

Fig. 2. Infrared spectra of spawning inhibitor obtained from *Asterina testis* (A) and of L-glutamic acid (B) in Nujol.

hydrolysis, revealed that the sample was pure and contained nothing but glutamic acid.

This identification was next checked by comparison of the sample with authentic L-glutamic acid. Amino acid-autoanalyzer diagrams of the sample and of the sample mixed with standard L-glutamic acid both showed single peaks at the same position. The infrared-absorption spectrum (Fig. 2) and the nuclear magnetic resonance spectrum of the sample were in good agreement with those of the authentic L-glutamic acid. Both sample and standard showed the same optical rotation: $[\alpha]_D^{25} +29^\circ$ (6N HCl, 25°C). All these results clearly showed that the purified sample was L-glutamic acid.

Furthermore biological assay of the authentic L-glutamic acid revealed that 5 to 50 $\mu\text{g/ml}$ effectively inhibited the activity of 20 μg of lyophilized nerve per milliliter in inducing spawning. This activity corresponded well with that of the purified sample. The effectiveness of amino acids other than glutamic acid was also examined by use of the following 18 amino acids: glycine, alanine, serine, cysteine, threonine, valine, methionine, leucine, isoleucine, phenylalanine, tyrosine, proline, hydroxyproline, tryptophane, aspartic acid, arginine, lysine, and histidine. Ovarian fragments of *A. pectinifera* were placed in sea water containing each of these amino acids at a concentration of 10^{-2} M together with nerve extract (20 $\mu\text{g/ml}$), and the degree of spawning was observed. None of the amino acids except aspartic acid had inhibitive effect (the inhibitive activity of aspartic acid was less than 10 percent of that of glutamic acid).

Finally determination with the amino acid autoanalyzer of the contents of

free amino acids in the acetone powder of testis material of *A. pectinifera*, by use of a trichloroacetic acid extract (7), showed that 4.9 μg of glutamic acid and 0.2 μg of aspartic acid were present in 1 mg of the acetone powder. Inhibition of spawning by testis extract (2.5 to 10 mg of dry tissue per milliliter) can therefore be explained by the inhibitive action of glutamic acid contained in the testis. Although free aspartic acid also is present in starfish gonad as we have explained, its low content and its low activity in inhibiting spawning suggest that the representative inhibitor of spawning in the testis of *A. pectinifera* is L-glutamic acid. Considering the normal proportion by weight of testis to radial nerve (about 90 : 1) in a starfish, only a part of the glutamic acid present in the gonad

seems to act as an inhibitor of spawning under natural conditions. The mechanism of this inhibition remains unknown.

S. IKEGAMI
S. TAMURA

Department of Agricultural Chemistry,
University of Tokyo, Bunkyo-ku,
Tokyo, Japan

H. KANATANI

Ocean Research Institute, University
of Tokyo, Nakano-ku, Tokyo

References and Notes

1. A. B. Chaet and R. M. McConaughy, *Biol. Bull.* **117**, 407 (1959); A. B. Chaet, *ibid.* **126**, 8 (1964); **130**, 43 (1966); T. Nourura and H. Kanatani, *J. Fac. Sci. Univ. Tokyo Sect. 4* **9**, 397 (1962); H. Kanatani, *Science* **146**, 1177 (1964).
2. H. Kanatani and T. Nourura, *J. Fac. Sci. Univ. Tokyo Sect. 4* **9**, 403 (1962); *Zool. Mag. Tokyo* **73**, 65 (1964); A. B. Chaet, *Biol. Bull.* **130**, 43 (1966).
3. H. Kanatani and M. Ohguri, *Biol. Bull.* **131**, 104 (1966).
4. H. Kanatani, *Science* **146**, 1177 (1964); in *Sex and Reproduction, Gunma Symp. Endocrinol.*, K. I. Hanaoka, Ed. (Inst. Endocrinol., Gunma Univ., Maebashi, Japan, in press), vol. 4.
5. Sea water containing gamete-shedding substance was prepared as follows: several milligrams of lyophilized radial nerves were homogenized in a few milliliters of deionized water and centrifuged for 1 hour at 30,000g. The supernatant was diluted with sea water to a concentration of 10 μg of lyophilized nerve per milliliter.
6. H. Spackman, W. H. Stein, S. Moore, *Anal. Chem.* **30**, 1190 (1958).
7. R. Hancock, *Biochim. Biophys. Acta* **28**, 402 (1958).
8. Detailed results of this study will be reported elsewhere.
9. We thank H. Shirai for technical assistance, J. C. Dan and H. A. Bern for encouragement and advice, and the director and staff of Asamushi Marine Biological Laboratory where part of this work was carried out.

