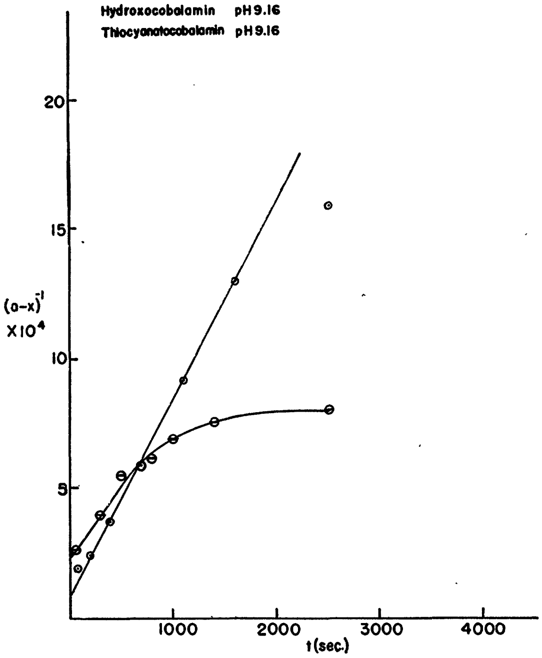

FIG. 2.

cyanide equivalents were determined by amperometric titration. Cyanide-binding impurities in the buffers were eliminated by adding to the buffer the amount of standard cyanide solution determined from a blank titration on an aliquot; the "cyanide-neutral" buffers were preserved in polyethylene bottles.

The reactants being in equimolecular proportions (about $1-2\times10^{-4}$ M) the reaction rate law followed is

$$\frac{1}{a-x} = kt + \frac{1}{a},$$

where a is the initial concentration of cyanide ion, and $a-x$ the concentration remaining at time t. The data assembled are graphed in Figs. 1 and 2. From the slopes of the lines, the rate constants k and half-lives $(1/ak)$ are obtained (Table 1).

In the case of hydroxocobalamin, it is to be noted that the rate constant of the cyanide-binding reaction decreases by roughly a factor of 10 for each unit increase in pH in the range studied. Since hydroxocobalamin is a pseudo base (*4*), whose basic properties are dependent on the hydrolytic reaction

$$\begin{bmatrix} --\text{OH} \\ \text{Co}^{3+} \\ 0\ 0\ 0 \end{bmatrix}^{0} + \text{H}_2\text{O} \rightleftarrows \begin{bmatrix} --\text{H}_2\text{O} \\ \text{Co}^{3+} \\ 0\ 0\ 0 \end{bmatrix}^{+} + \text{OH}^-,$$

the inverse rate dependence on pH is interpreted to mean that cyanide ion reacts not with hydroxocobalamin as such, but with the aquocobalamin ion in equilibrium with it (there being very much less of this ion present at pH 11 than at pH 9). It should be pointed out, however, that increase of reaction rate with diminished pH is limited by hydrolysis of cyanide ion, this becoming large below pH 9.

It is evident from Fig. 1 that the reaction between thiocyanatocobalamin and cyanide ion at pH 9.16 is not described by the rate law assumed above. The most probable explanation is that thiocyanate ion is not firmly bound by cobalamin at this pH, and that exchange with other ions in the solution occurs, giving rise to mixed cyanide reaction rates. The dissociation of thiocyanatocobalamin is clearly greater than that of the hydroxo analog at pH 10.96, since the half-life of cyanide exchange is only half as long.

TABLE 1

RATE-CONSTANT DATA

Substrate	pH	$a\times10^4$ M	Rate constant	Half-life (secs)
Hydroxocobalamin	9.16	0.86	73	120
"	9.88	1.63	7.9	850
"	10.96	1.58	0.63	9800
Thiocyanatocobalamin	10.96	1.64	1.30	4700

These ion exchange reactions, accompanied perhaps by reversible reduction-oxidation of cobalt, are conceivably of importance in the biological function of vitamin B_{12}.

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Evidence of Authigenic and Detrital Glauconite

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Glauconite, the general formula (*1*) of which is $R_2'O$, $4(R''O, R'''_2O_3)10SiO_2\cdot4H_2O$, is a common constituent of many sedimentary rocks throughout the world, ranging in age from Cambrian to Recent. If a clear-cut distinction could be made between authigenic and detrital glauconite which would be universally applicable to glauconite-bearing sediments, a useful tool would be placed in the hands of the petrologist who is attempting to determine the origin of these sediments. Pettijohn (*2*) points out that "The distinction between autochthonous or primary glauconite, and transported or secondary glauconite, is seldom made either in recent or fossil deposits. Failure to make such a distinction has led to misconceptions concerning the genesis of glauconite."

