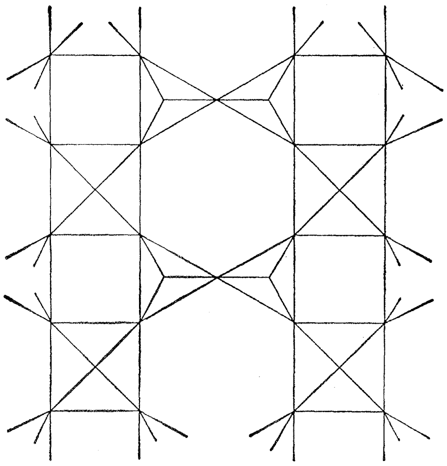

Fig. 2. Postulated crystal structure of lamprophyllite in the yz plane [after Woodrow (*5*)]. Titanium atoms reside in the square pyramids; silicon, in the tetrahedra.

"short" bonds (2.71 to 2.95 Å) and two "long" bonds (3.36 Å). In projection, the structure of fresnoite is strikingly similar to that of melilite, $(Ca,Na)_2(Mg,Al)[Si_2O_7]$ (Fig. 1b; cell parameters in Table 1). The coordinates and cell data come from Smith (*4*). Several differences are interesting: the melilite structure, unlike that of fresnoite, consists of undulating sheets with the symmetry-equivalent $[Si_2O_7]^{6-}$ double groups oriented *upward* and *downward* relative to the c-axis. Further, Ti in fresnoite resides in a square pyramid, whereas Mg in melilite is in tetrahedral coordination. Finally, the Ca^{2+} ions are in distorted square antiprisms of oxygen atoms in melilite. The pronounced sheet-like character of fresnoite, with the loosely held Ba^{2+} ions, affords the good-to-perfect c {001} cleavage relative to the distinct-to-poor c {001} cleavage for melilite.

The most curious feature of fresnoite, however, is the Ti^{4+}-centered oxygen polyhedron. Four oxygen atoms are tetragonally displaced 2.00 ± 0.04 Å from the titanium atom, the fifth (lone) oxygen atom being displaced only 1.66 ± 0.08 Å along c [001], forming a highly compressed square pyramid. The titanium atom is inside the square pyramid, displaced 0.59 Å from the base center. This lone oxygen atom was intentionally placed 2.00 Å from titanium during the refinement of atom coordinates, and it rapidly converged to the short displacement cited above. It is well resolved on the three-dimensional electron-density map.

Let us remark that the compressed square-pyramidal arrangement of oxygen atoms about titanium is not peculiar to fresnoite. The structure of lamprophyllite, $(Ba,Sr,K)Na(Ti,Fe)Ti[Si_2O_7](O,OH,F)_2$, solved for one projection by Woodrow (*5*), led to the sheet structure depicted in Fig. 2. Fortunately his solution was for a z-axis projection, an orientation that enabled us to calculate Ti—O~1.66 Å for the lone pyramidal oxygen atom. Thus the sheets of lamprophyllite are built of the same units as those of fresnoite, although arranged differently.

The Si—O distance for the oxygen atom shared by the tetrahedral pair is 1.65 ± 0.04 Å. The distance for oxygen atoms also associated with the Ti-centered square pyramid is 1.61 ± 0.04 Å, and the "apical" oxygen is displaced 1.59 ± 0.07 Å. Although the standard deviations are high, the overall mean Si—O distance is 1.615 ± 0.050 Å, agreeing with 1.615 Å for the mean suggested (*6*) for Si—O distances in Si_2O_7 groups.

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17 March 1967

Ethylene Formation from Ethyl Moiety of Ethionine

Abstract. *In plants, ethylene is formed in the presence of light and flavin mononucleotide from ethionine and* S-*ethylcysteine. The ethylene is formed from the ethyl moiety of ethionine.*

The formation of ethylene from acetaldehyde by slices (*1*) and particles (*2*) of apple was mediated by flavin mononucleotide (FMN) which caused nonenzymatic formation of ethylene in a model system consisting of acetaldehyde and cysteine (*3*). Yang *et al.* (*4*) reported that ethylene was formed from methionine and its allied compounds in etiolated pea seedlings by FMN and light, and that the two-carbon skeleton of ethylene was derived from carbons 3 and 4 of methionine. We then studied the formation of ethylene from ethionine and *S*-ethylcysteine (*5*) in a model system and found that ethylene was derived from the ethyl carbons of the S-containing amino acids.

The reaction was carried out in a Warburg vessel fitted with a rubber stopper, and ethylene was determined by gas chromatography (Shimadzu model GC-1C) with a hydrogen flame-ionization detector. Ethylene-^{14}C was determined by radio-gas chromatography with a solid-scintillation detector (Shimadzu model LSG-W22) or with a liquid-scintillation counter (Packard model 314 EX) (*6*). The reaction mixture contained in 4 ml: 20 mM potassium phosphate buffer (pH 7.0); 0.5 mM FMN; and 0.1 mM L-ethionine, L-methionine, or *S*-ethyl-L-cysteine. Incubation was carried out at 30°C under illumination by tungsten lamp (from bottom of Warburg vessel, 22×10^3 lu/m^2) and in the dark.