5 October 1967

Staurolite: Sectoral Compositional Variations

Abstract. *Electron-microprobe analyses across six successive sections of a single staurolite crystal show that the staurolite has three crystallographically controlled sectors, each with a distinctive content of Al, Si, Ti, Fe, Mg, and Mn. The sector distribution of elements raises the question of whether the staurolite acts as one or several phases during growth. Total analyses of the separate sectors suggest that: (i) the staurolite has tetrahedral Al substitution for Si, and (ii) the hydroxyl content varies between sectors.*

Electron-microprobe analyses of staurolite from the Kwoiek area, British Columbia, indicate that the individual staurolite crystals have markedly different compositions between sectors, which result from growth in different crystallographic directions; the compositions within any one sector are relatively homogeneous. This finding contrasts with compositional zoning patterns of garnet from the same rocks, which can be interpreted in terms of

a depletion model (1). Both minerals are from the assemblage chlorite-garnet-biotite-staurolite-ilmenite-quartz-plagioclase-graphite.

The volumes of the several sectors are defined by chiasolite-type patterns of inclusions, often described in staurolite (2). Figure 1, modified from Harker (2), illustrates in three dimensions the sectors in staurolite that have the crystallographic forms (010), (110), and (001). In the following discussion,

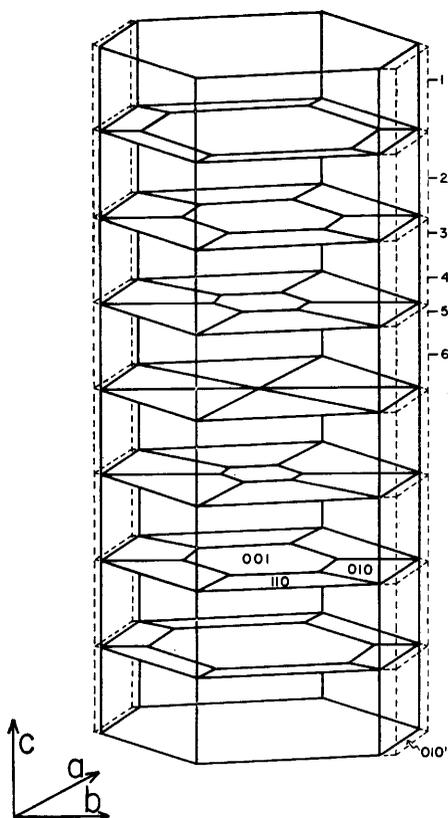


Fig. 1. Schematic drawing (2) illustrating geometry of sectors in Kwoiek-area staurolite. Numbers 1 to 6 refer to approximate positions of thin sections A to F of Fig. 2. Sections 1 and 6 are about 4 mm apart.

the sectors are named by the zone axis symbol for the presumed growth direction of the sector. Figure 1 shows that there are two symmetric [001] sectors, two [010] sectors, and four [110] sectors. Two other distinctive sectors, labeled [010]', are also present; the [010]' sector grew after [110] and [001] growth had ceased. The sector boundaries are defined optically by tiny quartz rods extending parallel to the presumed growth direction, normal to the sector's crystallographic face, and with bases on the plane between sectors; the staurolite of the Kwoiek area has less than 1 percent of these quartz inclusions. Regions of continuous staurolite can be traced optically from one sector to another, around the quartz inclusions.