The Upper Cretaceous, Eocene, and Pleistocene strata in the coastal plain of New Jersey afford an excellent opportunity for study of glauconite-bearing sediments. A systematic examination of glauconite grains from the several formations of this area reveals striking differences which make it possible to distinguish between authigenic and detrital glauconites.

The surface structures of the glauconite grains found in these sediments fall into two broad groups: (1) those marked by lines of deviation and (2) those that have no surface structural lines of deviation. The former group includes the following subgroups:

1. Lobate—grains with surface structures consisting of grooved indentations, which have been described as lobate, polylobate, papilliform, reniform, etc.
2. Grooved—grains characterized by surficial grooves which are relatively close to the grain periphery.
3. Tabular—parallel-grooved grains that are somewhat elongate along an axis, have parallel grooves at right angles to the long axis, and are cleavable.

The grains with surface structures that have no lines of deviation may be described as subspherical, spherical, ovaloid, cylindrical, etc.

Glauconite grains may also be classified as rounded and nonrounded. It has been found convenient to subclassify the nonrounded grains as follows:

1. Irregular—massive angular grains with no systematic surface structure, and with normal color and luster.
2. Broken or angular—grains which exhibit remnants of former surface structure, and which have the color and luster found in associated glauconite grains of other types.
3. Fragmental—grains which show little or no remnants of former surface structure, are found in the finer fractions, and are generally lighter than the glauconite grains of the same sample retained on the coarser sieves.

These classifications have been found useful for distinguishing between authigenic and detrital glauconite.

Authigenic glauconite grains show very little breaking or irregularity. They are usually rough and pitted, and the luster is dull to subvitreous. They have distinctive ovaloid to subspherical surface structural shapes, which persist even in the finer fractions. The lobate, grooved, and tabular parallel-grooved surface structures are not as well defined as they are in detrital glauconite, and it is probable that these grains are in an incipient stage of development.

Detrital glauconite, on the other hand, shows a great deal of breaking and irregularity. The surface is usually fairly smooth. Grains with lobate, grooved, and faintly grooved surface structures predominate in material over .124 mm in diameter. In material less than .124 mm in diameter, detrital glauconite is mostly fragmental, and many grains appear to be formed by the combination of smaller grains. The color of detrital glauconite is usually a shade of dark-green.

Chemical analysis[1] has shown that authigenic glauconite has a lower iron content than detrital material. Indications are that the iron has been replaced by other bases such as aluminum. E. W. Galliher (*3*) also reported in 1935 that a sample of authigenic glauconite had a similar high-iron and low-aluminum content and is thus like a sample of authigenic glauconite from the Merchantville formation. X-ray and differential thermal analyses[2] show that both authigenic and detrital glauconite are mineralogically the same.

Glauconite is more or less abundant in sections of the Magothy, Marshalltown, Mount Laurel–Wenonah, Navesink, and Tinton formations of the Upper Cretaceous; in the Hornerstown, Vincentown, and Shark River–Manasquan formations of the Eocene; and in the Pensauken and Cape May formations of the Quaternary.

The glauconite characterized as authigenic is found predominantly in the older Upper Cretaceous formations and is typically developed in the Merchantville clays. The detrital glauconite is prevalent in the formations younger than the Marshalltown and is typically developed in the Hornerstown and Pensauken formations.

Authigenic glauconite is found intimately associated with clay that is predominantly illitic. In formations such as the Raritan and the Marshalltown, especially in their northeastern outcrops, where the clay content is mostly kaolinitic, no glauconite was found. Toward the southwest, where the clay content of the Marshalltown is illitic, authigenic glauconite is found in high concentrations. The sedimentary deposits of New Jersey in which detrital glauconite is found do not contain significant amounts of clay.

E. D. McKee (*4*) distinguishes between two types of glauconite in the Cambrian Bright Angel shale—autochthonous, in beds composed of glauconite showing various stages of development from biotite; and redeposited sediments, in which the grains appear to be rounded and worn, and show no genetic relation to any other mineral. In the New Jersey sediments it may be noted that detrital glauconite occurs where it has no genetic relationship to other minerals.

