GeO_2 and of silicon in SiO_2 from 4 to 6 is to displace the main absorption band 24 and 23 percent, respectively, in the direction of increasing wavelength. The SiO_2 polymorphs, therefore, support the contention that infrared absorption spectra may be used to obtain information on cation coordination in simple compounds.

Based on the expression for the simple harmonic oscillation of two masses about a point,

$$f = \frac{1}{2\pi} \left(\frac{k}{\mu} \right)^{1/2}$$

(where f is the frequency, k is the force constant, and μ is the reduced mass), Dachille and Roy (2) suggested that the ratio of the squares of the wavelengths of the main absorption band of pairs of polymorphs may indicate the magnitude of the effect of coordination on the force constant. Our data give ratios of 1.54 and 1.49 for the GeO_2 and SiO_2 polymorphs, respectively.

The data of Lippincott *et al.* (1) and Dachille and Roy (2) give 1.51 and 1.48, respectively, for the GeO_2 polymorphs. These differences may be attributed to the broad character of the main absorption band for the rutile form of GeO_2 . The effect of coordination on the force constant is not only large but of the same magnitude in GeO_2 and SiO_2 .

The quartz and rutile forms of GeO_2 and SiO_2 may be used to show the effect of mass on the main absorption wavelength for tetrahedrally and octahedrally coordinated germanium and silicon. The ratio

$$[(\lambda^2/\mu)_{\text{GeO}_2}/(\lambda^2/\mu)_{\text{SiO}_2}]$$

for the quartz forms using our data is 1.18, and with the data of (1) and (2) it is 1.16 and 1.23, respectively. The corresponding ratio for the rutile forms is 1.22. The effect of mass on the main absorption frequency is apparently independent of the crystal structure.

Dachille and Roy (2) found that the following empirical function gave consistent values for the quartz forms of

BeF_2 , SiO_2 , and GeO_2 , and the rutile form of GeO_2 :

$$K = \frac{(CN)(\mu)(A_A + A_X)^{1/3}}{(Z_A Z_X)(\lambda^2)}$$

where CN is the coordination, μ is a reduced mass term, $(A_A + A_X)$ is the sum of the atomic numbers, $Z_A Z_X$ is the valence product, and λ is the main absorption wavelength. Three sets of K values for the SiO_2 and the GeO_2 polymorphs based, respectively, on published data (1, 2) and our study are given in Table 1. The Dachille-Roy function evidently holds well for these simple oxides, and the agreement is within 3 percent of $K = 0.171$.

C. B. SCLAR
L. C. CARRISON
C. M. SCHWARTZ

Battelle Memorial Institute,
Columbus 1, Ohio

References and Notes

1. E. R. Lippincott, A. Van Valkenburg, C. E. Weir, E. N. Bunting, *J. Res. Natl. Bur. Std.* **61**, 61 (1958).
2. F. Dachille and R. Roy, *Z. Krist.* **111**, 462 (1959).
3. H. E. Swanson *et al.*, *Natl. Bur. Std. (U.S.) Circ.* **539** **1**, 51 (1953); **8**, 28 (1959).
4. T. Zoltai and M. J. Buerger, *Z. Krist.* **111**, 129 (1959).
5. S. M. Stishov and S. V. Popova, *Geokhimiya* **1961**, No. 10, 837 (1961).
6. E. C. T. Chao, J. J. Fahey, J. Littler, D. J. Milton, *J. Geophys. Res.* **67**, 419 (1962).
7. C. B. Sclar, A. P. Young, L. C. Carrison, C. M. Schwartz, *ibid.*, in press.
8. This sample was obtained through the courtesy of D. J. Milton and E. C. T. Chao of the U.S. Geological Survey.

18 July 1962

Pollen Sequence at Kirchner Marsh, Minnesota

Abstract. A pollen diagram from Kirchner Marsh, southeastern Minnesota, records a continuous vegetation sequence from the time of Late Wisconsin ice retreat from the region. The late-glacial and early postglacial portions of the diagram are correlated with a radio-carbon-dated diagram from Madelia, Minnesota. Both diagrams show a series of maxima of pollen types in the early postglacial that suggest a significant climatic change at that time. The Kirchner diagram, in addition, shows high percentages of nonarborescent pollen later in the postglacial that indicate an advance of prairie elements into the area between 7200 and 5000 years ago.

Kirchner Marsh, located on the St. Croix moraine of the Cary stage of the Wisconsin glaciation, is about 18 miles south of Minneapolis. The present vegetation of the region consists primarily of oak forest, principally