

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	0.176	0.170	0.174
13.89	14.0	14.10	0.174	0.172	0.169
9.24	9.15	9.22	0.167	0.171	0.168
9.11	9.2	9.15	0.172	0.169	0.171
		11.25			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

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

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 radiocarbon-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 nonarboreal 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 stade of the Wisconsin glaciation, is about 18 miles south of Minneapolis. The present vegetation of the region consists primarily of oak forest, principally

Quercus borealis, *Q. alba*, and *Q. macrocarpa*. Two transects, consisting of a total of 12 borings, were made across the marsh, one nearly north-south, and the other east-west. Cuttings from the deepest boring were used both for pollen analysis and for samples for radiocarbon dating. The pollen diagram (Fig. 1) is generalized from the more detailed diagram which will be published jointly with a diagram from Lake Carlson (1). The sampling interval for the lower part of the diagram (below 850 cm) is 5 cm, and for the remainder of the diagram it is 25 cm. Each significant maximum is supported by at least two pollen spectra. The pollen-zone terminology for New England proposed by Deevey (2) is adopted here because the main lines of vegetational succession are closely similar, even though the significant pollen types are not always the same.

Almost the entire pollen sequence at this marsh is duplicated, even in many minor details, by the diagram for Lake Carlson, a site 3 miles northwest, also in the St. Croix moraine (3). The late-glacial portion of the Kirchner Marsh diagram is closely matched by the sequence at Madelia (4), a site on Mankato drift 90 miles southwest (Fig. 1).

Correlation of the pollen zones at Kirchner Marsh and Madelia with glacial and climatic events is aided by radiocarbon dates. The lowest zone at the marsh, as yet unlabeled and consisting of only two spectra below the A-a zone, is marked by high percentages of *Picea*, Cyperaceae, and Gramineae pollen. The correlative zone at Madelia (zone I) has high percentages of Cyperaceae and *Picea*, but low percentages of Gramineae. This zone is correlated with the Mankato ice retreat and is dated by carbon-14 as $12,650 \pm 350$ years ago (W-824) (5). The *Picea-Fraxinus* maximum that follows (zone A-a at Kirchner and zone II at Madelia), which represents the Two Creeks interstade, terminated about $11,250 \pm 400$ years ago (W-1058) (5). The Valdres ice advance is represented at Kirchner Marsh by a low maximum of *Artemisia* (zone A-b), just as it is at a site in northeastern Minnesota (6) and at a site bordering the Valdres drift in eastern Wisconsin (7). At Madelia, which was farther from the maximum Valdres ice advance, the *Picea* forest had already begun to deteriorate at this time and was being replaced by *Alnus* and *Betula* (zone III); the *Artemisia* maximum is represented, nonetheless,

and seems to be a key feature of the Valdres stage.

The postglacial phases are considered to start at the marsh with the abrupt decline of the *Picea* curve. Zone B encompasses first a maximum of *Betula*, *Alnus* and *Abies*, then an abrupt rise and fall of *Pinus*, and finally the equally abrupt rise of *Ulmus* and *Quercus*. Zone B thus represents a time of rapid vegetational succession, thus reflecting the climatic change that brought the final recession of ice from the Great Lakes region. The correlation is checked by the carbon-14 date of $10,225 \pm 105$ years ago (Y-1141) (8) for the *Betula* peak at Kirchner Marsh. The correlative succession at Madelia differs somewhat. Percentages of *Alnus* and *Betula* had already reached high levels during the Valdres stage (first part of zone III) because the *Picea* forest was already being replaced. Then the *Betula* curve reaches higher values, possibly due to the absence of *Pinus* pollen, which normally depresses the

percentages of other types. Finally, *Ulmus* and *Quercus* rise as at Kirchner Marsh, with a control carbon-14 date of 9300 ± 350 years ago (W-825) (5).

Zone C-a at Kirchner is marked by decreasing *Ulmus* and increasing *Quercus*. Zone C-b shows high values for the nonarboreal components and suggests the existence of prairie in the region during the interval from about 7200 to 5000 years ago (actual carbon-14 control dates are 7124 ± 105 years ago and 5450 ± 70 years ago, Y-1140 and Y-1139, respectively) (8). Some pronounced fluctuations, especially in the curves for *Ambrosia*-type and for Chenopodiaceae-Amaranthaceae (even more striking in the Lake Carlson diagram), are interpreted as a record of weed encroachment on the intermittently dried lake floor. Zone C-c sees the decline of the nonarboreal pollen curve and the rise once again of *Quercus* as the forest returned to the region. The sharp rise in Cyperaceae near the top reflects the encroachment

