

SVERIGES GEOLOGISKA UNDERSÖKNING

SER. C.

Avhandlingar och uppsatser.

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EXPERIMENTAL STUDIES
ON CHEMICAL PROCESSES
IN THE FORMATION OF
GLACIAL CLAY

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OLOF TAMM



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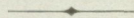
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Clays that are formed under the influence of hot or temperate climates are, at least to a great extent, products of the chemical decomposition of rocks. The glacial clays, on the other hand, consist principally of fine mineral particles, formed by the mechanical grinding of different rocks by glaciers and inland ices. The amounts of the finest particles in other glacial deposits such as moraine (i. e. the clay-amount of the moraine) have the same origin as the glacial clays. They constitute glacial clays, which have not been separated from the coarser grains present during the formation. — These glacial clays and clay-contents may, however, have been somewhat attacked chemically by the cold water of the melting ice.

In Fenno-Scandia there are many regions where the moraine, and also the glacial clay, are formed principally of the archean granites and gneisses. In an earlier paper (Tamm 1920) I have described chemical investigations of such moraine and other quaternary sediments. The chemical composition of moraines of granite and gneiss regions resembles that of the raw products, i. e. the rocks in question (pp. 71—85). The clay — and the clay-content of the moraine — have, however, a chemical composition suggesting that chemical processes may have contributed to their formation. The amount of aluminium is thus greater than it would be if the clay were composed only of minerals from the granites and gneisses. The excess of aluminium could to a great extent be explained by the evident augmentation of micas among the finest particles during the mechanical grinding (p. 80), but a part of it may be due to the chemical decomposition of different feldspars by the water of the melting inland-ice (p. 84). This assumption is based on many investigations on the solubility of feldspars and other silicate minerals in water, with or without carbon dioxide, especially those of Daubrée (1879) and Cushman and Hubbard (1907).

Subsequently my suggestion was criticised in some points by Goldschmidt (Goldschmidt and Johnson 1922, pp. 32—34). He somewhat misunderstood my suggestions, for he attributed to me the opinion that the chemical processes giving an excess of aluminium in the glacial clays would only have attacked the potash feldspar, whilst I had spoken of feldspars in general. Goldschmidt apprehends that these chemical processes attack principally the micas and the plagioclase. He considers it to be improbable that the hydrolysis of the orthoclase at 0° C. could take place in so short a time as during the formation of the glacial clay.

To elucidate the problem I have made an experimental investigation similar to that of Daubrée (*loc. cit.*), but under such conditions as to throw light upon the chemical processes in connection with the formation of glacial clay and to permit a theoretical discussion of them.

From the investigations of different authors, especially Daubrée and Cushman (*loc. cit.*), it is evident that silicate minerals are much more decomposed when ground in water than if ground first in air and then mixed with water. Daubrée agitated 3 kilograms of orthoclase with 5 kilograms of water for 192 hours in a revolving iron cylinder. He obtained 12.60 grams of K_2O , dissolved in the liquid. The feldspar was to a great extent ground into silt.

It is evident that the formation of glacial clay under the melting inland ice was a process very similar to Daubrée's experiment. The ice ground the mineral matter in its bottom layer, and during the melting-period this grinding took place in the presence of cold water. The melting water from the surface of the ice ran down to the bottom layers through the fissures that everywhere traversed the ice. This water gave rise to the great subglacial rivers, in which the grinding in water must have continued. The temperature, however, was lower than in the experiment of Daubrée.

Was the melting water of the ice charged with carbon dioxide or not? J. P. Koch (1915, pp. 324, 353) has found that glacier-ice in Greenland contained bubbles of air of 10 atmospheres' pressure at a depth of 7.5 meters. It is quite evident that, when a glacier is formed from loose snow, a good deal of air will be enclosed in the ice. Thus there must have been bubbles of air at high pressure in the inland ice.

The large quantities of cold water which were produced in the porous surface layer of the inland ice during its melting period must have contained dissolved carbon dioxide from the atmosphere. On its passage through the ice this water encountered bubbles of air at high pressure. Thus it is probable that the water, when arriving at the bottom layers of the ice, contained more CO_2 than corresponds to the partial pressure of CO_2 in the atmosphere at $0^\circ C$. The temperature at the bottom will have been near $0^\circ C$. (a little lower, owing to the pressure, which was probably regulated by water which filled up the vertical fissures traversing the ice).

Water in equilibrium with air of 1 atmosphere's pressure at a temperature of $0^\circ C$. contains 0.52cc. or 2.30×10^{-5} grammoles of carbon dioxide per liter. The corresponding hydrogenion concentration is $10^{-5.59}$, thus the p_H -value is 5.59. (The primary dissociation constant of carbonic acid is 3.0×10^{-7}). At the bottom of the inland ice the concentrations of the CO_2 and of the hydrogenion must have been somewhat greater, owing to the enclosed air within the ice. Thus the above mentioned concentrations may be considered minimum values.

As carbonates dissolved through decomposition of minerals are formed in the water, the hydrogenion concentration decreases, but the more slowly the greater the quantity of carbon dioxide present. Fresh water charged with CO_2 ran continuously from the surface of the ice, and the water charged with dissolved

carbonates was forced away in the subglacial rivers. It is thus probable that the clay-formation took place in continuously renewed water with a hydrogenion concentration of at least about $10^{-5.6}$. In pure water of the same temperature this concentration (calculated from the dissociation constant of the water = 0.16×10^{-14}) is only 0.04×10^{-7} . It is thus probable that small quantities of carbon dioxide may have had a great chemical importance on the formation of glacial clay. — It is to be noted that in the great granite and gneiss areas marine salts cannot have been present.

