Work on the helium method of age determination (HURLEY, P. M. and GOODMAN, C. *Bull. geol. Soc. Amer.*, **54**, 305) has continued since the war, with a further understanding of what conditions are necessary for satisfactory age measurements. Measurements on magnetite in certain "soft host" environments seem to be on a fairly firm footing.

Only three samples of magnetite from this eastern mineral belt have been measured so far, but the agreement in age with each other, and with the Manitoba area to the west, offers some assurance that the determinations are reasonably correct. Samples 1 and 2 were specimens of magnetite from the Larder Lake district, Ontario. Sample 3 was magnetite separated from a quartz veinlet in a piece of massive sulphide ore from the Horne Mine, Noranda, Ontario.

Sample	Alphas/hr/cm² from thick source*	Helium 10^{-5} cc/g	Age in millions of years†
1	.36	16.9	2100
2	0.15	8.4	2400
3	.26	11.4	2000

* NOGAMI, H. H. and HURLEY, P. M. *Trans. Am. geophys. Union,* 1948, **29**, 335.

† Assuming 90% of radioactivity due to uranium and 10% to thorium, as is about usual in this type of material.

If these ages are correct, they give us our oldest known orogenic belt.

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Some Simple Calculations Concerning the Efficiency of the Photosynthetic Mechanism

As is well known, the free energy increase resulting from the photosynthetic reaction

$$CO_2 + H_2O = HCHO + O_2$$

is about 120 kcal. Actually, the total amount of energy absorbed is such that the conversion of light into chemical energy is accomplished with an efficiency of 30% or more (RABINOWITCH, E. L. *Photosynthesis and rclated processes.* New York: Interscience, 1945. p. 50.) The reaction above consists of the following oxidation and reduction steps:

$$2H_2O = O_2 + 4H^+ + 4e^-$$

$$CO_2 + 4H^+ + 4e^- = HCHO + H_2O$$

In neutral solution the reversible potential of the first reaction is (LATIMER, W. M. *The oxidation states of the elements and their potentials in aqueous solution.* New York: Prentice-Hall, 1938.) + 0.81 v with respect to the standard hydrogen electrode while that of the second is − 0.49 v, the emf of the total reaction being 1.30 v. One will verify that $1.30 \times 4 \times 23 = 120$ kcal.

The formation of oxygen by oxidation of water is, in general, subject to a considerable anodic overvoltage or activation energy. If in particular the formation of molecular oxygen were to require the prior liberation of atomic oxygen from each molecule of water the minimum anodic potential would be the reversible potential for the reaction

$$H_2O = O + 2H^+ + 2e^-$$

which in neutral solution is + 2.00 v.

Similarly the reduction of carbon dioxide to a formaldehyde unit HCHO would be expected to be subject to a considerable cathodic overvoltage. As a matter of fact we have observed (VAN RYSSELBERGHE, P. *et al. J. Amer. chem. Soc.*, 1944, **66**, 1801; 1946, **68**, 2047; 2050) that the polarographic reduction of carbon dioxide cannot start until a cathodic potential of about 2 v with respect to the standard hydrogen electrode is reached. The total potential difference would thus be 4 v and the corresponding free energy of the 4-electron oxidation-reduction would be $4 \times 4 \times 23 = 368$ kcal. If the equivalent amount of light energy is absorbed to produce chemical synthesis to the extent of 120 kcal the efficiency of the process is $120/368 = 33\%$, in good agreement with the value given by Rabinowitch (*op. cit.*).

If we accept a mechanism involving eight quanta (which assumption, supported by other evidence, seems logical in view of the fact that there are altogether eight steps of yielding and accepting of electrons for the overall reaction) the average molar quantum would be $368/8 = 46$ kcal, corresponding to an average wavelength of 6210 A. It is interesting to note that the maxima of red absorption in ether solution correspond to 43.3 kcal for chlorophyll a and 44.5 for chlorophyll b (HARRIS, D. G., and ZSCHEILE, F. P. *Bot. Gaz.*, 1943, **104**, 515). See also our polarographic work on chlorophyll (VAN RYSSELBERGHE, P. *et al. J. Amer. chem. Soc.*, 1947, 69, 809).

The original free energy level of one mole of CO_2 and two moles of H_2O is − 208 kcal. The absorption of 368 kcal brings it up to + 160 kcal. If one subtracts from this the loss of free energy of 110 kcal corresponding to the formation of molecular O_2 from the atoms, one arrives at the value of + 50 kcal for the free energy of formation of the activated complex CH_4O_2 from the elements in their standard states. This value might lead to useful speculations concerning the structure and properties of this complex. Since the final free energy level of one mole of HCHO and one mole of H_2O is − 88 kcal the reaction

$$CH_4O_2 = HCHO + H_2O$$

from the reaction complex to the final products involves a free energy decrease of $50 - (-88) = 138$ kcal.

These considerations are submitted as an extension of the reversible electrochemical point of view already familiar in the field of photosynthesis to the more realistic one of overvoltage and activation. It is hoped that they may be of some use towards the final elucidation of the mechanism of the most important of all chemical reactions occurring in nature.

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