Genesis of Clay Minerals

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In a paper published three years ago, the term "silicic chemistry" was used for the first time to emphasize the increasing importance of the chemistry of silicon in science and technology. The development through which the colloid chemistry of siliceous matter has gone since then is in itself ample proof that the coining of this new term for this branch of colloid science was not presumptuous.

Until quite recently, however, silicic chemistry concerned itself only with the composition and colloidal properties of natural and synthetic siliceous matter, but had not paid much attention to the genesis of this matter, particularly to that of the clay minerals. What is even more disturbing, particularly from an educational point of view, is the fact that neither mineralogy, geology, nor metallurgy has fully realized the important role colloidal phenomena must have played in the genesis of our planet and the formation of minerals generally speaking. Considering the importance of colloid chemistry today in the fields just mentioned, it is not surprising that the theories most agreed upon by geologists and mineralogists for the origin of clay minerals are not acceptable from a strictly colloid chemical point of view for the genesis of these most important and most abundant components of the earth.

Of all the theories pertaining to the origin of clay minerals, those still most accepted by geologists and mineralogists are the "residual clay" and the "transported clay" theories. The former is based primarily on the assumption that the formation of clay minerals is the result of surface weathering of fresh rocks, or is due to the action of solutions. Taking the action of water on orthoclase as an example, the most recent ideas have been summarized by H. Jenny as follows:

Whereas the interior of any crystal is in electrical equilibrium (Pauling's rules), the surfaces of many crystals are composed of ions whose valences are not completely satisfied. For an orthoclase crystal, which consists of joined Si and Al tetrahedra and K ions in intertetrahedral cavities, the surface may be schematically depicted as in Fig 1 (left side).

\[ \begin{align*}
H_2O & \quad H_2O & \quad HOH \\
\rightarrow & \quad O-Si-O-Al-O-K-O & \rightarrow \\
\text{Crystal surface} & \quad \text{Crystal surface}
\end{align*} \]

\[ \begin{align*}
H & \quad H & \quad KOH \\
\rightarrow & \quad O-Si-O-Al-O-H-O & \rightarrow \\
\text{Crystal surface} & \quad \text{Crystal surface}
\end{align*} \]

Fig 1.—Schematic presentation of orthoclase surface reacting with water Hydration of oxygen ions not shown.

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Upon the addition of water two reactions may occur. First, hydration, whereby water molecules (dipoles) are attracted to the unsatisfied valences of exposed Si and Al ions. The polarization of the attracted water molecules may become so strong that some of the H ions are expelled. They may become attached to exposed O ions which are thus converted to OH ions. The exposed polarizing Si and Al ions become surrounded by OH ions (water molecules minus H).

The second reaction, proceeding simultaneously and independently of hydration, consists of an ion exchange (hydrolysis) between exposed K ions of the lattice and H ions of water, as follows:

\[
\text{Orthoclase} \quad K^+ + H^+OH^- \rightleftharpoons \text{Orthoclase} \quad H^+ + K^+OH^- 
\]

The liquid phase acquires alkalinity (pH 9–11), and the crystal surface gains H ions, which tend to combine with O to form OH⁻.

As a result of hydration and hydrolysis, the exposed oxygen tetrahedra become partial hydroxyl tetrahedra. Aluminum tends to attract further OH ions to assume its preferred octahedral configuration of hydroxyl ions. Coupled with the absence of stabilizing intertetrahedral K ions, the surface layer becomes unstable and polyhedra peel off.

Tetra- and octahedra liberated from feldspars and other minerals aggregate among themselves to form clusters of colloidal size, namely, colloidal silica, colloidal aluminum hydroxide, and mixtures, the colloidal alumino-silicates. Although young colloidal particles are probably amorphous, upon aging the polyhedra orient themselves to definite crystal lattices such as cristobalite, diaspore, bauxite, goethite, gibbsite (hydragillite), clay minerals of the hydrous mica-illite-vermiculite group, and clay minerals of the kaolinite-halloysite group.

THEORIES

The "transported clay" theory postulates that the residual clays are carried by rainwash into streams and are then transported, frequently to distant areas. Depending on the location where the clay is finally deposited, a differentiation is made between marine, estuarine, flood, plain and terrace clays and several others.15

Only the "residual clay" theory deserves attention from a chemical, particularly a colloid-chemical, point of view, because it at least discusses the formation of clay minerals from feldspar. It does not offer a truly satisfactory explanation, however, for the genesis of the basic components of clay, which is just as important for our understanding of the genesis, composition, and properties of the various clay minerals as a knowledge of the formation of an organic copolymer is for an understanding of its properties.