Experiments.

For the purpose of studying the weathering by water, both pure and containing different concentrations of carbon dioxide, I have agitated gravel of granite and feldspar in flasks of quartz-glass, with plugs of thick caoutchouc. A rotation apparatus could be enclosed in a thermostat at a temperature of $+2^\circ$ C. The flasks made about 40 rotations a minute.

I employed a granite collected and examined microscopically by Dr. N. Sundius. Dr. Sundius stated that the minerals of the granite were typical and unaltered. The granite was crushed to a gravel, the large grains being about of the size of a pea. During the crushing some silty matter was also formed. A sample of the crushed granite was carefully mixed, powdered, and then analysed chemically by Dr. N. Sahlbom. Dr. Sundius calculated the mineralogical composition of the granite on the basis of that analysis and his own microscopical examination. (Table 1.) — Of course the calculated mineralogical composition is only approximate. The granite was subsequently described by Dr. Sundius (1922, p. 235).

Table 1. Granite from Biskopshöjden, Dalecarlien. (Järna-granite).

	%		%
H ₂ O	0.65	Quartz	20.80
SiO ₂	63.50	Microcline	12.84
TiO ₂	0.89	Albite	27.77
Al ₂ O ₃	16.32	Anorthite	10.34
Fe ₂ O ₃	1.69	Biotite	18.10
FeO	3.89	Hornblende	7.64
MnO	0.07	Magnetite	1.00
CaO	3.46	Titanite	0.34
MgO	1.66	Apatite	0.77
Na ₂ O	3.33	Total	99.60
K ₂ O	3.71	Rest (water)	0.08
P ₂ O ₅	0.35		
Total	99.52		99.52

All the water used in the experiments was carefully purified in the following manner: Distilled water was alkalinized with a small quantity of NaOH and was slowly dripped into a distilling-apparatus of Jena glass, in which the normal air had been replaced by CO₂-free air. The re-distilled water was always

tested before use with the indicators of Clarke and Lubs. The p_H was near 7.

CO_2 -saturated water (at the temperature of the laboratory) was made by leading a stream of carbon dioxide (from marble with pure HCl and a little $SnCl_2$ to remove possible traces of chlorine) into water, re-distilled in the above-described manner. Three liters of water in a flask of Jena glass was thus treated with CO_2 during the experiments, and now and then the amount of carbon dioxide in the water, which could be siphoned off, was determined. The water thus contained 0.031 gram-molecules of CO_2 per liter. Small differences in the CO_2 -amount that occurred are of no importance for the experiments. The p_H of the CO_2 -saturated water was 3.9.

Experiment-series no. I.

300 grams of the carefully mixed, crushed granite was put into a flask of quartz-glass of 618 c.c. capacity. It was found that after mixing with pure water (which was then poured off) the sample retained about 50 c.c. water. Thereafter 300 c.c. of pure water was put into the flask, which was agitated 12 hours by the rotation-apparatus in a laboratory at a temperature of 14–15° C. After that time the suspension of silt and clay was poured off, filtered, and 100 c.c. of it titrated with 0.1 N HCl. The result in the whole liquid (350 c.c.) was 0.0041 gram of bases, calculated as K_2O .

After the first shaking the sample in the flask was washed with pure water and then the flask was charged with 300 c.c. of water, saturated with carbon dioxide and agitated 12 hours. The dissolved bases were now determined in following manner. The suspension was filtrated. 10 c.c. of 0.1 N HCl was put into 100 c.c. of the filtrate. The acidified liquid was boiled a few minutes in vacuum at the temperature of the room to remove the excess of carbon dioxide. Then it was titrated with 0.1 N barium-hydroxide; the indicator was methyl red.

Table 2. 300 grams granite in about 350 c.c. water, agitated for 12 hours.

Experiment no.	Added volume of CO_2 -saturated water	Temperature	Bases in the solution, calc. as K_2O
1	0	14–15° C.	0.0041 gram.
2	300	14–15	0.0412
3	300	14–15	0.0362
4	300	2–3	0.0317
5	25	2–3	0.0263
6	12.5	2–3	0.0156

The sample in the quartz flask was again washed with pure water, and a new experiment was made, and so on. Table 2 gives the results of the series of experiments.

When shaken at the lowest temperature, the charged flask was always previously placed for 5–6 hours in the cold thermostat to obtain the correct

temperature. An experiment no 7 was arranged in the same way as no 5, but without agitation. The flask was kept in a room at a temperature of 14° C. for 10 days. The dissolved bases, calculated as K₂O, only amounted to 0.0049 gram.

After experiment 7 was finished, the sample of crushed granite was dried in air at 40—50° C. and weighed. It was found to be 280 grams. From Table 2 it is evident, as was to be expected, that *temperature has no great influence on the reaction velocity*. This is on the whole governed by the rotatory speed and the velocity of diffusion of the ions in the liquid to the surfaces of the reacting minerals, which depends principally on this speed. It may be mentioned, too, that the dissociation constant of carbonic acid has a small temperature-coefficient. Therefore, the carbonic acid has nearly the same decomposing power on the minerals at +2° C. as at 14—15°. — The influence of carbonic acid on the dissolving velocity is very appreciable. The experiments indicate that small quantities of carbon dioxide may have great influence. An increase in the amount of carbonic acid over 25 c.c. of CO₂-saturated water only leads to a very slight increase in the dissolving power.