The [110] and [001] sectors have the pleochroic formula $X = Y =$ very pale yellow, $Z =$ pale yellow; the [010] sector has the pleochroic formula $X =$ yellow, $Y =$ pale yellow, $Z =$ golden yellow. The color differences between the sectors permit easy identification of crystallographic directions, even in thin sections cut obliquely to the staurolite c -axis.

For study of the compositional variations in three dimensions, six polished thin sections were cut nearly normal

to the c -axis of a single staurolite grain. The approximate locations of the six polished sections with respect to the staurolite crystal form are shown in Fig. 1; the distance between the first and sixth is less than 4 mm. Section A of the six sections (Fig. 2), cut near the end of the crystal and about 50 percent quartz, illustrates a phenomenon observed in other staurolite of the same hand specimen: the sector [001] is commonly anhedral against quartz.

Figure 3a shows the variation in composition of the sectors [010] and [001] for SiO_2 , Al_2O_3 , TiO_2 , Cr_2O_3 , MgO , FeO , and MnO (traverse 1, section E, Fig. 2). Figure 3b shows the compositional variations of the sectors [110] and [001] for SiO_2 , Al_2O_3 , TiO_2 , MgO , and FeO (traverse 2, section E, Fig. 2). Not shown is ZnO , which is nearly constant for all points of all sectors at about 0.2 percent by weight. Chromium was detected only at the edge of [010], in the sector labeled [010]' in Fig. 1. Similar profiles were made for the other five sections, and the position of the discontinuous changes of concentration is always at the boundary between sectors. The relative changes of concentrations of the elements across the sector boundaries, and the concentrations of the elements in each sector, are nearly constant throughout the crystal. A profile along the c -axis of another staurolite from the same rock shows that Al, Si, and Ti are constant from the center to about 200μ from the staurolite edge, where Al declines and Ti and Si rise slightly as one approaches the edge. The change in Mg is about the same along [001] as it is in [010] and [110] (Fig. 3).

Table 1 shows total analyses for the points indicated in Fig. 3; the analyses are based on the correction factors of Bence and Albee (3). Wavelength profiles, made at selected points of the staurolite crystal, revealed minor amounts of Zn and Cr, but unusual concentrations of other elements were not discovered. The formula accepted by Deer *et al.* (4), that of Náray-Szabó and Sasvári (5), contains 30 cations (excluding H^+) in the unit cell. The formulas of Table 1, calculated on the basis of 30 cations, yield summations of cations, for each of the three positions, that closely approach the ideal. Clearly indicated in the formulas is tetrahedral substitution of Al for Si, creating a positive charge deficiency in [001]. One way of balancing the charge discrepancy is by postulating