Although the latest contributions to the chemistry of silicates admit that colloid chemistry plays an important role here, the majority of scientists interested in this new branch of colloid chemistry are seemingly still unaware
of the fact that colloid science had already made basic contributions to the theory of the genesis of silicates more than a quarter of a century ago.\textsuperscript{16}

The formation of true gels as well as the formation of systems exhibiting the phenomena of thixotropy, rheopexy, and dilatancy must today be considered as the colloidal phenomena that are most essential for a real appreciation of the importance of silicic chemistry whenever an attempt is made to offer a truly acceptable theory for the genesis of clay minerals. The theories that have been advanced to account for the phenomenon of gelation and to explain the structure of the resulting gel can generally be classified under the headings: the solid-liquid theory, the liquid-liquid theory, the micellar theory, and the potential-energy theory. For a detailed discussion of these theories the reader is referred to appropriate texts in colloid chemistry.\textsuperscript{7,8,9,14}

Thixotropy is the property of a gel to liquefy upon mechanical agitation and to resolidify when agitation is stopped. One theory postulates that a thixotropic gel is caused by the formation of a loose network of colloidal particles interconnected only at a few points. Another theory assumes that the particles in the gel are held in place by long-range forces, thus having no contact whatsoever.\textsuperscript{7}

The phenomenon of dilatancy is the direct opposite of thixotropy. A dilatant system behaves like a liquid and flows easily under weak stresses. If the system is subject to rapid change of its shape or to large shearing stresses, as unquestionably occurred in the formation of this globe, it offers increasing resistance to deformation and actually solidifies.

The phenomenon of rheopexy differs from thixotropy only by the fact that the change from a colloidal sol to a gel can be speeded up by subjecting the sol to rhythmic agitation. The finest fractions of solenhofen slate, so famous for the imprints of jellyfish and other delicate organisms and plants, exhibit this phenomenon and therefore deserve far more attention from geologists and mineralogists and others interested in the genesis of clay minerals than they have so far found.\textsuperscript{7}

**RESEARCH ON SILICEOUS MATTER**

From an experimental point of view, the colloid chemist has had at his disposal various possibilities for learning more and more about the composition, morphology, and structure of siliceous matter by applying to his investigations X-ray diffraction, ultramicroscopy and electron microscopy, electrophoresis, differential thermal analysis, infrared spectroscopy, and many other modern tools of research. Here again the interested reader is referred to appropriate texts.\textsuperscript{4,7,8,12,14}

The famous German poet, philosopher and scientist, Johann Wolfgang von Goethe, said: "The history of science is science itself." The following
review of the history of the colloid chemistry of silicon reveals once again how true this is. It also indicates the serious need for a drastic revision in our educational program, because only by appropriating some time for the study of the history of science will we be able to develop a young generation of scientists who have been taught not only to memorize what is written in the textbooks but also how to develop basically new ideas.

To offer more specific proof for the points to be brought out, quotations are included from three publications pertaining to siliceous matter, the oldest one having been published more than 170 years ago.

As early as 1779, the Swedish scientist, Torbern Bergman, had this to say in his paper, De Terra Silicea:

Finally I must still think of those incomplete phenomena, which depend on a seeming solubility. This silicious liquor [alkali silicate solution—E. A. H.] is precipitated by all acids, because the alkali prefers to hang on to them rather than to the gravel. This precipitated gravel has a very expanded and loose texture, is filled with water, so that it is twelve times as heavy when moist, than when dry. However if one first adds more water before adding acid, the solution remains clear, even if more acid is then added as would be needed to neutralize the alkali. This is a peculiar phenomenon and the reason for it probably is the following: Through the dilution with water the silicious particles are very much separated from each other, or made finer and better distributed throughout the liquid. Although the particles, being heavier than the liquid, should settle out, they can in this case not overcome the resistance due to friction, because a greater force will be needed to accelerate sedimentation than the one resulting from the difference in specific gravity. The silica particles remain suspended in the liquid and at the same time invisible due to their fineness and transparency.

In 1861, Thomas Graham made the following statement in one of his speeches: "The comparatively fixed class as regards diffusion is represented by a different order of chemical substances, marked out by the absence of the power to crystallize. Among the latter are hydrated silicic acid, when it exists in the soluble form. Soluble silicic acid forms a peculiar class of compounds, which are interesting by their analogy to organic substances." A few years later, he said: "We have no degrees of solubility to speak of with respect to silicic acid, like the degrees of solubility of a salt. . . . The ultimate pectization of silicic acid is preceded by a gradual thickening in the liquid itself. The production of the compounds of silicic acid described, indicates the possession of a wider range of affinity by a colloid than could well be anticipated."