During the shakings, by the mechanical grinding, the granite grains were made a little rounded, while to commence with they were very sharp. This mechanical result evidently caused a decrease in the dissolving power.

Experiment-series no. II.

The crushed granite from experiments 1—7, 280 grams, was put into the quartz flask, the air was replaced by CO₂-free air, and then were added 100 c.c. of pure water. The flask was agitated as before at a temperature of 2—3° C., the suspension was poured off, and, in the experiments without CO₂, 0.5 c.c. of concentrated, neutral NH₄Cl-solution was added to secure a clear filtrate. The liquid was filtered and 50 c.c. of it boiled in vacuum and titrated as described above. The dissolved bases were calculated as K₂O. The crushed granite was dried and weighed, and a new experiment was commenced. After two experiments had been made, the crushed granite was sieved through a 2 mm. sieve. Only the coarser part, 215 grams (the gravel, > 2 mm.) was employed for the next experiments. — Table 3 gives the results.

The p_H of the pure water was near 7. In the experiments without CO₂ the active hydrogenion concentration in the solution at the end of the agitation can be calculated from the determined bases in the solution (the dissociation constant of water at + 2 C. is 0.16×10^{-14}). In the experiments with CO₂ the p_H at the beginning of the agitation is calculated in a manner to be described later, in connection with experiment-series no. III. The p_H at the end of the agitations with CO₂ in the water could not be calculated, because the hydrolysis of the carbonates is not sufficiently known. — The determined bases in the solution are not an exact expression for the extent of the chemical processes, because a part of the bases, such as potassium hydroxide, must have been adsorbed by the clay generated.

Table 3. Granite in 100 c.c. of water. Temperature + 2°—3° C.

Experiment no.	Added volume of CO ₂ -saturated water c.c.	Granite grams	Period of agitation hours	Dissolved bases calc. as K ₂ O gram	p _H at the beginning of the experiment	p _H at the end of the experiment
8	0	280	12	0.0084	about 7	12.05
9	0	270	12	0.0091	›	12.08
10	0	215 (> 2 mm.)	12	0.0060	›	11.90
11	0	213 ›	32	0.0109	›	12.16
12	0, pure atmospheric air in the flask	200 ›	12	0.0092	5.7	—
13		20	200 ›	12	0.0218	4.7
14	10	200 ›	12	0.0107	4.8	—
15	2.5	200 ›	12	0.0070	5.1	—
16	10	200 ›	12	0.0077	4.8	—

Table 3 shows a very interesting phenomenon. *It is the rubbing of the coarse gravel grains against each other that is the principal cause of the decomposing effect.* After experiment 9 all particles smaller than 2 mm. were sieved off, and only the larger grains retained. But the decomposing effect was only diminished from 0.0091 to 0.0060. It is obvious that the essential condition is the continuous production of new surfaces that can be attacked by the water. During continued experiments with the same granite sample the dissolved quantities decreased. Thus experiment no. 16 showed less decomposing effect than no. 14, no. 15 less than no. 12, although its p_H value was higher. It is evident that in the later experiments the mechanical grinding intensity was less than in the earlier ones, because the sharp edges gradually became somewhat rounded off.

The mechanical grinding-intensity, i. e. the making of new surfaces, is the most important factor for the chemical decomposition of the minerals, but besides this the influence of the carbon dioxide is appreciable. — It is evident that if any of the granite minerals contain very small quantities of included salts, as chlorides, which are to a slight extent dissolved through the wet grinding, those salts will not be determined by the titration-method employed.

Experiment-series no. III.

Experiment-series no. III was made in much the same way as no. II and at the same time, but with fresh crushed granite. The results follow below as table 4.

After experiment no. 18, the particles that were smaller than 2 mm. were sieved off, as in series no. II, and only the larger ones retained. The results are analogous to those of series II. In nos. 17—21 the p_H-values were calculated in the same way as in experiments 8—11. In experiments 23—25 the amount of carbon dioxide present was more than sufficient to form HCO₃ ions corresponding to the base ions. The hydrogenion concentration at the end of the shakings can therefore be calculated on the basis of the first-stage dissociation constant of the carbonic acid. The concentration at the beginning

Table 4. Granite in 100 c.c. of water. Temperature + 2° C, the period of agitation 12 hours.

Experiment no.	Added volume of CO ₂ -saturated water c.c.	Granite grams.	Dissolved bases as K ₂ O gram	PH	
				at the beginning of the agitation	at the end
17	0	280	0.0105	about 7	12.15
18	0	252	0.0112	»	12.17
19	0	215 (> 2 mm.)	0.0071	»	11.98
20	0	210 »	0.0060	»	11.90
21	0	209 »	0.0060	»	11.90
22	5	200 »	0.0111	5.0	—
23	40	200 »	0.0256	4.5	7.1
24	100	200 »	0.0265	4.3	6.5
25	{ 100, CO ₂ in- instead of air in the flask }	200 »	0.0212	4.0	5.6
26	10	200 »	0.0090	4.8	—

of the shaking, after equilibrium between air and water has been reached, is capable of calculation from the same dissociation constant:

The whole amount of CO₂ present = a.

The CO₂, dissolved in the water at the beginning = x.