Authigenic glauconite occurs in clayey formations which might well contain genetic materials. Although Galliher (*5*) has reported biotite as the source material for glauconite in Monterey Bay deposits, biotite cannot be considered as a direct source of the large amounts of glauconite in the New Jersey coastal plain. In the systematic examination of hundreds of slides, only insignificant amounts of biotite, pyroxenes, or feldspars were found in the glauconitic and associated sediments (except the arkosic, relatively nonglauconitic phase of the Pensauken). The present study confirmed the observations of S. B. Hendricks and C. S. Ross (*6*), who state that:

> Mineral associations in many greensands indicate that large supplies of micas and feldspars are not necessary for glauconite formation. Some of the greensand beds of New Jersey are many feet in thickness and are composed of nearly pure glauconite. The accumulation of biotite in such thickness and freedom from impurities would be impossible.

This study indicates that the illitic clays intimately associated with authigenic glauconite may be the source material of the New Jersey glauconite. The structural relationship between glauconite and illite had been shown by Maegdefrau and Hoffmann (*7*), and Hendricks and Alexander (*8*). The results of x-ray, differential thermal, and chemical analyses

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[1] X-ray, petrographic, and chemical studies were carried on at the Rutgers University Laboratories.

[2] Differential thermal analyses were made in the Princeton University Civil Engineering Laboratory.

verify the close similarities in structure and composition between illite and glauconite, and lend support to the possibility of glauconite genesis from an illitic clay.

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Comments and Communications

Emergency Projects and University Personnel

THE following correspondence between the Association of American Universities and the Science Advisory Committee of the Office of Defense Mobilization relates to certain kinds of defense research projects and their effect on the normal activities of colleges and universities in education and research. It is submitted by its authors as a subject of general interest to the readers of SCIENCE.

UNIVERSITY OF MISSOURI
OFFICE OF THE PRESIDENT
COLUMBIA

November 6, 1951

Mr. Oliver Buckley, Chairman
Science Advisory Committee
Executive Office Building
Washington, D. C.

MY DEAR MR. BUCKLEY:

As you probably know, the members of the Association of American Universities have been giving considerable attention to the whole problem of additional compensation for faculty members working on emergency research programs, especially government contracts. At our Annual Meeting held in New Haven on October 23–24, the Association with thirty-three of the thirty-seven member institutions represented unanimously adopted the following resolution:

The resolution, as amended and adopted, reads as follows:

> The present period of rearmament and national emergency has resulted in a heavy demand upon universities and university faculties to undertake defense research and other emergency services for the government. Our universities must accept their proper share of responsibility in meeting the security needs of the nation. Thus they are faced with the difficult, dual responsibility of assisting the government in its immediate and emergency needs, while at the same time preserving as fully as possible their basic and long-range activities in education and creative scholarship. In recognition of the difficulties inherent in this dual responsibility
>
> BE IT RESOLVED:
>
> (1) That the Association of American Universities reaffirms the importance of our universities' maintaining their primary functions in meeting the critical educational needs of the nation and of maintaining those policies and environmental conditions most favorable to free and creative scholarship.
>
> (2) That the Association of American Universities recognizes that in the national emergency, some institutions will be operating under government contracts, large research programs requiring these institutions to draw on the staffs of other universities or colleges for the temporary loan of faculty members, but registers the opinion the number of such programs should be kept to the minimum consistent with national security and only initiated when the need of the Government is clearly of utmost importance to the defense of the nation; and that to this end it further urges the Science Advisory Committee of the Office of Defense Mobilization to take steps to ensure that there be careful screening of these projects.
>
> (3) That in the operation of such projects the universities recognize their responsibilities: (*a*) to manage these projects in a manner that is least disruptive of the normal educational and research activities of their own faculties and those of other institutions, and (*b*) to avoid whenever possible personnel policies and rates of compensation for these emergency projects which might embarrass or weaken other institutions. It is vital that the nation's universities preserve the incentives, prerogatives and attractiveness of academic appointments, and that they avoid policies which make educational and basic research activities poor relations of sponsored research.
>
> (4) Recognizing the possibility of special exceptions, the Association of American Universities feels that in general government funds should not be used to increase the monthly rate of compensation of staff members engaged on government research at the university of which they are members, or those on leave of absence from another institution.
>
> (5) That the Association of American Universities goes on record as favoring a policy of personnel rotation on university defense projects which will enable faculty members to return to their academic duties at their own institutions at the end of some period, preferably one, but not to exceed two academic years.

You are free to use this Resolution in any of your conferences and deliberations. If it would be helpful for any