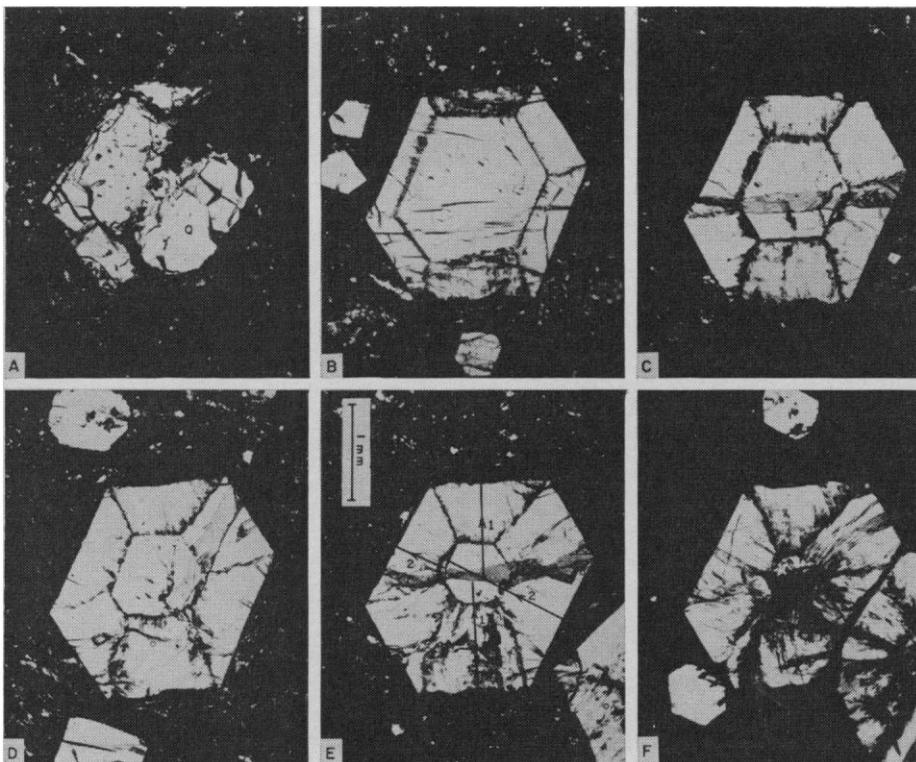


Fig. 2. Six successive thin sections of a single staurolite crystal; plane-polarized light. Note lines of inclusions marking sector boundaries. The positions of the electron-microprobe traverses of Fig. 3 are shown in section E. Crystals besides the staurolite crystal are garnets; Q, quartz.

deficient $(OH)^-$ in $[001]$ relative to $[010]$ and $[110]$. The higher anhydrous total of $[001]$, relative to $[110]$ and $[010]$, lends support to this hypothesis.

The observed pleochroic differences between the sectors are most probably due to either Ti^{3+} or Fe^{3+} preferentially concentrated in the $[010]$ sector. Differences in concentration of Ti alone could not account for the color differences because there is as much Ti at the edge of $[110]$ as in $[010]$ (Fig. 3); but there is no color zonation within $[110]$. Recent data (6) suggest that Ti^{3+} is the coloring element in kyanite, and the similarity in crystal structure of staurolite to kyanite (5) indicates that positive evidence for the presence of Ti^{3+} should be sought in staurolite. The formulas shown in Table 1 do not indicate significant differences in Fe^{3+} between sectors, but the exact amount of Fe^{3+} in each sector cannot yet be determined analytically.

The cell dimensions of both the $[010]$ and $[001]$ sectors are identical within the limits of error: a , $7.89 \pm 0.01 \text{ \AA}$; b , $16.62 \pm 0.02 \text{ \AA}$; and c , $5.65 \pm 0.02 \text{ \AA}$. These values fall within the range given by Deer *et al.* (4, 7).

The most important aspect of the compositional variations of the staurolite is the petrologic implication of crystallographic control of composition. The different compositions of the sectors of the Kwoiek-area staurolite are related to growth directions in the staurolite, and presumably are related to the different atomic configurations of each growing face. If the phenomenon is governed by surface equilibrium processes, one would expect that staurolite from other localities, having the same morphology, would have similar variations in sectoral composition; or staurolite lacking variations in sectoral composition would be expected to have a different morphology, with minimal differences of surface energy between faces. Also, if the process leading to variations in sectoral composition were an equilibrium process, one would expect the distribution of elements between sectors, for elements occupying similar atomic sites, to be the same for all staurolite of one outcrop and to vary systematically with metamorphic grade. The answers to these predictions of equilibrium remain unknown.

