and was filtered. It was recrystallized from methanol, and then showed a mp of 264°–266° C (Stage) which was not changed by another crystallization from methanol. This fraction had a specific count of 5 cpm/mg.[3] All mother liquor material was dissolved in ether, and this solution was extracted with 5% alkali. The alkali extract was acidified and extracted with ether. The residue from the ether solution was distilled in high vacuum at a bath temperature of 120°–160° C, and the substance thus obtained was recrystallized twice from acetone. The melting points of the crystals were the same as above. The specific count for this fraction was 3 cpm/mg.

b) *Isolation of β-estradiol.* The second portion of the methanol extract was dissolved in about 10 ml methanol, and 200 mg of β-estradiol (mp 172°–174°) was added. The material which crystallized out on cooling was crystalline but impure and could not be purified by further crystallization. It was recombined with the mother liquor and this mixture dissolved in ether, which was extracted with 5% KOH. The alkaline extract was acidified and extracted with ether. The residue from this ether solution was distilled in high vacuum at 120° bath temperature, and the material obtained was recrystallized from acetone, the crystals washed with cold ether and then recrystallized from acetone-hexane. The mother liquor was decanted from the crystals and these again crystallized from aqueous acetone. The crystals thus obtained sintered at 173° and melted at 177°–181° C (Stage). A further recrystallization from methanol gave a mp of 176°–177° C. This fraction gave a specific count of 3 cpm/mg.

c) *Isolation of cholesterol.* All mother liquor material in the second experiment was combined and boiled for 5 hr with 15 ml of a 10% solution of KOH in 95% ethanol. This reaction mixture was extracted with pentane, which after evaporation gave a crystalline residue of yellow color. It was treated with digitonin in the usual fashion, and the cholesterol was isolated from the digitonin complex. The specific count was 434 . Dibromination and reconversion gave a pure cholesterol which had a specific count of 75, thus showing the presence of higher counting companions (HCC) in the crude cholesterol (*5*).

The experiments here reported show that isolated surviving sow ovaries when perfused with sodium acetate labeled in the carboxyl group produce labeled estrone, β-estradiol, and cholesterol. Westerfeld *et al.* (*6*) many years ago isolated β-estradiol in substance from ovaries, and MacCorquodale *et al.* have secured the simultaneous presence of estrone by unmistakable reactions (*7*). Beall also observed the presence of both estrogens together in horse testes (*8*).

Like the testis in the earlier investigation, the ovary produces C^{14}-cholesterol simultaneously with the hormones. The experiments as described do not allow any conclusion as to whether the hormones are derived from this cholesterol, or whether cholesterol and the hormones are produced from a common precursor.

References

1. Zaffaroni, Z., Hechter, O., and Pincus, G. *J. Am. Chem. Soc.*, **73**, 1390 (1951).
2. Brady, R. O. *J. Biol. Chem.*, **193**, 145 (1951).
3. Savard, K., Dorfman, R. I., and Poutasse, E. *J. Clin. Endocrinol. and Metabolism*, **12**, 935 (1952).
4. Werthessen, N. T.. and Schwenk, E. *Am. J. Physiol.* (in press).
5. Schwenk, E., and Werthessen, N. T. *Arch. Biochem. and Biophys.* (in press).
6. Westerfeld, W. W., *et al. J. Biol. Chem.*, **126**, 181 (1938).
7. MacCorquodale, D. W., *et al. Ibid.*, **115**, 435 (1936).
8. Beall, D. *Biochem. J.* (London), **34**, 1293 (1940).

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[3] All counts in this investigation were made in a gas flow counter. For the preparation of the samples for counting compare (*4*).

Structural and Energy Relationships in the Formation of Iron and Aluminum Oxides, Hydroxides, and Silicates[1]

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Iron and aluminum oxides, hydroxides, and silicates are of great importance in the mineral content and formation of soils and sediments. Their structural relationships, known from x-ray diffraction methods and bonding considerations, are shown herein to help explain their occurrence. Recently, Ervin (*1*) considered the diaspore-corundum and boehmite-Al_2O_3 systems, and he has shown that they are structurally related. Structural interrelationships with genesis can be shown for iron and aluminum silicates, as well as for their oxides and hydroxides. These considerations, together with energy changes, are summarized in Fig. 1. (Downward slope of arrows is indicative of ease of occurrence.)

