STUDIES on the SYNTHESIS of
LAYER SILICATES.

THESIS

presented by

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CONTENTS.

SUMMARY.

A study on the low temperature synthesis of layer silicates was undertaken on the systems SiO_2/Mg^{2+}, SiO_2/Al^{3+} and $SiO_2/MgO/LiF$.

Initial work was carried out on the uptake of silica from dilute solutions of magnesium at room temperature and atmospheric pressure to ascertain the amount of silica adsorbed in precipitates formed under these conditions. Reflux of these solutions gave products analogous to the serpentine minerals, chrysotile and antigorite. Electron microscopy was used to study these products. Electron diffraction provided a means of identifying some of the phases and morphological features observed were discussed in terms of silicate structures.

Similar studies were made on the SiO_2/Al^{3+} system at room temperature and atmospheric pressure and under reflux conditions. The products of these reactions were mainly hydroxides of aluminium. Attempts were made to chelate mildly the aluminium in solution to hinder the precipitation of hydroxides and encourage silicate synthesis. A series of organic and inorganic additives were used and the solutions heated at 80°C. Hydroxides were again precipitated but some poorly crystalline dickite was formed.

Systems capable of yielding layer silicates in greater quantities and more reproducible were then studied.

Slurries of powdered silicic acid, magnesium hydroxide and lithium fluoride refluxed for about five days produced a three layer smectite, hectorite. Experiments were conducted to determine the critical SiO_2/MgO ratio to produce hectorite. These experiments were carried out in polypropylene vessels since at low SiO_2/MgO ratios glass vessels were found to dissolve to a considerable extent. With a SiO_2/MgO 1.2 hectorite alone was produced.

The mechanism of formation of hectorite from these slurries was investigated by following the changes in slurry material by electron microscopy. Direct evidence was obtained for the fixation of silica on the octahedral layers of brucite. The process was also followed by X-Ray diffraction and differential thermal analysis.

The formation of layer silicates under these conditions is interpreted in terms of an initial fixation of silica on brucite layers. This "silicated magnesium hydroxide" then dissolves to form the particular units required for layer lattice synthesis.

The products were also investigated for cation exchange ability, resistance to acid attack and their behaviour in density gradients.

Similar refluxes were performed with additional ions present: by using aluminium hydroxide with magnesium hydroxide and saponite like clay was formed.

INTRODUCTION.

Clay minerals have been studied intensively during the last thirty years due to their considerable industrial importance, for instance, their use as catalysts in oil refining and as raw materials for the cermaics industry. Their properties also govern the mechanical and chemical nature of soils. Indeed the formation of soils is intimately related to the formation of clay minerals.

The possible role of clay synthesis in the origins of life (Cairns-Smith, 1966) was another important reason for the present study.

An understanding of clay synthesis has only made progress since the development of reliable techniques of phase identification such as X-Ray diffraction and thermal analysis. Another factor which inhibited progress was the conception that clay minerals would take long periods of time to synthesise, especially at normal temperature and pressure.

Rayner (1962) synthesised kaolin hydrothermally from coprecipitated gels: at 300°C the time to convert half the starting materials to kaolin was eight hours, at 260°C it took eleven days. By extrapolation he concluded that at 20°C the time for half conversion would be 160,000 years. A more optimistic method by Noll (1936) predicted that it would take sixty years to synthesise kaolin.

Wey and Siffert (1961) on the other hand claim to have synthesised montmorillonite like products overnight from dilute solutions at room temperature and, by complexing Al^{3+} with oxalic acid, a precipitate with kaolinite like properties was formed after three weeks.

However the high temperature treatment of mixed gels and oxides proved to be the most successful in initial synthetic work.

Among the first workers to successfully synthesise layer silicates were Chrustschoff (1887) and Hautefeuille and St. Gillies (1887) who independently prepared and carefully characterised fluoro-biotite.

Noll (1935) studied the system Al_2O_3-SiO_2-H_2O in the temperature range 250°C to 500°C with varying amounts of alumina and silica, the pressure bomb containing a constant percentage of water. Silica gel and alumina gel were used in the experiments; the latter crystallised rapidly to bayerite and boehmite when the gel was aged prior to use. Kaolinite and pyrophyllite were synthesised.

The synthesis of kaolin was also achieved from coprecipitated Al_2O_3-SiO_2 gels at 150°C to 400°C under varying vapor pressures (Roy and Osborn, 1952).

Brindley and De Kimpe (1961) synthesised kaolinite at 150°C and 5 atm pressures using gibbsite as a source of alumina with various sources of silica.

Noll (1936) has also studied the system $(Ca,Mg)O-(K_2Na_2)O-Al_2O_3-SiO_2-H_2O$ at 300°C and 87 atmospheres pressure and produced kaolinite, smectite and mica. The production of kaolinite was favoured under acid conditions, while smectites formed under alkali conditions.

Barrer (1952) produced felspars, zeolite, and mica felspathoids by hydrothermal reaction of sodium aluminosilicates. By hydrothermal treatment of aluminium hydroxide gels and silica gels micas with NH_4 for K, Ga for Al, Ge for Si were synthesised. Using the same technique (1967) he has synthesised alkyl ammonia complexes of montmorillonite and hectorite.