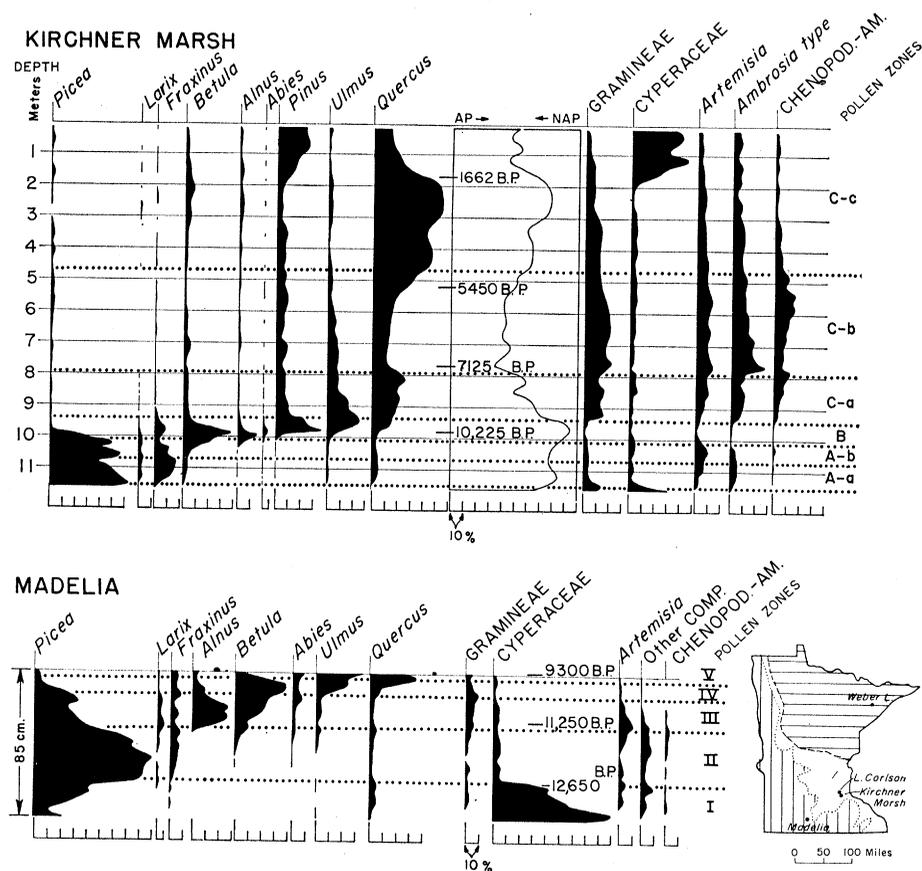


Fig. 1. Generalized pollen diagrams from Kirchner Marsh and Madelia, southern Minnesota. Pollen sum is generally between 300 and 700 grains. Included in the pollen sum are trees, shrubs, and anemophilous herbs. AP and NAP (Kirchner Marsh diagram) refer to arboreal pollen and nonarboreal pollen, respectively; B.P., before present or years ago. Horizontal lines, vertical lines, and plain area indicate coniferous and deciduous forest, prairie, and deciduous forest, respectively, on the map next to the Madelia diagram. [Madelia diagram redrawn from Jelgersma (4)]

of marsh vegetation into the lake, but the concomitant rise of *Pinus* (dated as 1662 ± 80 years ago, Y-1155) (8) may record a southward advance of pine from its major area of distribution in northeastern Minnesota. The sediment of the main core is truncated at the top, but a supplemental core from elsewhere in the marsh shows an abrupt rise in *Ambrosia*-type and in *Chenopodiaceae*-*Amaranthaceae* which is probably attributable to the disturbance caused by forest clearance and agriculture in the region.

THOMAS C. WINTER

U.S. Geological Survey,
St. Paul, Minnesota

References and Notes

1. H. E. Wright, Jr., T. C. Winter, H. L. Patten, in preparation.
2. E. S. Deevey, Jr., *Am. J. Sci.* **249**, 177 (1951).
3. H. L. Patten, unpublished M.S. thesis, University of Minnesota, Minneapolis (1959).
4. S. Jelgersma, *Am. J. Sci.* **260**, 522 (1962).
5. U.S. Geological Survey radiocarbon measurements VII, in preparation.
6. M. Fries, *Ecology* **43**, 295 (1962).
7. R. J. West, *Am. J. Sci.* **259**, 766 (1961).
8. Letter from M. Stuiver, March 1962.
9. This paper was presented at the International Conference on Palynology, Tucson, Ariz., April 1962. My research was conducted at the University of Minnesota Geology Department with the financial support of the Hill Family Foundation, St. Paul, Minn.

22 August 1962

Inhibition of Antigen-Antibody Reactions by Aminocarboxylic Acids

Abstract. Aliphatic aminocarboxylic acids inhibit at least two different antigen-antibody reactions. The degree of inhibition depends upon carbon chain length and the position of the amino group in relation to the carboxyl group.