In the aluminum system, dehydration of $Al(OH)_3$ (gibbsite) results in the formation of AlOOH (boehmite, reaction *f*, Fig. 1). Dehydration may be accomplished by increase of temperature or decrease of suspension pH. Milligan (*2*) has reported boehmite to

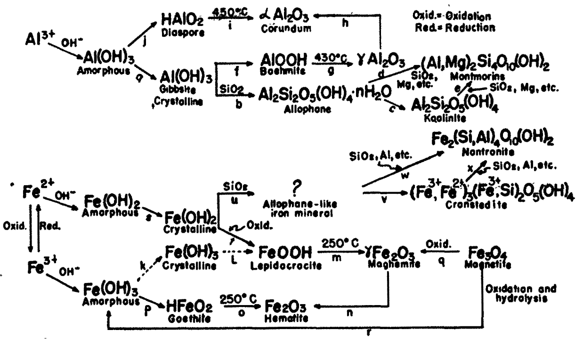

Fig. 1. Structural and energy relationships of iron and aluminum oxides, hydroxides, and silicates. (Downward slope of arrows indicative of ease of reaction occurrence.)

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be formed from solutions of pH below 6.5. In the alteration of gibbsite-boehmite colloid to kaolin, in the presence of silica solutions, 1 oxygen atom of a silica tetrahedron (4 oxygens coordinated by the 4-valent Si ion) is believed to replace a position left vacant in a gibbsite octahedron (6 oxygens coordinated by trivalent Al) on partial dehydration. The process continues by entrance of silica solution between the hydrogen-bonded crystal layers which form gibbsite crystals. Although the hexagonal network of silica tetrahedra would permit a complete replacement of the vacant oxygen positions to give a kaolin family crystal structure, this probably does not occur immediately, since the apical oxygens of silica may not at first be unidirectionally oriented. Incomplete bonding to both adjacent gibbsite crystal layers may at first give rise (reaction *b*) to an amorphous mineral, allophane, described by Ross and Kerr (*3*). Allophane is characterized by a high water content and is frequently associated with the kaolin family. Its high water content and the continuous removal of water as the temperature is raised from room temperature to 900° C may be due to "trapped" water within the interlayer made up of a silica-alumina network, in contrast to water lost from between the well-organized 1 : 1 layers of hydrated halloysite. Also, some of the interlayer surfaces of partially silicated $Al(OH)_3$ are greatly exposed by expansion and would lose water at low temperature. Infrared absorption spectra of allophane have shown that it is not a mixture of alumina and silica (*4*).

Allophane is visualized as forming kaolin on completion of unidirectional bonding through alternate wetting and drying in an acid medium (reaction *c*). The transition of kaolin to the montmorin (montmorillonite isomorphous series) structure (reaction *e*) is believed to be accomplished in the following way. Magnesium and iron can replace aluminum along the edges of the octahedral sheet of kaolin; in so doing, the larger size of the magnesium and iron atoms stretches the octahedra in which they are coordinated. Magnesium would further instabilize the hydroxyls by its divalence on substitution for a trivalent aluminum in dioctahedral silicates. Table 1 shows the decreased dehydration temperatures of the 2:1 layer silicates with different isomorphous substitution in the dioctahedral layers.

The data show that the 2 : 1 layer silicates decrease in thermal stability with increasing isomorphous substitution. They further show that magnesium decreases the dioctahedral stability nearly as much as iron, even though trioctahedral magnesium layer silicates (*5*) have a high dehydration temperature. In the kaolin minerals, there are four hydroxyls instead of the two present in 2 : 1 layer silicates. When magnesium substitutes for aluminum in kaolin, the hydroxyls become less tightly bound; and in the presence of silica in solution, the montmorin series of minerals appears, from soil mineral colloid studies here, to result (reactions *d* and *e*). The occurrence of magnesium and silica in abundance in soils is usually limited to situations in which there is little leaching, and reactions *d* and *e* are thus the reverse of normal weathering (*8*). Such reactions have occurred in the dark magnesium soils of Hawaii, where magnesium and silica, together with kaolin sediments, have been carried into the valleys from adjacent mountains and formed montmorin. In a latosol in the Dominican Republic, antigorite (Mg-kaolin) has been found to have reverted in part to montmorin.