An alternate hypothesis, which does not depend on thermodynamic equilibrium, is that the rate of growth of staurolite may affect the staurolite com-

position. From the inequidimensional form of the staurolite it is clear that the crystal grew at different rates in different crystallographic directions. The biggest chemical difference is between the $[010]$ and $[110]$ sectors and the $[001]$ sector, correlating with the greatest difference of sector growth rates. The facts that the faster growing

sector, $[001]$, contains more Al than is reported from staurolite analyses, and that it contains a greater amount of tetrahedral Al than the slower growing sectors, lends weight to the hypothesis of kinetic control of composition. If kinetic control is important, the faster a mineral, or sector of a mineral, grew, the more its composition would

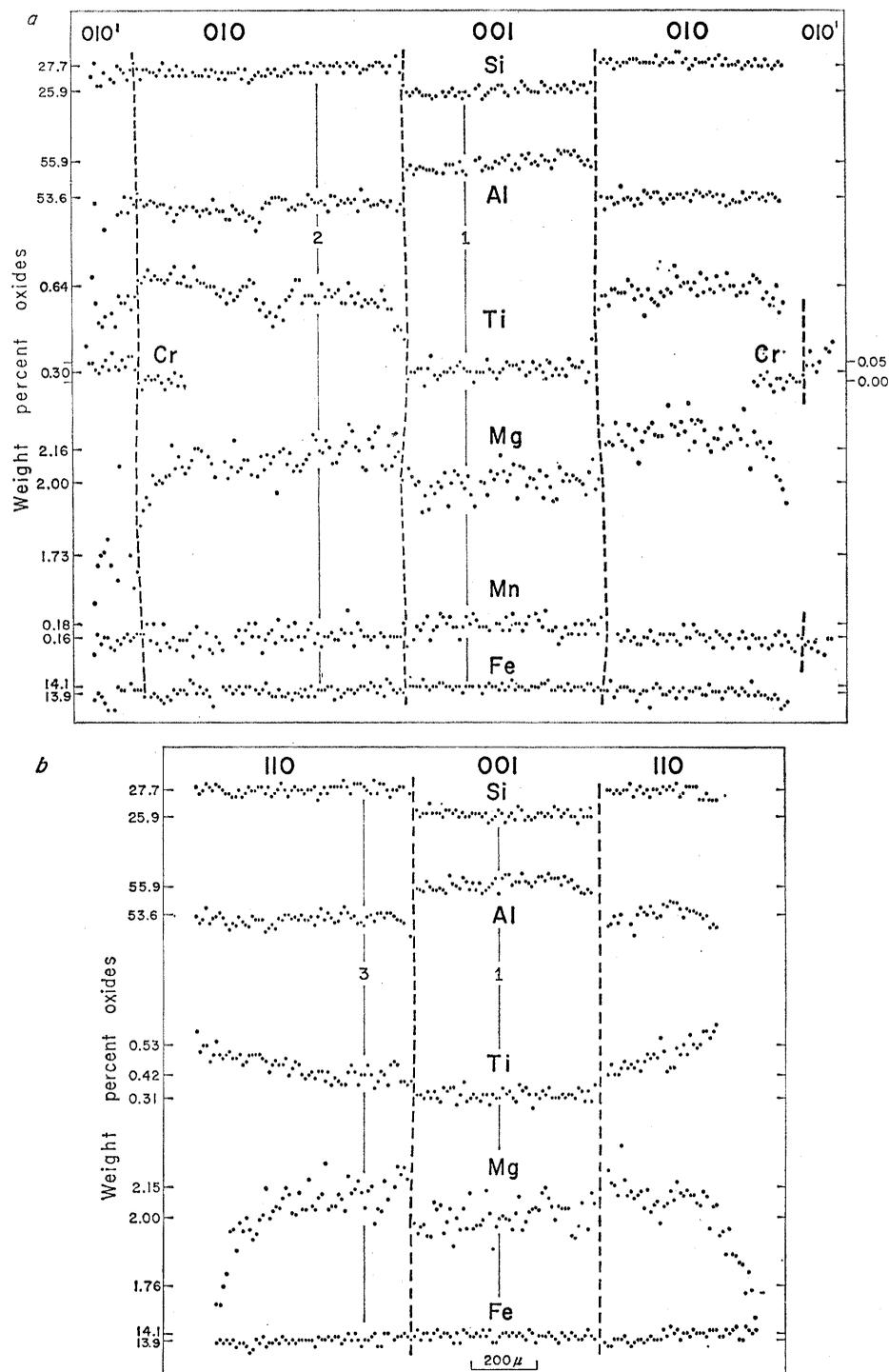


Fig. 3. (a) Variations of the elements Si, Ti, Cr, Mg, Fe, and Mn along traverse 1 ($[010]$ - $[001]$ - $[010]$), section E of Fig. 2. (b) Variations of the elements Si, Al, Ti, Mg, and Fe along traverse 2 ($[110]$ - $[001]$ - $[110]$), section E of Fig. 2. Electron-beam diameter is less than 2μ ; analysis interval is 10μ . Vertical scales are based on total analyses at nine points, three of which (1-3) are in Table 1.

Table 1. Results of analyses of staurolite.

Component; ion	1 [001]	2 [010]	3 [110]
SiO ₂	25.96	27.66	27.50
TiO ₂	0.32	0.64	0.46
Al ₂ O ₃	55.93	53.57	53.82
FeO	14.07	13.98	13.84
ZnO	0.2	0.2	0.2
MnO	.19	.17	.16
MgO	1.99	2.11	2.13
<i>Anhydrous totals</i>			
	98.66	98.33	98.11
<i>Numbers of ions on the basis of 30 cations</i>			
Si	7.27	7.80	7.76
Al	0.73	0.20	0.24
Al	17.72	17.60	17.66
Ti	0.07	0.14	0.10
Fe ³⁺	.21	.27	.24
Fe ²⁺	3.09	3.03	3.02
Mg	0.83	0.89	0.89
Mn	.05	.04	.04
Zn	.04	.04	.04

be expected to differ from an "equilibrium composition." As the Kwoiek area is one of contact metamorphism related to the Coast Range Batholith, it is reasonable to presume that the metamorphic event took place during a brief period relative to regional metamorphic events. The concept of kinetic control of composition is not unknown in synthesis experiments (8); it may be an important process in the governing of compositions of metamorphic minerals.