The solubility in saline solution of macromolecular complexes of deoxyribonucleoprotein is increased when certain aliphatic aminocarboxylic acids are present (1). Activity of the compounds which were studied was maximal when the chain contained six carbon atoms and when the amino group was in the terminal (omega) position rather than in the alpha position. We have studied the effects of these compounds on another group of macromolecular complexes, namely those arising from reactions of antigen and antibody.

The first group of experiments was based on a precipitin reaction between crystalline bovine serum albumin and specific rabbit antiserum (2). The reaction was carried out at pH 7.4 by double diffusion in agar (3). The test compounds were added to the reaction

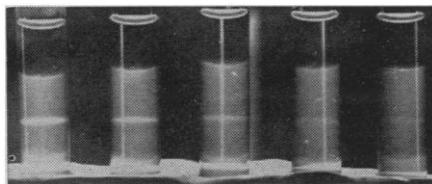


Fig. 1. Influence of ϵ -aminocaproic acid (0, 0.1, 0.25, 0.5, 1.0M concentration) on the precipitin reaction between bovine serum albumin and specific antiserum.

tubes in varying amounts prior to immunodiffusion, and any effect on the final amount of precipitate was noted. Figure 1, a photograph taken on the 8th day of one such experiment, shows that increasing amounts of the aminocarboxylic acid ϵ -aminocaproic acid caused a progressive inhibition of the antigen-antibody reaction. This is seen as a decrease in the amount of precipitate.

A comparative study was then made of the inhibition of the precipitin reaction by different aminocarboxylic acids. At a final concentration for the amino acid of 1M, the relative ability to inhibit was as follows: ϵ -aminocaproic acid, γ -aminobutyric acid, β -alanine. Glycine and the control, which contained no amino acid, showed no inhibition. ω -Aminocaprylic acid was less inhibitory than ϵ -aminocaproic acid; α -aminobutyric acid was the same as the control. Maximum inhibition was thus provided by a compound with a six carbon chain where the amino group was in the terminal position.

The second group of experiments was designed to avoid the necessity for a secondary expression, such as precipitation, of the primary union of antigen and antibody. Leucocyte nuclei

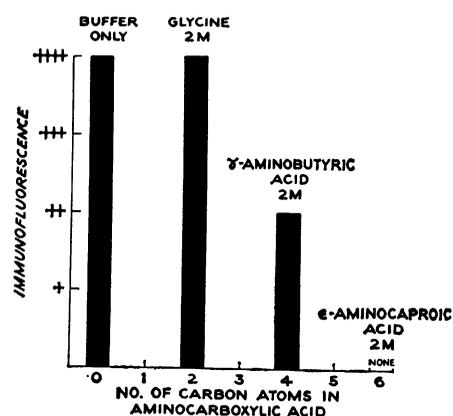


Fig. 2. Influence of certain aminocarboxylic acids on the binding of anti-globulin serum to globulin-coated nuclei.

from normal human blood, which was smeared onto glass slides, were coated with gamma globulin from serum which was drawn from a patient with lupus erythematosus and which was known to contain antibodies to nuclei. The globulin-coated nuclei were then treated with rabbit antihuman globulin which had been conjugated with fluorescein isothiocyanate and examined with a fluorescence microscope (4, 5). The effect of aminocarboxylic acids was studied by incorporating at pH 7.4, prior to treatment of the nuclei with the conjugate, varying amounts of these compounds into the fluorescent conjugate and by noting any change in the brilliance of the immunofluorescence. A decrease in fluorescence was interpreted as an inhibition of the fixation of antiglobulin to the globulin-coated nuclei. The fluorescence of the conjugate itself was not lessened by the presence of the test compounds.

A preliminary experiment showed that increasing amounts of ϵ -aminocaproic acid inhibited the test reaction. At a concentration of 2M the reaction was totally inhibited, and this concentration was then used to study the effect of chain length of the aminocarboxylic acids (Fig. 2). Further studies with this method have shown that arginine and lysine are both considerably more inhibitory than ϵ -aminocaproic acid.

Our studies of nucleoproteins showed that the effect of the aminocarboxylic acids was not related to their activity as salts or chelating agents, and this is also true for the phenomena here reported. The high dielectric activity of the more inhibitory aminocarboxylic acids suggests one possible explanation for their action, but a complete correlation is not yet available (6, 7).

Note added in proof. Since this report was submitted for publication, the work of Gill *et al.* (7) has come to our attention. Their studies of synthetic polypeptides suggest that certain amino acids are important as antigenic determinants and that inhibition of reactions between antigen and antibody by amino acids may be due to specific complementary relationships between those amino acids and the antibody or antigen.

WILLIAM A. ATCHLEY
N. V. BHAGAVAN

Cancer Research Institute and
Department of Medicine, University of
California School of Medicine,
San Francisco 22