An outline of the systematic syntheses of layer silicates has been made by Roy (1954). Under controlled temperature (up to 900°C) and pressure (up to 3000 atmos.) various layer silicates with many different ions can be made. The change of various properties such as lattice constants, morphology, expansion with ethylene glycol was studied as a function of the size and nature of ions present in the $Al_2O_3-SiO_2-H_2O$ system.

Yoder and Eugster (1955) have made extensive researches into synthetic and natural muscovite. Yoder (1959) has summarised work on the synthesis of micas. It appears that the simpler polymorphic forms develop initially at lower temperatures and pressures and that with increasing temperatures and pressures there is a transition to the more complicated polymorphic forms.

Siffert and Francois (1968) have succeeded in synthesising nickel containing montmorillonite by heating a mixture of silica, nickel hydroxide and lithium hydroxide in an autoclave at 350°C and 160 bars for five hours.

Numerous patents have been awarded for the production of lamellar silicates by hydrothermal processes.

Granquist (1964) describes a technique for the synthesis of alumina silicates. The minerals are prepared by heating to 280-315°C an aqueous suspension of SiO_2 and Al_2O_3 and compounds containing various cations and anions of O^{2-}, OH^- and F^-.

Newmann outlines a method of preparing lithium containing magnesium clays with exchangeable cations of Na, Li or organic molecules. By coprecipitating a solution containing all the anions and cations required while maintaining the pH 8 and then, without washing the precipitate free from soluble salts, heating the product under pressure, crystalline clays may be prepared.

A review of hydrothermal techniques has been compounded by Roy (1961). It appears that the layer silicates synthesised in the range 0-5000 atm and 0-1000°C appear to be in every way compatible to the natural minerals. Virtually the entire range of clay minerals and micas has been synthesised in addition to several special synthetic phases with specifically chosen cations. The range of compositional variation permitted in each main mineral family has been determined experimentally and the influence of various types of solid solution on X-Ray optical, polytypic stacking and stability properties has been studied. Using the capacity for controlled synthesis, it has been possible to tackle general specific problems such as : interpretation of the infra-red spectra of clays, influence of minor impurities in changing of stacking, the composition of 'illite' and the control on morphology of ionic radius.

Clay synthesis has been studied during rock weathering experiments conducted in the laboratory.

According to Gruner (1944) kaolinite, pyrophillite, muscovite and boehmite are the phases that may form when microcline and albite are subjected to high temperatures and pressures in the presence of aluminium hydroxide, silica and potassium chloride under acid conditions. The concentration of the potassium ions and the Al_2O_3/SiO_2 ratio of the system were the factors determining which minerals formed from felspars. Kaolinite will form and is stable below about 350°C, whatever the potassium ion concentration, provided the ratio of Al/Si is about unity.

Treatment of orthoclase and anorthite with 0.5 NHCl yields kaolinite as an alteration product at temperatures below 400°C, pyrophillite and boehmite at temperatures of 400 to 550°C, and corundum at about 600°C. (Scharz & Trageser 1935).

The degradation of potash felspar was studied by Badger and

Ally (1935) by treatment with hydrofluoric acid with production of kaolinite. No reaction occurred when the same felspar was heated in the presence of carbonic acid for 156 hours at 60°C and a pressure of 1,800 psi.

Pedro (1958 et seq.) studied geochemical weathering using a soxlet extraction apparatus which served as a model natural environment of humid tropics with an atmospheric zone and zone of water-table fluctuation. The formation of clays was favoured using acid drainage (CO_2-H_2S).

Similar experiments performed by Correns (1961) showed that the components of framework silicates enter solution as ions and a very thin residue layer forms on the particles, the thickness of which does not change during the course of the experiment. The composition of the residue layer is such that the SiO_2/Al_2O_3 ratio does not correspond to that of kaolinite or montmorillonite. It is also found that the residue layer gave no X-Ray diffraction lines and no crystal formation could be observed using electron diffraction. Indeed Pedro (1960) had already concluded that the leaching of rocks under pure water conditions gave amorphous material and no clays were formed. By concentrating the leachate, adding magnesium acetate solution and heating the solution at pH 7 at 70°C for four months montmorillonite was produced from a granite source and lavas produced antigonite like material. He proposed that the natural leaching of rocks yields transitory products which are one of several steps in the formation of clays.

Much work has been carried out on the transformations of clay minerals at ordinary temperatures and pressures.

Sedletsky (1937) mixed sodium silicate and sodium aluminate and then leached with $NMgCl_2$ until the pH of the leachate was 5.6. After further washing to remove all the free chloride, the gel was held in a closed vessel at laboratory temperatures for four years, after which X-Ray examination showed the presence of a product similar to a smectite.

Caillere and Henin (1948) have shown that illite like material is produced from smectite when all the exchange positions are occupied by potassium ions and the material is thoroughly dried at about 110°C. Caillere, Henin and Barshad (1950) showed that treatment of either smectite or vermiculite with a solution of Mg^{2+}. with all the exchange sites occupied by Mg^{2+}, gives a product which does not expand and has an X-Ray diffraction pattern similar to chlorite. Caillere and Henin (1947) have also reported the formation of kaolinite from montmorillonite by treatment with 20% $CaCl_2$, 0.5% Na_3AlO_3 and 10% $Al(NO_3)_3$ for three to four days and then precipitating with ACl or NH_4OH.

The complimentary technique to these degradative studies, that is, the study of clay mineral formation from dilute solutions under normal temperature and pressures has however received less study.