More than 20 years ago, a German geologist who had training in colloid chemistry made the following statements:

During the decomposition of silicates, one must bear the following in mind: In the magma silicic acid is in chemical equilibrium with the bases. It is able to form
complex molecules which are chemically well-defined, however; this is demonstrated by the fact that all these silicates are capable of separating in crystallographically well-defined particles. Silicic acid owes this property to its high acidity at elevated temperatures. At low temperatures the acidity of silicic acid is so small, however, that it can only form a salt with the strongest bases, as for example Na₂O and K₂O. It will be precipitated from these by the weakest acid, however, even by water alone. This implies that most of the silicates are present in a metastable equilibrium, even at normal temperatures. When weather-decomposition sets in, the equilibrium is disrupted. In the absence of acid, oxides or hydroxides of the silicate bases are formed and silicic acid is liberated. In the presence of carbonic acid, humic acid or sulfuric acid, primarily those bases will be attacked which will form soluble salts with these acids. The molecular structure of the silicate is disrupted and at certain locations of the crystal lattice the acid-insoluble bases and silicic acid remain. When liberated, they are present in a molecular disperse condition. Since they are insoluble, they are not capable of forming a molecular solution with water; oversaturation results, causing polymerization. This can either occur in space-lattice fashion resulting in the formation of crystals, or if the oversaturation is too great in comparison to solubility, and the ability to crystallize too small, colloidal gels are formed. The formation of colloids due to the decomposition of the silicate is a condensation reaction.

EDUCATIONAL METHODS

To accomplish the changes in our present educational methods suggested on page 100, we would not only have to revise our college and university curricula, putting more emphasis on the history and philosophy of science and technology, but also see to it that our educational institutions are put in charge of individuals who are scientists, preferably natural scientists with a good background in natural philosophy, and not just citizens who have made a name for themselves in other fields than science or education. What we need today more than ever for such positions are individuals who have offered convincing proof that they are devoting all their life to education and that they are also leaders in certain fields of science or technology. To depend, as recently was done in filling the presidency of a state university, on the opinion of a selection committee as to who might be the best possible man for conditions they knew well in that state, is not to further the ideals of education. Unless drastic changes are made in this respect, it will become more and more difficult to improve our educational system, so important under prevailing world conditions.

FORMATION OF CLAY MINERALS

As interesting and important as all this information may be, it still does not offer a truly satisfactory answer to the question of how clay minerals were actually formed or how their genesis can be explained in a way satisfactory to all knowledge now at our disposal. A few years ago a paper on Man-Made Minerals appeared in print, in which it was stated that talc, a
known clay mineral, was produced from its ingredients—magnesia, silica, and water—by putting these components under high water-vapor pressure. Many years prior to this, however, it had been shown that montmorillonite can be produced by subjecting a synthetic glass as well as a natural obsidian to a high-temperature and high-pressure treatment. It could be demonstrated that a devitrification phenomenon is involved here in which the alumina and silica groups are rearranged under the influence of temperature and pressure to give a crystalline structure. The alteration of the pure silica and alumina to kaolinite or montmorillonite therefore is most probably a combination of the chemical reactions attendant upon leaching and a devitrification of the glass, the reaction then proceeding through a hydration and adsorption of ions. Most probably the silica and alumina gels reacted first to form halloysite; then, by condensation, kaolinite or montmorillonite, talc, mica, and other minerals, depending on the ions present. In any event, clays owe their genesis to the presence of silica and alumina or magnesia gels, and the changes they undergo with either time or temperature.6 Fairly recent studies on the formation of clay minerals have offered further proof for the validity of this theory.11 Another fact that until recently has not found the attention it deserves is that, in spite of the inertness of most siliceous matter, the chemical reactivity of the silica surface surpasses that of most stable oxides. Systematic research on the surface chemistry of silicates has led to the discovery of unexpected chemical reactions, which result from the dehydration or polymerization of silicic acid. Most important of all is the release of atomic oxygen even at room temperature and the fixation of nitrogen as ammonia at temperatures ranging between 250° and 350°C.18 What is of particular importance and has so far not been given the attention it deserves is the fact that the temperatures and pressures that the average chemist considers essential for certain chemical reactions can be drastically reduced if adsorption of gases or dissociated ions in a liquid medium is possible. In this respect the silicates deserve special attention, because their unbalanced surface ions will act as adsorbents, bring the reactants closer together, and also increase the probability of electron transfer essential for the formation of new chemical compounds.10,18

This kind of knowledge deserves far more attention than it has received so far. This is possible, however, only if our higher educational institutions also realize this, and devote more attention to colloid chemistry in planning the curricula, not only for those who intend to major in chemistry or chemical engineering but also in mineralogy and geology. The previously mentioned discoveries of the release of atomic oxygen from silica gel during dehydration10 and the fixation of nitrogen by silica surfaces offer direct proof for the important role Silicic Chemistry could already play in explaining many problems mentioned in the paper presented by A. F. Frederickson.3
Problems of Clay and Laterite Genesis

SUMMARY

The older theories of the formation of clay minerals are reviewed. Colloidal phenomena that are of primary importance in evaluating the genesis of clay minerals are referred to. Attention is drawn to a few publications that discuss the importance of several basic colloidal phenomena pertaining to the genesis of clay minerals, known even before the term “colloid” had been coined. A new theory for the genesis of clay minerals is given. Attention is drawn to the problem our educational system faces unless more attention is paid to the importance of Silicic Chemistry and its implications in our higher education, particularly for those intending to major in chemistry, chemical engineering, geology, and mineralogy, as well as any industry depending on siliceous matter as basic material.

REFERENCES