The partial pressure of the CO₂ at the beginning = p'.

The normal pressure of the atmosphere = p.

The volume of the gaseous phase in the flask = v' (the volume of the flask was 602 c.c., the volume of the liquid 100 c.c., and the volume of the granite 73 to 76 c.c.)

The volume of the liquid phase = v''.

The absorption-coefficient of CO₂ in water, at the temperature t, is q. Allowing for some small approximation, the following expressions can be obtained at the beginning of the shaking:

$$\frac{x}{v''} \cdot \frac{1}{q} = \frac{p'}{p} \tag{1}$$

$$x + \frac{p'v'}{p(1 + 0.00367 t)} = a \tag{2}$$

or
$$x + \frac{x v'}{q v'' (1 + 0.00367 t)} = a \tag{3}$$

If a is given in grammoles of CO₂, x is obtained from (3) in the same unit. The concentration of CO₂ + H₂CO₃ in the water — if the dissociated part of the carbonic acid is neglected — will then be $\frac{x}{v''}$. The hydrogenion concentration at the

beginning is then obtained from the mass-action law: $[H^+] = \sqrt{3.0 \times 10^{-7} \times \frac{x}{v''}}$
 (The primary dissociation constant of carbonic acid = 3.0×10^{-7}).

At the end of the shaking it can be accepted that an amount of HCO_3 ions, equivalent to the base ions present, as determined by titration, exists in the liquid phase. The acid carbonates may be regarded as wholly dissociated. The amount of HCO_3 ions determined by the titration can thus be subtracted from the whole quantity of carbon dioxide present. The rest must be distributed between the liquid and the gaseous phase, according to Henry's law, and can thus be calculated from expression (3). The hydrogenion concentration at the end of the shaking can then be calculated by the mass-action law:

$$[\text{H}^+] = \frac{3.0 \times 10^{-7} \times [\text{H}_2\text{CO}_3 + \text{CO}_2]}{[\text{HCO}_3]}$$

In this way calculated p_{H} -values are obtained.

From Table 4, as from Table 3, it is evident that the grinding of the coarse granite grains is most important for the chemical decomposition. After the removal of the smaller grains by sieving (before experiment no. 19), only a slight decrease of dissolved bases — from 0.0112 to 0.0071 — was found. Also in Table 4 a decrease of the decomposing power on continued shakings could be noted, which must be caused by the gradual rounding off of the grains during the shakings. Thus the amount of dissolved bases is less in no. 26 than in no. 22, less in no. 25 than in no. 24, etc. The influence of the carbonic acid is very appreciable, as in series II. The calculations of the p_{H} -values suggest that much higher p_{H} -values are reached in the experiments without CO_2 than in those with it. The carbonic acid acts as a buffer. Since the hydrolysis of the silicates can take place at a (calculated) p_{H} -value of about 12, it is probable that, in the shakings with CO_2 , it is the grinding-intensity in the different experiments that has limited the quantity of the minerals decomposed.

The carbonic acid acts upon the minerals even if present in very small amounts. A slight increase of the CO_2 -amount has a great influence when the concentration is small but a very slight one when the concentration is great. Experiment no. 12, compared with nos. 10, 20 and 21, proves that even the influence of normal, CO_2 -containing air in the flask increases the decomposition. An entirely satisfactory correspondence between the experiments and the glacial clay-formation cannot of course be reached. In the experiments the dissolved base ions immediately form carbonates, which have a tendency to check the dissociation of the carbonic acid, i. e. the hydrogenion concentration decreases rapidly. In the formation of glacial clay in nature there is a continuous supply of fresh water, certainly with small concentrations of dissolved CO_2 , but without carbonates which check the dissociation of the carbonic acid. In my shakings with relatively large amounts of carbon dioxide, by its buffer influence the excess of CO_2 prevents the hydrogenion concentration from falling below a certain limit. Very probably, therefore, from the physico-chemical point of view, some of my experiments are comparable to the process of formation of glacial clay.

It is interesting to observe that in the shakings with pure water a calculated p_{H} -value of about 12 has always been reached. Even in no. 11, with the shaking

period of 32 hours, this value is hardly exceeded. It would be of great importance if there really existed a limiting hydrogenion concentration for the hydrolysis here, which however is not proved by my experiments. I propose subsequently to investigate this interesting problem chemically with a better apparatus and employing individual silicate minerals. In the case of the decomposition of silicates by water and water solutions there are two phenomena that are to be considered: the hydrolysis and the exchange of positive ions. In my experiments it can hardly be anything but the hydrolysis that has any importance, because the ion exchange is due to the occurrence of positive ions — for instance, the hydrogenion. The latter had a very low concentration in my experiments.

From the theoretical point of view, it is to be noted that the decidedly acid character of the silicic acid is again suggested (Bogue 1920, s. 2575—2582). Bogue has investigated the hydrolysis of different solutions of natrium-silicates with the hydrogen-electrode. His results do not accord with the earlier ideas concerning the acid character of the silicic acid. According to Bogue the hydrolysis of dissolved silicates in water is far from being complete. Thus it is to be expected that a p_H -value exists where no hydrolysis will take place, and where the mineral would be dissolved without hydrolytical decomposition, but to a very small extent, corresponding to its own true solubility in water.