Caillere and Henin (1947, 1948) and Caillere, Henin and Esquevin (1953) have reported the synthesis of clays by the electrolysis of sodium and potassium silicate and aluminate solutions. Platinum was used for the cathode and various anodes of Al, Fe, Ni and Mg were tried. The product depended on the anode used: with an Mg anode, antigonite like minerals were formed and with Al, the product was similar to kaolinite.

Henin and Robichet (1953), using dilute boiling solutions, succeeded in synthesising a montmorillonite type clay similar to hectorite and by using silicate, aluminate and magnesium acetate solutions with a vast excess of KCl, a mica like precipitate formed. The same authors in 1954 described the synthesis of Mg montmorillonite and perhaps sepiolite by slowly mixing (1 ml/hour) dilute solutions of silica and magnesium (1-100 mg/l). They also succeeded in synthesising antigonite (1954) by adding 25 mls/24 hours of a very dilute solution of Na silicate and aluminate into 2 litres of water containing NaCl, $MgCl_2$ and $CaCl_2$ at pH 7.

Caillere, Oberlin and Henin (1954) carried out experiments with dilute solutions at room temperature and reflux temperature. With (Si,Mg) mixtures montmorillonite was formed at both room temperature and reflux temperature. In the (Si,Mg,Al) system, with Al as aluminate at pH 8, montmorillonite was again formed, with more Al a "swelling chlorite" was produced: with cationic Al at pH 8.5, a filmy, almost amorphous product, perhaps sepiolite, was found: at pH 7.7 boehmite was produced. Anionic Al with a large excess of KCl gave micas. They also studied systems with Fe present, and obtained Fe rich saponite, montmorillonite minerals, Fe_2O_3 and swelling chlorite: using excess NaCl mica like products formed.

Henin (1955) extended the technique using cations of Mg, Fe and Ni to form montmorillonite like silicates at pH > 7. Below this value oxides, hydroxides and amorphous material was obtained. Without added silica, the glass vessel was attacked and antigorites of Mg and Ni were obtained.

Caillore, Henin and Esquevin (1958) have synthesised cobalt containing clays at room temperature and pressure, from dilute solutions of $Co(OAc)_2$, $MgCl_2$ and Na silicate and aluminate solutions.

These studies showed that it was not necessary to use hydrothermal techniques to produce clay minerals.

One repercussion on these studies was that the formation of clay minerals under mild conditions gave a clearer understanding of the composition of natural waters.

Krauskopf (1959) and Harder (1964) have studied the solubility of silica in fresh or marine water. The level of silica is less than that expected if silica is assumed to be in equilibrium with amorphous silica. This is ascribed to inorganic precipitation of silica or to fixation and sedimentation of silica by organisms.

Diagenesis can lead to the formation of various clay minerals and finegrained quartz from X-Ray amorphous hydroxide-silica gels. The conditions under which clay minerals exist in sea water have been calculated by Kopeikin (1970) who gives values of pH for equilibrium between various clays.

By using catalysts or chelating agents it would appear to be possible to synthesise clay minerals more rapidly at ordinary temperatures and pressures.

Danse (1959) has shown that oxides of Fe, Al, Ti, and Si can be separated by aerobic bacteria. The clays which occur with laterite would be produced by an organo-chemical process. Swanson and Bisque (1970) report that naturally occurring organic acids (humic acids) are effective agents in the colloidal transport of Cu, Pb, Zn, Fe, Al. Concentrations of organic acids 4-40 ppm C in H_2O can effect large increases in amounts of material stabilised in solution. Indeed Linares and Huertas (1971) have synthesised kaolin from dilute solutions at normal temperature and pressure by first complexing Al^{3+} in solution with fulvic acid; this ensured the sixth fold coordination of aluminium. Wey and Siffert (1961) had previously synthesised kaolin by complexing aluminium with oxalic acid. It appears then that organic processes can accelerate the breakdown of primary rocks and catalyse the production of secondary clay minerals.

Much work has been directed to techniques using intermediate conditions between hydrothermal treatment of oxides and low temperature, dilute solutions studies.

Strese and Hofmann (1941) made magnesium silicate gels from $MgCl_2$ and hydrated silica which produced clay like structures when boiled with potassium hydroxide, calcium hydroxide or sodium hydroxide. The products resembled hectorite and antigorite but micas formed with high concentrations of potassium hydroxide. Similar work by Hinz and Kunth (1957) on gels made from $MgCl_2$ and $NaO.SiO_3$ solutions of varying NaO/SiO_2 ratio, showed that on being aged for a longish time at room temperature or by being treated for several hours at 100°C poorly crystalline products form: the X-Ray spacing did not allow them to distinguish between hectorite or antigorite as the likely mineral. However, Wiegmann and Horte (1960) using the same preparation technique prepared products with similar compositions and X-Ray patterns to Strese and Hofmann hectorite like compounds but on the basis of D.T.A. and infra red spectra consider the products to be more like sepiolite than hectorite.

By refluxing slurries of SiO_2, $Mg(OH)_2$, LiOH, LiF and NaOH, Granquist and Pollack (1960) synthesised hectorite on the basis of composition D.T.A., X-Ray, cation exchange and flow properties.