The amount of ethylene formed from ethionine (0.1 mM) and from methionine (0.1 mM) was 10.8 and 6.5 μl (N.T.P.), respectively, in the presence of FMN and light for 30 minutes. However, there was no formation of ethylene from ethionine or from methionine, either in the dark or in the absence of FMN. Light, as well as FMN, was essential for production of ethylene. The rate of ethylene formation from ethionine was greater than that from methionine; this suggested the possibility that the ethyl moiety of ethionine was also transferred to ethylene. Experiments with ethionine-^{14}C (ethyl-1-^{14}C) showed that ethylene was formed from the ethyl carbons of ethionine. Radioactivity of ethylene-^{14}C formed from ethionine-^{14}C (1.7 mg, 12×10^4 count/min) was 3772 count/min in the presence of FMN and light after 30 minutes of incubation. However, in the dark and in the presence of FMN, the radioactivity was reduced to 42 count/min. There was no formation of ethylene-^{14}C in the light and in the absence of FMN.

The results confirm the hypothesis that the *S*-ethyl moiety can also be converted to ethylene with FMN and light. We felt that *S*-ethylcysteine containing the *S*-ethyl moiety in its molecular structure should also produce ethylene; therefore, we experimented further. When *S*-ethylcysteine (0.1 mM) was used instead of ethionine as the substrate in the reaction mixture, the amount of ethylene formed was 13.6 μl (N.T.P.) after 30 minutes of incubation in the presence of FMN and light. However, there was no formation of ethylene in the presence of FMN in darkness. From the similarity of the structures of ethionine and *S*-ethylcysteine, ethylene from *S*-ethylcysteine might be derived from *S*-ethyl moiety. We conclude that the ethyl moiety of the substrates containing the *S*-ethyl group in their molecular structure is converted to ethylene. We suggested earlier that the acetaldehyde-cysteine complex was a direct precursor of ethylene in apple particles (*3*). We now find that acetaldehyde gives *S*-ethyl moiety after reaction with the SH-compound and that the *S*-ethyl moiety is then converted to ethylene.

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Photosynthetic System II: Racial Differentiation in Typha latifolia

Abstract. *The rate of reduction of 2,6-dichlorophenol-indophenol by illuminated chloroplasts isolated from ecological races of* Typha latifolia *was negatively correlated with length of growing season at the site of origin. Efficiency of the photochemical apparatus for this reaction was twice as high in a high-altitude population from Wyoming as in a maritime population from California.*

Although experimental evidence indicates that subspecific populations of plants adapted to different habitats may differ in photosynthetic rates (*1*), and, although Bjorkman *et al.* have detected differences in the photochemical properties of *Solidago vigaurea* populations from shaded and sunny habitats (*2*), there is no evidence available that indicates a relation between macroclimate of origin and basic photochemical properties. I now report experiments that demonstrate higher rates of photoreduction of 2,6-dichlorophenol-indophenol in races from climates characterized by short growing seasons.

Plants from seven populations of broad-leaved cattail (*Typha latifolia* L.), at elevations between sea level and 1980 meters, were obtained from marshes in Oregon, California, Wyoming, and New York. The plants were grown for 2 months under these conditions: daylength, 12 hours; day temperature, 35°C; and night temperature, 25°C. Chloroplasts were isolated (*3*), the concentration of chlorophyll was determined (*4*), and Hill activity was assayed spectrophotometrically (*5*) with 2,6-dichlorophenol-indophenol photoreduction carried out at a light intensity of 27,500 lu/m^2 (2500 ft-c) from a 150-watt incandescent reflector bulb with a water filter. Because of an endogenous rhythm in Hill activity similar to that reported in tomato chloroplasts (*6*), plastids isolated at different times of the day varied considerably in this activity. The data reported represent means of the four highest determinations for each population. Although the rate of the reaction varied throughout the day, the qualitative relation reported here was invariable.

The ability of isolated chloroplasts to reduce 2,6-dichlorophenol-indophenol declined linearly with length of the growing season at the native site (Fig. 1). The regression coefficient (r) was -0.927, which indicates a significant ($.01 > P > .001$) inverse correlation between native climate and photochemical capacity. Reduction of 2,6-dichlorophenol-indophenol is attributed to system II of photosynthesis (*7*). Bjorkman found differences in ability to reduce plastocyanin, a system II–system I mediator, in plants from habitats with different light intensities (*2*). It seems unlikely, however, that the differences reported here could be accounted for solely on the basis of radiation input at the native sites. In fact, the two populations with the longest growing seasons are from sites with quite different radiation inputs; one is from Point Reyes, California, an extremely maritime site with abundant summer fog, while the other is from Red Bluff, California, a site with intense summer sun (*8*). Studies of productivity in cattail marshes at different altitudes suggest greater assimilation rates in populations from high altitudes (*9*). Although Hill activity cannot be equated with productivity, it seems likely that the greater assimilation rates of populations from sites with short growing seasons are at least partially a reflection of photochemical differences of the type documented here and represent a partial compensatory mechanism for the short period favorable for growth.

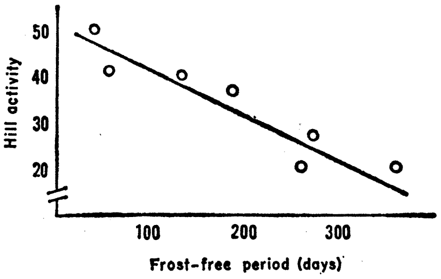

Fig. 1. Relation between Hill activity (micromoles of 2,6-dichlorophenol-indophenol per milligram of chlorophyll per minute) of isolated chloroplasts and the length of frost-free period (in days) at the site of origin of plants from which chloroplasts were isolated.

Preliminary experiments with four populations grown at 17-hour photoperiods with a 12-hour thermoperiod of 25° and 10°C gave an r of -0.952 ($.05 > P > .02$) for the regression of Hill activity on length of frost-free period at the native site.

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