From the mineralogical literature it is known that silicates such as orthoclase and albite can be formed in water-solutions under circumstances which, from a chemical point of view, are not quite known. Daly (1917, pp. 659—665) mentions the formation of feldspars in calcarous marine muds below $100^{\circ}C$. The formation of crystallised zeolites from water solutions at low temperatures has long been known. It is evident that, under certain given conditions, different ions in a water-solution can meet and form silicate crystals; there is a hydrolysis equilibrium, which can be moved in both directions. The weathering is the movement of this equilibrium in the one direction, the formation of silicate minerals described by Daly and others appears to be the movement in the other direction. It is an important problem to investigate this matter from a physico-chemical point of view.

Main experiments.

I have made two simultaneous shakings lasting 72 hours in order to procure enough material for further examinations. In each of two flasks of quartz glass (618 and 602 c.c. capacity) were put 200 grams of fresh crushed granite, from which all particles smaller than 2 mm. had been removed by sieving. One was filled with 500 c.c. of pure water, the other with 450 c.c. of pure water and 50 c.c. of CO_2 -saturated water. The air-volume in the flasks was nearly 50 c.c. The flasks were put into the rotation apparatus in the thermostat ($+2^{\circ}C$) and remained there for 5 to 6 hours. Then they were agitated there for 12 hours, after which time the resulting suspensions of clay and silt were carefully poured off into flasks of Jena glass. I had previously prepared two other Jena glass flasks in the thermostat, one with 500 c.c. of pure water, the other

with 450 c.c. of pure water, measured at the temperature of the laboratory. To the last-mentioned was added 50 c.c. of the CO_2 -saturated water, immediately before its liquid was employed. The samples in the quartz-glass flasks were now washed by a little of the liquid in the prepared flasks. The washing water was poured onto the suspensions in the flasks before mentioned, and the quartz-glass flasks were filled, one with the pure water and the other with the water charged with CO_2 , and then agitated 12 hours at 2°C . After 12 hours the liquid in the quartz flasks was again changed in the manner described, and the resulting suspensions of silt and clay collected and mixed with those previously poured off. The liquids in the quartz-glass flasks were changed in this way five times, and thus at the end of the experiments the granite samples had been agitated for 72 hours in 6 different bulks of about 500 c.c. of pure and CO_2 -charged water, which were collected in two large Jena flasks.

After ten days the CO_2 -suspension was quite clear, owing to the settling of the silt and clay. The CO_2 -free suspension needed 6 months for this, and was not quite clear even then, but showed a slight opalescence caused by colloids. The two liquids were siphoned off and stirred, and a liter of each was analysed chemically. The rest was left standing for 4 months. Then all the colloids in the CO_2 -free liquid had precipitated themselves and settled, and the solution had become clear. A liter of each solution was now analysed again. All analyses were made very carefully in platinum dishes. Table 5 gives the results. The difference between no. 3 and no. 4 gives approximately the composition of the colloids in the CO_2 -free solution that had deposited after the first analysis.

Table 5. 3 liters of solution contain:

	a. Experiment with CO_2		b. Experiment without CO_2		Difference between no. 3 and no. 4
	Analysis no. 1	Analysis no. 2	Analysis no. 3	Analysis no. 4	
SiO_2 . .	0.0183 gram.	0.0126 gram.	0.0498 gram.	0.0057 gram.	0.0441 gram.
Al_2O_3 . .	} 0.0183	0.0048	} 0.0432	0.0090	} 0.0342
FeO . . .					
MgO . .	0.0122	0.0117	0.0119	0.0037	0.0082
CaO . .	0.0168	0.0165	0.0090	0.0045	0.0045
Na_2O . .	0.0144	0.0153	0.0168	0.0058	0.0110
K_2O . .	0.0318	0.0322	0.0120	0.0104	0.0016
Total	0.1118	0.0931	0.1913	0.0391	0.1522

The iron is calculated as FeO because it is most probable that the iron in the solution occurred as ferrous ions. That the colloid-containing CO_2 -free solution cleared was probably due to oxidation of the ferrous ions to $\text{Fe}(\text{OH})_3$. Thereby the equilibrium between the different colloids was disturbed, and precipitation and settling began. In the CO_2 -containing liquid, too, an analogous reaction appears to have taken place, but to a much smaller extent (see the amounts of SiO_2 , Al_2O_3 , and FeO in nos. 1 and 2). In the following

discussions of the quantities of dissolved substances, analyses 2 and 4 are always concerned.

The silt and clay from the experiments were peptised by shaking for 24 hours with 0.01 N ammonia (according to Odén, 1920, p. 530). Then the suspension was separated (according to Atterberg, 10 cm. falling in 8 hours) by repeated sedimentations in very pure water in glass cylinders. When the clay (< 0.002 mm.) had been separated, again a shaking of the rest was made with 0.01 N ammonia to test whether all the clay was absent, which was the case. Table 6 gives the results of the mechanical analyses and the amount of chemically combined water in the different groups of particles.

Table 6. Mechanical analyses of the silty and clayish products of the experiments and their amounts of chemically combined water.

	1. Experiment with CO ₂		2. Experiment without CO ₂		
	Weight of particles	Combined water	Weight of particles	Combined water	Weight of particles
0.2—0.02 mm.	1.665 gram.	0.75 %	1.620 gram.	0.75 %	1.620 gram.
0.02—0.002 mm.	1.961	1.22	1.653	1.28	1.653
Clay, < 0.002 mm.	2.339	4.00	1.939	3.04	2.091
Total	5.965		5.212		5.364

Under 2 b the quantity of precipitated colloids from Table 5 has been added, i. e. the difference between b₃ and b₄. The amount of combined water was not determined in this precipitate. There is thus a slight error in 2 b, as may be noted. It is of no great importance for the discussion. The chemically combined water is determined according to Brush and Penfield (with subtraction of the water that evaporates below 110° C.). The sandy component (> 0.2 mm.) in the granite samples after the agitation is not determined.