Aluminium and magnesium layer silicates have also been prepared from gels by De Kimpe, Gastuche and Brindley (1961). With Al, the gel phase was the more abundant and the identification of crystals was only possible by electron diffraction. With Mg, the yields of crystals were much higher and X-Ray diffraction methods were possible. The properties of the gels influenced the type of product formed, the main factors being pH, salt concentrations, and the ratio of Al or Mg to silica content. For Al, the change from six fold to four fold coordination increased with pH. Kaolinite was identified at low pH and mica like structures at higher pH. Serpentine minerals were obtained at intermediate pHs. Gillis and Dekeyser (1962) suspended sachets of mixed aluminium and silica gels in water: whisker like crystals formed on the exterior of the sachets with kaolinite properties.

Caillere, Esteoule and Henin (1962) reported that Mg aluminosilicates may be synthesised more rapidly from gels than from solution. A number of preparations are given and their analysis and properties tabulated. They postulate that under natural conditions layer silicates will be readily formed where solutions have a greater concentration of Mg than of silica.

Abdul-Latif (1969) has studied the systems $MgO-SiO_2-H_2O$ and $MgO-Al_2O_3-SiO_2-H_2O$ in the temperature range 25-200°C under alkaline conditions. Using aqueous solutions of silica and hydroxides of magnesium and aluminium he describes the role of temperature in determining either 2:1 or 1:1 layer formation and the effect of varying the Mg/Al ratio on the clay product.

De Kimpe (1969) described the crystallisation of kaolinite at low temperatures from an alumina-silicic acid gel. The product formed from a gel by the simultaneous hydrolysis of ethylorthosilicate and aluminium isopropoxide by 0.1 N NaOH at 175°C. The transformation was thought to occur through a zeolite phase.

The present work is concerned with the study of the formation of clay minerals at room temperature, reflux temperature and atmospheric pressure. The possible significance of clay synthesis for the origin of life was a factor in determining the choice of these conditions.

Bernal has speculated upon the possible role that colloidal silicates played in catalysing the formation of complex organic molecules from simple ones: these low molecular weight compounds could be formed abiogenically as has been shown by Miller. For example amino acids were synthesised from methane, nitrogen and water vapour under the influence of electrical discharges. Bernal suggested that a concentration of simple organic molecules might have been brought about by adsorption on colloidal clays.

Cairns-Smith (1966) attributes a more direct role to clays by pointing out that clay crystals are capable in principle of storing large amounts of genetic information which if replicated sufficiently accurately during crystal growth could evolve means of phenotypic expression under simple selection pressures. Such systems would represent primitive organisms.

This work is concerned with investigating an initial requirement for testing this hypothesis, that is, to find conditions under which clays could be synthesised reasonably quickly under mild conditions. The work described here is also concerned with attempting to clarify the mechanism involved in the formation of hectorite using a slurry technique.

Future work would aim at estabilishing conditions, on the basis of the work described here, that just permit the crystallisation of a potentially genetic clay and where that clay would only survive if it had some simple functional attribute, for example if it were able to adsorb some kind of molecule or molecules from the surrounding solution. When these simple systems had been established, more strict selection pressures could be set up so that mutants would be selected for more specialised and complex functions.

CHAPTER I

Dilute solution studies on the SiO_2/Mg^{2+} system.

Part 1 of this chapter contains experimental work on the effect of pH, time and silica concentrations on the molecular ratio SiO_2/MgO in precipitates formed in dilute silica, magnesium solutions at room temperature and atmospheric pressure.

Electron microscopy studies on precipitates formed under similar conditions are described in Part 2.

The effect of heating similar mother solutions of silica and magnesium at or near 100° C is reported in Part 3.

Part 4 contains the description of other techniques developed to study this system.

PART 1.

Silica uptake from dilute magnesium solutions.

Experimental.

Polythene or polypropylene apparatus was used as much as possible to minimise contamination from silica and other components present in glassware.

Stock solutions of magnesium were prepared from magnesium chloride, $MgCl_2 6H_2O$, of 'Analar' reagent quality supplied by British Drug Houses, to contain 1000 ppm of Mg^{2+}. Silica solutions were prepared from sodium metasilicate, $Na_2SiO_3.5H_2O$, supplied by Alcock (Peroxide) Ltd. containing 1000 ppm of silica, SiO_2. This silica source had a maximum of 0.025% iron present. The $MgCl_2$ was dried at 60°C and stored over silica gel, as was the Na_2SiO_3, before use. Distilled water was used throughout : deionised water made by a mixed cortion and anion exchange resin, made by Demstill Equipment Ltd., was found to be unsuitable because it contained traces of clay minerals.

Normally, the Mg^{2+} solution was added to the SiO_2 solution, the pH adjusted with HCl or NaOH, diluted to about 100 mls, the pH adjusted again and the final volume noted so that the starting concentrations could be calculated. Glass electrodes connected to a Pype pH meter were used to record the pH of the solutions.

To determine the SiO_2 concentrations in solution samples were withdrawn from the mother solutions and centrifuged at 1800 g for half an hour to give a clear supernatant; aliquots of the supernatant were taken and the SiO_2 concentration determined by a spectrophotometric method developed by Alexander (1953). The yellow silicomolybdate complex formed with SiO_2 as monomenic silicic acid, H_4SiO_4 was reduced to molybdenum blue by a colour development procedure based on the work of Shapiro and Brannock (1963). For details please refer to the experimental Appendix. An average of duplicate analyses allowed the SiO_2 content to be determined to $\pm$ 2%. The SiO_2 which remained in the supernatant was called the free silica content; the silica removed from solution was determined by subtracting the free silica concentration from the initial amount of silica added and was described as the silica uptake.