TABLE 1

DEHYDRATION TEMPERATURES OF DIOCTAHEDRAL 2 : 1 LAYER SILICATES WITH DIFFERENT ISOMORPHOUS SUBSTITUTIONS

Octahedral ions				Sum of cations	Dehydration temperature °C*	Literature sources
Al^{3+}	Fe^{3+}	Fe^{2+}	Mg^{2+}			
2.00	—	—	—	2.00	650	(*5*)
1.61	—	—	0.40	2.01	580	(*6*)
1.48	0.14	—	.39	2.01	560	(*6*)
0.77	1.10	0.02	.19	2.08	490	(*7*)
0.11	1.91	0.02	0.04	2.08	440	(*7*)

* The dehydration temperatures recorded are the approximate midpoint in the integral thermal curves.

Although boehmite ($AlOOH$) is formed by the dehydration of gibbsite (reaction *f*), its iron analog lepidocrocite ($FeOOH$) is formed from the oxidation of ferrous compounds (reaction *t*). Crystalline $Fe(OH)_3$, the analog of gibbsite (and thus the natural precursor of $FeOOH$, by reaction *L*), has not yet been reported. The gibbsitelike layer structure of $Fe(OH)_2$ reverts to lepidocrocite on oxidation and dehydration, a transformation identical to the gibbsite-boehmite transition except for the oxidation.

Possible reasons for the instability of crystalline $Fe(OH)_3$ in comparison with crystalline $Al(OH)_3$ and $Cr(OH)_3$ may be attributed to the influence of *d* electrons.[2] If the concept of resonance is applied, instability of $Fe(OH)_3$ may be attributed to the absence of ionic-covalent resonance. One of the rules regarding resonance states that resonance can occur only among structures with the same number of unpaired electrons (*9*). Both aluminum and chromium are known to form crystalline hydroxides, and their electronic structures are such as to permit resonance between the ionic and covalent forms; the resonance energy helps to stabilize the structure. Trivalent iron has five unpaired 3*d* electrons in the ionic bond (e.g., FeF_6^{---}) and one unpaired 3*d* electron in the covalent bond—e.g., $Fe(CN)_6^{---}$—there can be no resonance between the two bond types. If the concept of polarization is applied, instability of $Fe(OH)_3$ is accounted for by the increase of polarizing power of cations with increasing charge and increasing number of *d* electrons. The instability of $Zn(OH)_2$ with respect to the

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[2] The *d* electron is an electron of a designated orbital energy range within a given electronic shell of an atom; in the case of iron atoms considered here, the 3*d* electrons occur in the *M*-shell, the latter being indicated by number 3.

$Mg(OH)_2$-type structure has been explained on the basis of the high polarizing power of divalent zinc which has ten 3*d* electrons (*10*). Trivalent aluminum exhibits the effect of polarization by directed hydroxyls in $Al(OH)_3$ (*11*). Chromium with three 3*d* electrons is known to form $Cr(OH)_3$, but $Cr(OH)_3$ is unstable even at room temperatures (*2*). It would seem reasonable to assume that $Fe(OH)_3$ would be less stable than $Cr(OH)_3$, since ferric iron has five 3*d* electrons.

The change of $Fe(OH)_3$ to the more stable partially dehydrated form (goethite, reaction *p*) occurs before crystalline $Fe(OH)_3$ forms (reaction *k*). That goethite may be more stable than lepidocrocite is shown by the dehydration temperatures of their respective Al analogs diaspore > boehmite (Fig. 1). The identical temperature recorded for the goethite and lepidocrocite dehydrations (*12*) may be due to smaller particle size of goethite or other difficulties in the method of measurement.

In the presence of silica, a ferrous mineral similar to allophane would be expected from $Fe(OH)_2$ (reaction *u*). Thus far it has not been identified positively, although exchange capacities of amorphous ferruginous soil colloids are at present being postulated at several laboratories. However, there are several crystalline iron 1 : 1 layer silicate minerals that are similar to kaolinite; the minerals cronstedite and greenalite are examples (reaction *v*). The trioctahedral nature of the iron in the mineral cronstedite suggests that cronstedite is formed from ferrous hydroxide. Hendricks (*13*) considers the octahedral iron of cronstedite as being due to the replacement of silicon by large ferric iron in the tetrahedral position, which allows the octahedral layer to be "opened" up. In view of the transformation just considered, it would seem that the ferrous iron in the octahedral position opened up the structure, and this in turn allowed the ferric iron to enter into the tetrahedral position. This would be similar to the kaolin-montmorin transition, except that it would be expected to occur with a deficiency of silica and excess of ferrous iron in the environment. In greenalite there is a mixture of ferrous and ferric ions octahedrally coordinated, and silica presumably in tetrahedral coordination. It is formed in iron-rich environments, from iron silicates in iron ore deposits (*14*).