The clays that had been formed in the experiments could not be distinguished from natural clay by the appearance. The colour was grey, quite like a glacial clay without any organic constituent. In the experiment with CO₂ more clay was formed than in the other.

The clay suspensions from the mechanical analyses, which had a volume of about 2 liters, were evaporated in the steam-bath, first in large beakers of Jena glass, then in a platinum-dish. After drying and weighing a sample of each clay was prepared. Chemical analyses of the two samples were then made by Mr. K. Lundblad, civil engineer. The Fe₂O₃ and P₂O₅ are determined by the author, and the FeO by Dr. N. Sahlbom. Table 7 gives the results.

In 2 b (Table 7) the above-mentioned precipitate of colloids from Table 5 is added to the clay, and the composition so obtained is calculated in percentages. The amounts of water and P₂O₅ in this composition are not quite exact, because they were not determined in the precipitate from Table 5. The total of 2 a is too low. The Al₂O₃ etc. in that clay was checked, but the sample was too small to allow of further checking. — The amounts of SiO₂ in the clays are perhaps influenced a little by particles off the flasks.

Table 7. The compositions of the two clays.

	1. Experiment with CO ₂	2. Experiment without CO ₂	
		a	b
H ₂ O below 110° C.	1.35 %	1.00 %	0.93 %
H ₂ O, combined	4.00	3.04	2.87
SiO ₂	45.40	45.78	44.88
TiO ₂	2.24	2.56	2.39
Al ₂ O ₃ etc.	14.92	14.31	15.49
Fe ₂ O ₃	5.76	5.01	4.68
FeO	10.02	10.76	12.40
MgO	5.61	5.86	5.87
CaO	3.43	3.69	3.66
Na ₂ O	1.80	1.56	1.98
K ₂ O	4.34	4.67	4.44
P ₂ O ₅	0.56	0.43	0.40
Total	99.43	98.67	100.00

The resemblance in composition of the two clays is very striking. Their composition is very similar to that of natural clays and clay-contents of moraines collected in granite and gneiss areas (see Tamm 1920). The amounts of iron, magnesium, and potassium, are however rather high. This may be explained by a high content of biotite, due to the very biotite-rich raw product (see p. 6). The large proportion of micas in glacial clays, assumed by many investigators, is thus confirmed by the experiments. The large amount of titanium is also explained by the presence of much biotite. A calculation of the mineralogical composition of the clays from the chemical analyses is impossible, since the results of an enrichment of biotite cannot be distinguished from the results of the chemical decomposition as shown by Table 5. This table, on the other hand (analyses nos. 2 and 4), may serve as a good starting-point for very interesting calculations as to the extent of the chemical processes during the experiments.

The sum of the dissolved bases (calculated as oxides, MgO + CaO + Na₂O + K₂O) in the experiment with CO₂ is 3.24 %, in the experiment without CO₂ it is 1.17 %, calculated as a percentage of the clay simultaneously formed. This gives an idea of the extent of the chemical decomposition compared with the clay-formation. The clay has certainly adsorbed a little of the dissolved bases, especially potassium hydroxide. Thus the quantities of dissolved bases found are *minima*.

The chemical decomposition of the different minerals in a heterogeneous system such as the two granite-water systems depends on the surfaces that have been attacked by the water. As the surface is much greater in the clay than in the coarser material, it is certain that the principal part of the products of the chemical processes that are not soluble will be found in the clay. The chemical decomposition-products consist to a great extent of precipitated colloids, which, when peptised, constitute the smallest particles in the clay.

On the basis of these facts, I have calculated the amount of the different products of the chemical decomposition in the clays formed.

The dissolved Na_2O must have come principally from the albite-component of the plagioclase. The K_2O comes principally from the microcline and the biotite. It is very probable that as much of the CaO derives from the plagioclase as corresponds to the ratio of $\text{Na}_2\text{O} : \text{CaO}$ in this mineral. According to Sundius (loc. cit. p. 236), the plagioclase of the granite has 74 molecules of albite and 26 molecules of anorthite. From this the ratio $\text{CaO} : \text{Na}_2\text{O}$ is calculated = 0.63. Thus from the amounts of Na_2O is calculated a quantity of CaO that is assumed to have derived from feldspar. To each of the dissolved groups of Na_2O , K_2O and feldspatic CaO has been combined a group of Al_2O_3 in the granite. Thus, this quantity of Al_2O_3 can be calculated. After the dissolved Al_2O_3 has been subtracted, its remainder represents an aluminium excess in the clay. This excess has been formed during the shaking by the chemical attack. This »chemical» aluminium excess of the clay is 3.10 % in the CO_2 -experiment, 0.90 % in the CO_2 -free experiment.

The natural, glacial clays are, however, not constituted only of particles smaller than 0.002 mm., but contain coarser grains too. For a comparison with natural clays, it is therefore convenient to calculate as percentages of the particles smaller than 0.02 mm. In percentage of these portions of the grinding products the mentioned aluminium-excess in the silt + clay from the CO_2 -experiment is 1.69 %, in that from the CO_2 -free experiment it is 0.50 %.