The Mg^{2+} content was determined from the supernatant by a standard Atomic Adsorption method described in the Experimental Appendix.

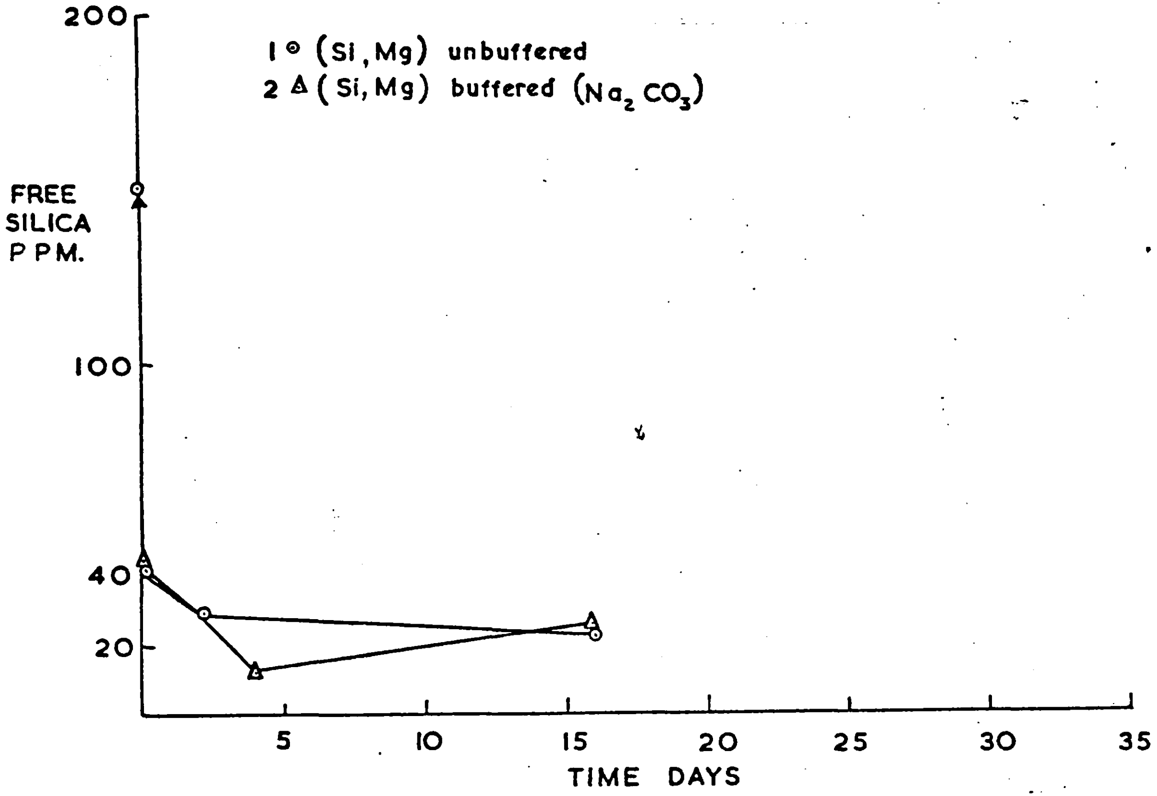
Buffering agents were used in some of the experiments. For pHs between 10 and 12 solutions of sodium carbonate were used. It was not possible to use phosphate buffers for this pH range since a phosphomolybdate complex would be formed with the molybdate reagent.

Silica Uptake Experiments.

To determine the length of time required to achieve equilibrium in the SiO_2/Mg^{2+} system, solutions with initial concentrations of 150 ppm SiO_2 and 100 ppm Mg^{2+} at pH 11.0 were analysed for SiO_2 in solution for a period of 16 days. Curve 1 of fig. 1 shows the free SiO_2 content falling to about 40 ppm 30 minutes after mixing, and after five days reaching an equilibrium value of about 20 ppm. A solution containing the same mixture but buffered at pH 11.1 with Na_2CO_3 gave similar results (curve 2).

Preliminary experiments were also carried out to determine the extent of precipitation of Mg^{2+} between pH 7 and 14. A series

FIG.I. SILICA UPTAKE FROM DILUTE MAGNESIUM SOLUTIONS AGAINST TIME.



of solutions were prepared containing 100 ppm Mg^{2+} with pHs in the above range, shaken for one day, and the Mg^{2+} concentration found from the supernatant of centrifuged samples. The results are shown in curve 1, fig. 2; the precipitation of Mg^{2+} as magnesium hydroxide, or brucite, is seen to be complete at pH 9.6.

A series of solutions was then prepared with 150 ppm SiO_2 and 100 ppm Mg^{2+} and pHs in the range 7 to 14. The free silica content was determined after agitating the solutions for five days. Since the solutions were not buffered the final pH was measured immediately before the samples were taken.

Curve 2, fig. 2, shows the change in the free silica content in the pH range 7 to 14. The uptake cannot be due to an equilibrium with a solid form of SiO_2 since the collected data of Krauskopf (1959). fig. 3, shows that the free silica level increases from about 110 ppm at pH 7 to 2000 ppm at pH 11 when in equilibrium with amorphous silica. The uptake must be caused by a reaction with the magnesium component of the solution.