The zoning in Mg within individual sectors probably reflects changes in the physical conditions of the environment, because the behavior of Mg is nearly the same in all three sectors, rather than being a growth-rate phenomenon. If the crystal grew under conditions of increasing temperature, which possibility is reasonable, an implication of the Mg zoning pattern is that the Mg:Fe ratio of the staurolite decreases, in the assemblage chlorite-biotite-garnet-staurolite, with increase in temperature.

The region marked [010]' in Fig. 3 typically has a high concentration of graphite inclusions, is added to the [010] region without a concurrent growth in the [110] or [001] sectors, and has 0.05 percent Cr₂O₃. The [010]' sector is present in its entirety on only one side of the profile of Fig. 3, being partially resorbed from the other side, and it has an anomalously low content of Mg; it is not apparent in Fig. 2 because it blends optically with the background. Petrologic explanation of this phenomenon remains speculative. It may be that depletion of other elements in the pore fluid increased the chemical activity of Cr in

the pore fluid to such an extent that it could go into staurolite in the last stage of staurolite growth.

Other minerals that have formed during the process of metamorphic recrystallization and that exhibit sector zoning are andalusite and kyanite. White and White (6), without apparently recognizing the sector distribution pattern of Ti in kyanite, nevertheless presented oral evidence that Ti can be sectorally zoned in kyanite. Andalusite of the Kwoiek area shows differences of birefringence between crystallographic sectors. The lower birefringent sector, [001], contains 1.05 percent Fe₂O₃, 0.12 percent TiO₂, and 0.70 percent MgO. The higher birefringent sectors, [100] and [010], contain 0.28 percent Fe₂O₃, 0.04 percent TiO₂, and 0.08 percent MgO. These data are consistent with those of Chinner *et al.* (9), who recognized similar compositional variations correlating with the birefringent differences, but apparently did not recognize the sectoral significance.