It is possible, too, to calculate the quantities of the granite minerals that are attacked chemically in the two experiments. From the dissolved Na_2O is calculated the part of CaO that has been combined in plagioclase, as is described above. The rest of the CaO is calculated as hornblende, according to a hornblende analysis cited by Sundius (loc. cit. p. 236). This quantity of hornblende contains very small amounts of Na_2O and K_2O , which are subtracted from the dissolved Na_2O and K_2O . Their remainders are calculated as orthoclase and albite, and the feldspar part of the CaO as anorthite. The rest of the MgO is calculated as olivine (= a component in biotite; the ratio $\text{FeO} : \text{MgO}$ in the olivine = 15:4, according to Sundius loc. cit. p. 237). Thus are obtained the sums of the decomposed minerals in the experiments. If these sums are calculated on the assumption that other minerals present may have participated in the chemical dissolving processes, this does not lead to results that differ seriously from those obtained in the way described. If, for instance, a part of CaO is calculated as apatite, and the thereby increased remainder of MgO as olivine, a slightly larger total of decomposed minerals is obtained. — From the calculated total of the mineral materials that have participated in the decomposition is subtracted the dissolved quantities (Table 5, nos. 2 and 4).

It is thus possible to state the percentage of chemical decomposition-products in the clays, and as a consequence the amount of pure mechanical grinding-products (the clays are supposed to have been deprived of water and hydrogen). These results will be found in Table 8.

Table 8. Results of different calculations of the composition of the insoluble products of the shakings.

	The experiment with CO ₂		The experiment without CO ₂	
	Particles		Particles	
	< 0.002 mm.	< 0.02 mm.	< 0.002 mm.	< 0.02 mm.
Chemically generated Al ₂ O ₃ -excess	3.10 %	1.69 %	0.90 %	0.50 %
Chemical decomposition-products, without hydrated water	15.60 %	8.45 %	6.04 %	3.37 %
Non-decomposed minerals . . .	84.40 %	91.55 %	93.96 %	96.63 %
»Pure mechanical» clay	2.01 grams		1.96 grams	

It is once more to be pointed out that the determined dissolved bases, especially K₂O, are minimum-values, for the clay formed may have adsorbed a part of them. Thus the calculations of chemical products from these values give minima too. — It is interesting that nearly the same quantity of »pure mechanical» clay was found in both experiments, in view of the fact that mechanical conditions were identical.

After the main experiments, I made two similar experiments with the same samples of granite, which were agitated for 12 hours. Owing to the grinding, the granite grains were very rounded, and therefore less decomposition was to be expected. With CO₂-containing water was obtained 0.203 gram of clay (< 0.002 mm.). In the CO₂-free experiment was obtained 0.137 gram of clay.

If the grinding intensity had been as great as in the main experiments, a sixth part of the clay that resulted from these would have been formed. A sixth part of the clays (from Table 6) is 0.386 gram in the CO₂-experiment and 0.335 gram in the CO₂-free experiment. Even if the none too great degree of accuracy of the mechanical analysis method is taken into consideration, it is evident that less clay per hour was formed in the last experiments than in the main experiments.

The dissolved bases in the last experiments were determined by titration as is described above. It was found in the CO₂-experiment to be 0.00013 grammols of bases (MgO + CaO + Na₂O + K₂O), in the CO₂-free experiment, 0.00007 grammols. If we assume that the bases in the two last experiments are distributed between MgO, CaO, Na₂O, and K₂O, in the same proportions as in the corresponding main experiments (Table 5), which is very feasible considering the similar physico-chemical conditions, it is possible to make some calculations, which are, however, very approximate.

Thus, with CO₂ the quantity of dissolved bases will be 4 %, calculated in percentages of the simultaneously resulting clay (< 0.002 mm.). The aluminium excess in the same clay will be 4 %, the amount of chemical decomposition-products, 20 %. In the CO₂-free experiment the quantity of dissolved bases will be about 3 % of the clay, the aluminium excess will be 2—3 % of the clay, and the amount of chemical decomposition-products about 17 % of the clay.

The calculations based on the last experiments prove that *the mechanical*

grinding velocity has diminished more than that of the chemical decomposition, if compared with the main experiments. It is evident that this is due to the rounding of the granite grains through grinding during the continued agitation in water. The consequence is that the percentage of chemical products and aluminium excess in the resulting clay will increase on continued shaking if the physico-chemical conditions are similar. If I had started with granite gravel a little rounded from the beginning, I should have obtained a clay consisting more largely of chemical products.

In nature, even in the case of grinding by a glacier, the rock-grains will seldom be so sharp as in my gravel, which was formed by crushing the granite with a hammer. The »synthetic» clays from my main experiments may therefore be poor in chemical decomposition-products compared with natural, glacial clays. The clays resulting from my last experiments may be more similar to the natural, glacial clays.

Although the total amount of dissolved bases is much less in the last CO_2 -free experiment than in the experiment with CO_2 , the percentage of chemical decomposition-products in the two clays is nearly the same, because the total quantity of clay is less in the CO_2 -free experiment.

The formation of glacial clay has taken place through grinding in water with a CO_2 -content less than in my CO_2 -experiments, but greater than in my CO_2 -free experiments. Other factors of any importance were similar. It may thus be stated that an important part of the glacial clays are chemical decomposition-products, due to weathering during their formation-process in cold ice-water.