Wey and Siffert (1961) in a similar series of experiments showed that the SiO_2 level fell from 150 ppm to 40 ppm in the presence of 78 ppm Mg^{2+} at about pH 11.0. They suggest that the reaction is ionic between Mg^{2+}, $SiO_3^{=}$ and OH^-. They further suggest, (1968), that the silica reacts with Mg^{2+} to form a basic salt with clay like properties, but do not propose a structure for this salt.

FIG. 2. SILICA UPTAKE FROM DILUTE MAGNESIUM SOLUTIONS WITH pH.

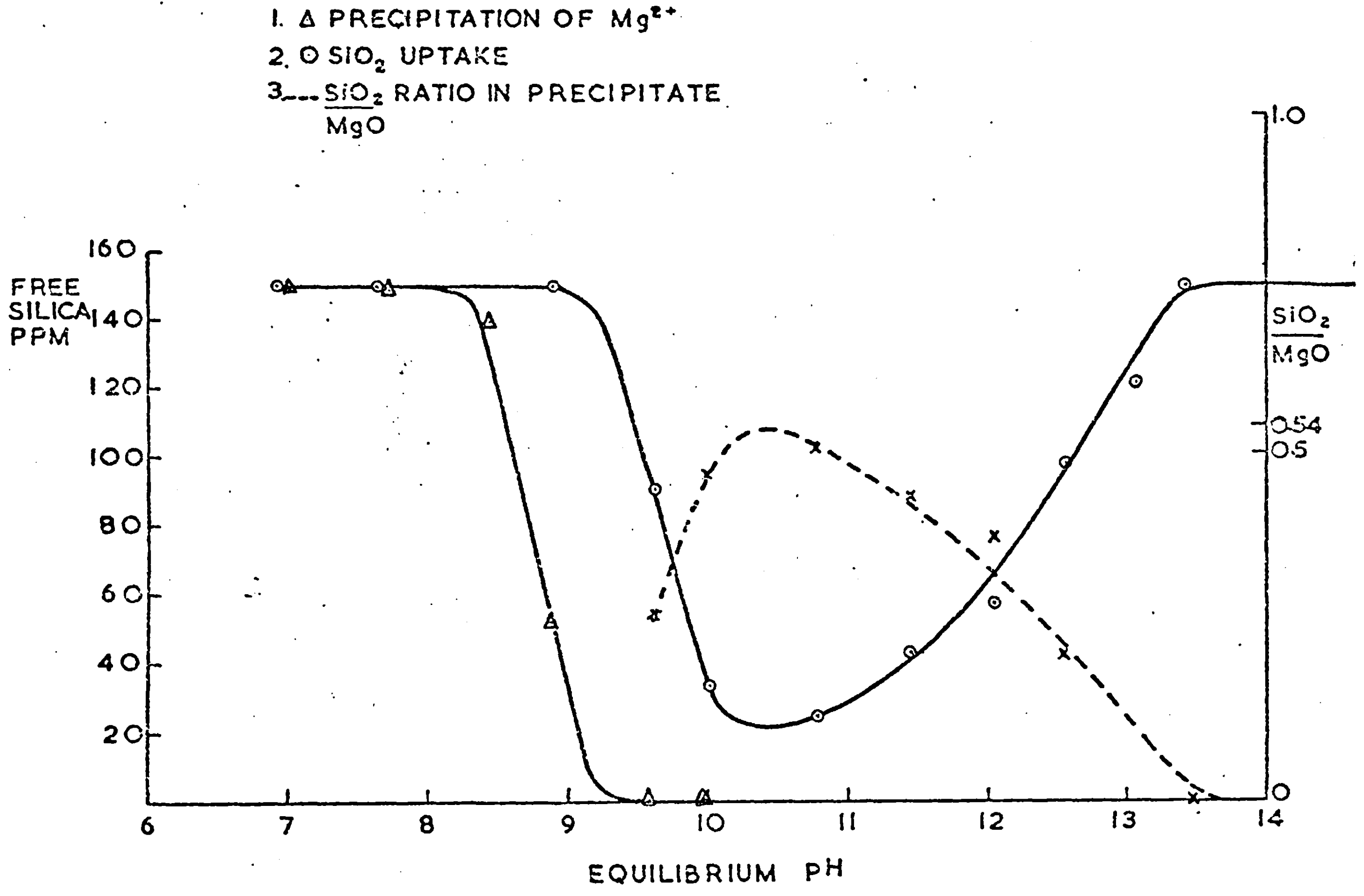
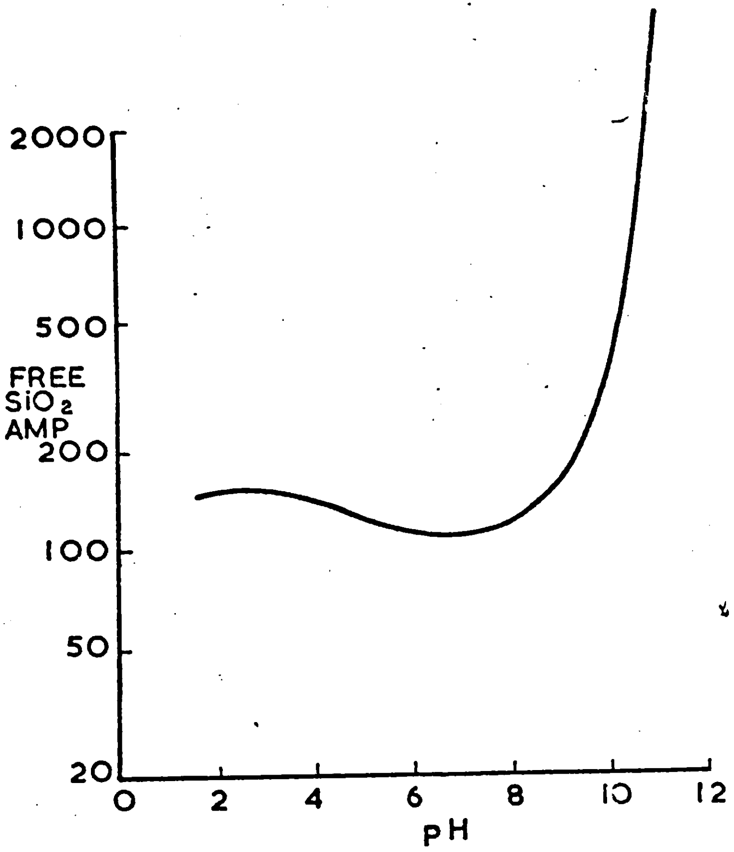