LINCOLN S. HOLLISTER

Department of Geology, University of California, Los Angeles 90024

A. E. BENCE

Division of Geological Sciences, California Institute of Technology, Pasadena 91109

References and Notes

- L. Hollister, *Science* **154**, 1647 (1966).
- A. Harker, *Metamorphism* (Methuen, London, 1932), p. 44.
- A. Bence and A. Albee, at Nat. Conf. Electron Microprobe Analysis, 2nd, Boston, 1967.
- W. Deer, R. Howie, J. Zussman, *Rock-Forming Minerals* (Wiley, New York, 1962), vol. 1, pp. 151-60.
- I. Náray-Szabó and K. Sasvári, *Acta Cryst.* **11**, 862 (1958).
- E. W. White and W. B. White, *Trans. Amer. Geophys. Union* **48**, 232 (1967).
- Wayne Dollase, University of California, Los Angeles, made precession photographs of thin slices of a staurolite cut normal to the *c*-axis, from the same rock as the one of Fig. 2. He found no obvious differences between [001] and [010] in regard to symmetry, diffraction intensities, or unit cell dimensions. The space group was either *Cmcm* or *C2cm*. No reflections of the type *Ok*l, $1=2n+1$, were found.
- J. L. Torgesen, *Ann. N.Y. Acad. Sci.* **137**, 30 (1966).
- G. A. Chinner, C. R. Knowles, J. V. Smith, Cambridge abstr., Intern. Mineral. Assoc., 1966.
- Supported by NSF grants GP-2773 and GP-3570 to A. L. Albee (California Institute of Technology) and an Academic Senate Research Grant from the University of California, Los Angeles. We thank J. L. Rosenfeld (University of California, Los Angeles) for stimulating discussions of processes of crystal growth and A. L. Albee (California Institute of Technology, Pasadena) and W. G. Ernst (University of California, Los Angeles) for criticism of the manuscript. Arthur Chodos and Arden Albee (California Institute of Technology) assisted with the analyses and computations. John de Grosse (University of California, Los Angeles) prepared the serial thin sections.

12 October 1967

Hemoglobin Variants in Koreans: Hemoglobin G Taegu

Abstract. *Hemoglobin G Taegu*, an electrophoretically slow hemoglobin with a structural anomaly believed to be in the β -T-3 section of the beta chain, was the only variant found among 6700 normal Koreans. Four subjects, 0.06 percent, had the G-hemoglobin variant in addition to normal hemoglobin A. Hemoglobin E, known in numerous groups from Southeast Asia and the variant most frequently seen in Chinese subjects, was not found among the Koreans we tested.

During the past decade numerous Asian ethnic groups have been surveyed for hemoglobin variants. Although most studies have involved insufficient numbers of subjects, it has been clearly demonstrated that the Asian groups differ markedly from each other with respect to the variety and incidence of the variants. From our preliminary studies reported here it appears that Korean people have a low incidence of hemoglobin variants.

So far we have studied 6700 Koreans, 4841 males and 1859 females, all presumably normal and healthy. Our first samples of blood were obtained from 2110 male members of the army of the Republic of Korea stationed near Taegu, Korea (1); recently, 4590 additional blood samples were obtained from school children and university students of both sexes in the vicinity of Seoul. Blood samples were collected by finger prick into merthiolate-treated capillary tubes and were allowed to clot. The samples were maintained under refrigeration until returned by air to Taipei for analysis. Hemolysates were made from the clots (2) and were analyzed by the Smithies vertical starch-gel method (3) with the triethylenediaminetetraacetate-borate buffer system at pH 8.9 (4).

One male in the initial group of 2110 subjects and two males and one female in the second group of 4590 subjects were found to have a slow hemoglobin in addition to normal hemoglobin A. In all four subjects the slow component migrated at a rate characteristic of the G hemoglobins. The overall incidence of the variant in the present group of Koreans was low—4 in 6700 or 0.06 percent.

Studies of structure are in progress on the G hemoglobin from the blood of our initial subject found in Taegu (1). Special studies [by urea-dissocia-