My experiments do not show which is the source of the dissolved K_2O , the microcline or the biotite. From a chemical point of view, it is most probable that all the silicates of the granite participated in the hydrolysis, because all silicium-acids must be weak acids and their salts therefore hydrolysed by water. Professor Goldschmidt (see p. 3) has based his suggestion as to the predominant rôle the biotite plays in the dissolving of K_2O in connection with the formation of glacial clay on the fact that biotite can exchange its positive ions with others, as do the zeolites. (G. loc. cit. p. 42.) The exchange can take place not only on the surface of the mineral, but also within it. But for an ion-exchange to be possible there must be ions to exchange with, and that in appreciable concentrations. That is also the case in the experiments of E. Johnson (Goldschmidt and Johnson loc. cit. pp. 58—66), on which G. bases his conclusion concerning the superiority of biotite over orthoclase in its capability to emit potassium-ions to a water solution. In the experiments mentioned by Goldschmidt the difference of potassium-feldspar and biotite is greater the greater the hydrogenion concentration, as is to be expected if the phenomenon is an exchange of potassium-ions with hydrogenions.

To throw light upon the formation of glacial clays of potassium feldspar, I have made experiments with red microcline (from Söderåsen, Skåne). The mineral was crushed to grains similarly to the granite (of about the size of a pea), and the particles smaller than 2 mm. were sieved off. 200 grams of the feldspar was shaken for 12 hours with 100 c.c. of water containing 20 c.c. of

CO₂-saturated water (p_H at the commencement = 4.7, temperature 2—3° C.). The milky clay suspension contained 0.0198 gram of dissolved K₂O. Experiment no. 13 (see Table 3), which was made in an identical manner, but with the biotite-rich granite, gave 0.0218 gram of bases, calculated as K₂O. The feldspar is thus decomposed nearly to the same extent as the granite.

Another experiment was made under the same conditions as the main experiments. 200 grams of crushed feldspar (> 2 mm.) were shaken for 12 hours with 500 c.c. of water containing 50 c.c. of CO₂-saturated water; the temperature was + 3° C. The result was:

Dissolved bases (K₂O + Na₂O), calculated as K₂O, determined by titration, 0.0078 gram.

Quantity of clay formed (< 0.002 mm., of white colour) 0.1770 gram.

Quantity of silt formed (> 0.002 mm.) 0.3653 gram.¹

The amount of chemically combined water in the clay 2.20 %.

The amount of chemically combined water in the silt 0.17 %.

The excess of Al₂O₃ in the clay, calculated from the dissolved bases, 5.0 %.

p_H at the beginning of the agitation, calculated 4.5.

p_H at the end of the agitation, calculated 5.7.

The Al₂O₃-excess is calculated in following manner. For each dissolved group of K₂O (or Na₂O) is accepted an Al₂O₃-group in the clay which is not combined with alkali. — If this Al₂O₃-amount is calculated as kaolinite, 12.6 per cent of the clay would be kaolinite. This would contain 0.0031 gram of combined water. The amount of combined water found was 0.0039 gram (2.20 %). It is to be noted that some of the potassium ions may have been adsorbed in the clay, and therefore the aluminium excess and the kaolinite must have been calculated a little too low. The white feldspar-clay (< 0.002 mm.) contains about 22 % of chemical decomposition-products, and thus about 78 % of unweathered feldspar. (All these calculations are made without correction for the very small quantities of dissolved aluminium and silica, because these were not determined.)

The experiments with feldspar suggest that this mineral must participate in the formation of glacial clay, as do the biotite and probably most of the other silicates. This is not in agreement with the views of Goldschmidt (loc. cit.) but is explained by the fact that the formation of glacial clay takes place with much smaller hydrogenion concentrations than in the experiments of Goldschmidt and Johnson. *In the formation of glacial clay the chemical processes are principally hydrolytical, not ion exchanges.*

Whether orthoclase or biotite in the p_H-range of 4.5—8 (common in our arable soils) is the more apt to give off its potassium, is thus not yet definitely decided. In an earlier paper (Tamm 1915, pp. 187, 203) I have stated that the biotite weathers much faster in the soil than do the acid feldspars. This result was, however, found in forest soils with p_H-values of about 4 and does not, perhaps, hold good for arable soils.

¹ A complete Atterberg analysis was not made. This portion is therefore not comparable with the above-described silt portions from the granite experiments.

Concerning the power of ion-exchange, it is known that the feldspars show the property of ion-exchange too, but the phenomenon appears (at least during a short time) only to affect the surface of the mineral, whilst in the case of the zeolites and biotite it affects the inside too. The advantage of the zeolites and biotite over the feldspars thus appears to be as follows: They, like a hydrogel, have a structure that makes possible a rapid diffusion of ions into the interior of the mineral. All the alkali-ions or calcium-ions of the zeolite can thus be exchanged in a short time. A feldspar must also have a great power of ion-exchange in water solutions, if the mineral is ground into very small particles with large surfaces that can be attacked by the liquid. It is thus probable that the feldspars, like the biotite, can exchange positive ions on the formation of glacial clay, if the limiting concentrations of positive ions to exchange with are exceeded. The velocity of such reactions will, like that of the hydrolytical reactions described, largely depend on the velocity of the diffusion of the different ions in the liquid to the reacting surfaces. In the rock-metamorphosis, on the other hand, the diffusion-velocity of ions in the mineral itself will be decisive.

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