FIG 3. CHANGE OF SOLUBILITY OF AMORPHOROUS SILICA (AFTER KRAUSKOPE F)



Stock and Davies (1944) established the existence of the $Mg(OH)^+$ ion in dilute alkaline solutions.

At pH 9.5 a basic salt might be formed as follows :

$$Mg^{2+} + OH^- = Mg(OH)^+ + H_3SiO_4^- = Mg(OH)^+H_3SiO_4^-$$

If the salt on the right hand side were insoluble enough under these conditions it would precipitate out, pushing the equilibrium to the right. Table 1 shows that as the pH increases the concentrations of $Mg(OH)^+$ and $H_3SiO_4^-$ increase making salt formation more favourable. This may account for some of the uptake below about pH 9.5. However at pH > 9.5 the $Mg(OH)^+$ ion becomes unstable and precipitates as $Mg(OH)_2$ so that in the region of maximum uptake at pH 10.5 it would seem more likely that a reaction occurs between $Mg(OH)_2$ and the species $H_3SiO_4^-$ and H_4SiO_4.

Britton (1942) and Iler (1955) suggest that the precipitation is brought about by the "mutual coagulation" of the positively charged hydroxide and the negatively charged silica.

Along these lines it may be envisaged that a reaction between $H_3SiO_4^-$ and $Mg(OH)_2$ with + ve holes occurrs : figure 4. This type of bonding could be reversible with the $Si(OH)_3O^-$ continually competing with OH^- for the + ve sites.

TABLE 1.

pH	OH^-(M)	$\frac{Mg(OH)^+}{Mg^{2+}}$ *	$Mg(OH)^+$ (M)	$\frac{H_3SiO_4^-}{H_4SiO_4}$	$H_3SiO_4^-$(M)
7.9	10^{-7}	3.8×10^{-5}	1.5×10^{-7}	-	-
8.0	10^{-6}	3.8×10^{-4}	1.5×10^{-6}	1.6×10^{-2}	4.0×10^{-5}
8.5	$10^{-5.5}$	$3.8 \times 10^{-3.5}$	$1.5 \times 10^{-5.5}$	-	-
9.0	10^{-5}	3.8×10^{-3}	1.5×10^{-5}	1.6×10^{-1}	4.0×10^{-4}
9.5	$10^{-4.5}$	$3.8 \times 10^{-2.5}$	$1.5 \times 10^{-4.5}$	1.0	2.5×10^{-3}
9.6	$10^{-4.4}$	$Mg(OH)_2$	-	-	-
10.5	$10^{-3.5}$	$Mg(OH)_2$	-	5.0	1.25×10^{-2}

Concentrations of $Mg(OH)^+$ and $H_3SiO_4^-$ at pHs 7 to 11 in solutions containing 100 ppm Mg^{2+} and 150 ppm SiO_2. $Mg(OH)_2$ precipitates at pH 9.6.

* Stability constant, $K_1 = \frac{Mg(OH)^+}{Mg^{2+} \; OH^-}$, $\log K_1 = 2.58$.

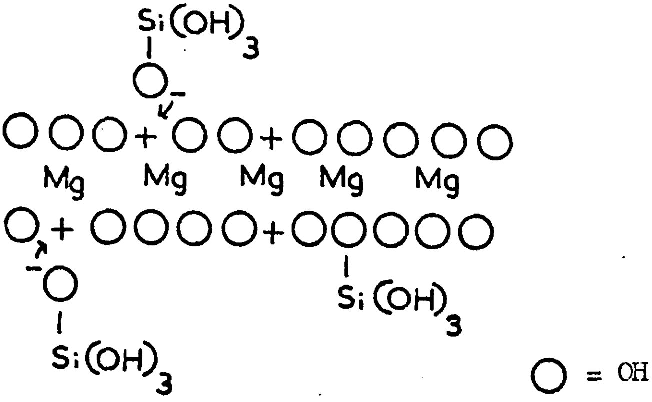


Figure 4. Adsorption of silicic acid into + Me holes in brucite.

The silica would also be capable of hydrogen bonding to the brucite surface as H_4SiO_4 and $H_3SiO_4^-$. (Fig. 5).