When great excess of silica is present, the ferric member of the montmorin series can be formed as evidenced by nontronite (reactions *w* and *x*), which typically occurs embedded in a silica matrix.

Franzen and Eyk van Voorthuysen (*15*) have accomplished the synthesis of nickel layer silicates, which further emphasizes the importance of the hydroxyl layer structure such as in $Ni(OH)_2$, to formation of the corresponding layer silicates. Nickel and ferrous ions are similar in their electronic configuration, but both have lower polarizing power than the ferric ion.

Although in the tropics there is an abundance of iron and aluminum oxides and hydroxides, layer silicates with iron are rare. This is due to the rapid oxidation of ferrous iron to ferric, which gives rise to goethite and hematite, owing to the instability of $Fe(OH)_3$ as already discussed. Decomposition of magnetite is generally accompanied by hydrolysis and oxidation. Without hydrolysis, maghemite (γ-Fe_2O_3) is formed. Because silica and the bases are rapidly leached in well-drained soils, the montmorin series in which iron might be substituted is disfavored and the formation of aluminum members of the kaolin family is favored.

In the temperate regions, where decomposition of primary minerals and leaching of silica and bases are relatively slower and less complete than in the tropical weathering referred to, the 2 : 1 layer silicate minerals bearing some iron ions are common, but give way (*8*) to kaolin as weathering progresses.

References

1. ERVIN, G., JR. *Acta Cryst.*, **5**, 103 (1952).
2. MILLIGAN, W. O. *J. Phys. & Colloid Chem.*, **55**, 497 (1951).
3. ROSS, C. S., and KERR, P. F. *U. S. Geol. Survey Profess. Paper 185G*, (1935).
4. KERR, P. F. Am. Petroleum Inst. Proj. 49, *Prelim. Rept. #8*, (1950).
5. PAGE, J. B. *Soil Sci.*, **56**, 273 (1943).
6. FOSTER, M. D. *Am. Mineralogist*, **36**, 717 (1951).
7. ROSS, C. S., and HENDRICKS, S. B. *U. S. Geol. Survey Profess. Paper 205B*, (1945).
8. JACKSON, M. L., *et al. J. Phys. & Colloid Chem.*, **52**, 1237 (1948).
9. PAULING, L. *The Nature of the Chemical Bond.* Ithaca, N. Y.: Cornell Univ. Press, 13, 22 (1946).
10. LOTMAR, W., and FEITKNECHT, W. *Z. Krist.*, **93**, 368 (1936).
11. BERNAL, J. D., and MEGAW, H. D. *Proc. Roy. Soc.* (London), **A151**, 384 (1935).
12. BRINDLEY, G. W. *X-ray Identification and Crystal Structures of Clay Minerals.* London: Taylor and Francis (1951).
13. HENDRICKS, S. B. *Am. Mineralogist*, **24**, 529 (1939).
14. GRUNER, J. W. *Ibid.*, **21**, 449 (1936).
15. FRANZEN, P., and EYK VAN VOORTHUYSEN, J. J. B. VAN *Trans. 4th Intern. Congr. Soil Sci.*, **3**, 34 (1950).

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Substrate Competition between Procaine and Succinylcholine Diiodide for Plasma Cholinesterase

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It was shown by Kalow (*1*) that the enzyme responsible for the hydrolysis of procaine in plasma is identical with cholinesterase (nonspecific cholinesterase, pseudo-cholinesterase). It was also demonstrated by Glick (*2*) and more recently by others (*3–7*) that plasma cholinesterase is capable of hydrolyzing succinylcholine, a recently introduced muscle relaxant. In the course of clinical studies with succinylcholine diiodide (*8*), it was observed that, when 100 mg procaine was administered intravenously to patients receiving succinylcholine, the respiratory depth decreased markedly for several minutes, and in