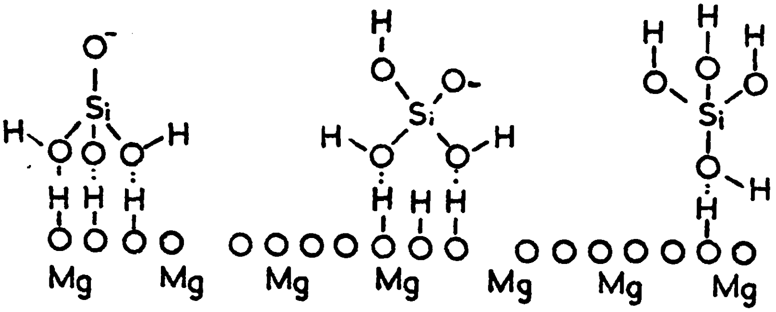


Figure 5. Hydrogen bonded configurations of adsorbed silicic acid.

Singly and doubly ionised silicic acid will be present at pH > 10.5. This could account for the decreasing silica uptake in this region since the molecules will tend to repel one another making adsorption increasing unstable.

Saturation Experiments.

Experiments were conducted to establish the maximum uptake of SiO_2 in this system.

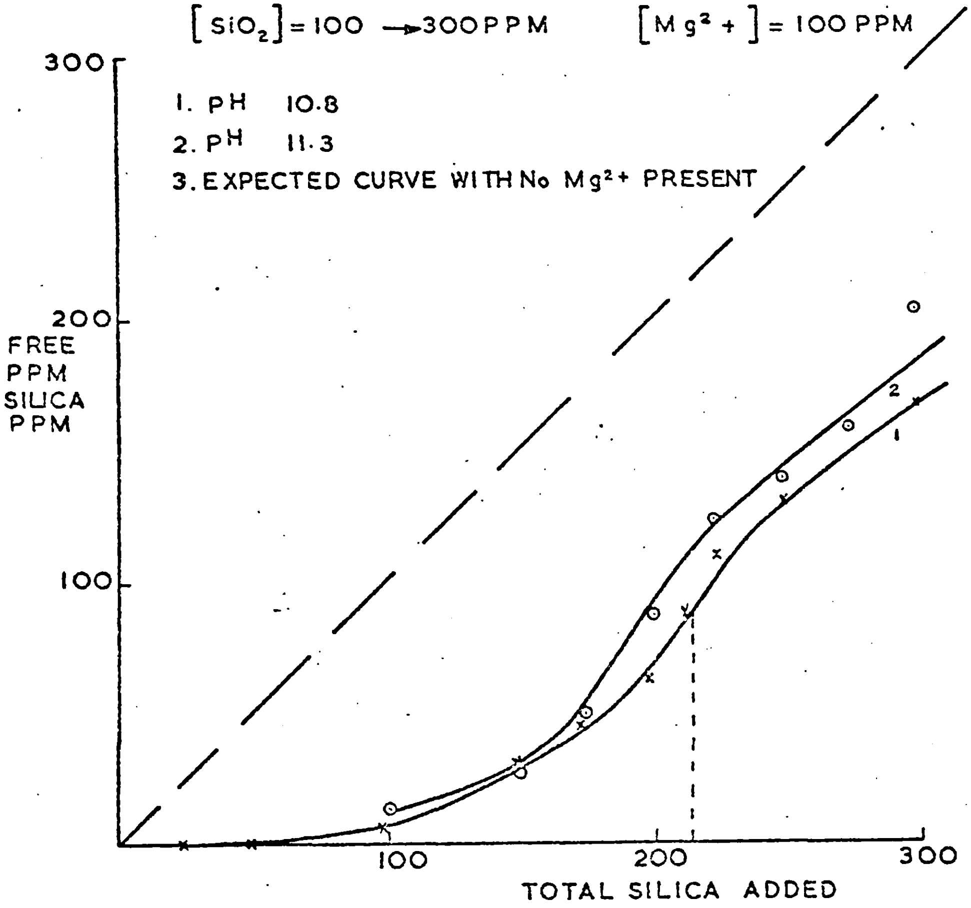
Experimental.

A series of solutions were prepared containing SiO_2 up to 300 ppm and containing 100 ppm Mg^{2+}. The pH was adjusted to 10.8, the solutions equilibrated for five days and the free silica concentration determined. For comparison a similar series of reactions at pH 11.3 were carried out.

Results and Discussion.

The results are shown in figure 6 up to 100 ppm SiO_2 total SiO_2 added, SiO_2 is virtually completely adsorbed. As more SiO_2 is added, more SiO_2 remains in solution. The curve then tends to become parallel to the curve expected if no Mg^{2+} were present, showing that the saturation point is being reached. It then passes through a gentle inflexion point and then tends to slope away perhaps due to slight polymerisation of SiO_2. The inflexion point was taken as the saturation level. The pH 11.3 curve shows a

FIG. 6. FREE SILICA PRESENT IN SOLUTIONS OF SATURATION EXPERIMENT.



parallel but higher level of free silica with increasing total SiO_2 added; this is consistent with the results shown in curve 2, figure 2, where less SiO_2 is adsorbed at higher pHs.

The molecular ratio SiO_2/MgO in these precipitates was calculated as follows :

$$\frac{\text{moles } SiO_2}{\text{moles } MgO} = \frac{SiO_2}{Mg^{2+} \text{ g ion equivalents}} = \frac{\text{ppm } SiO_2 \text{ uptake (g)}}{\text{ppm } Mg^{2+} \text{ (g)}} \times \frac{24}{60}$$

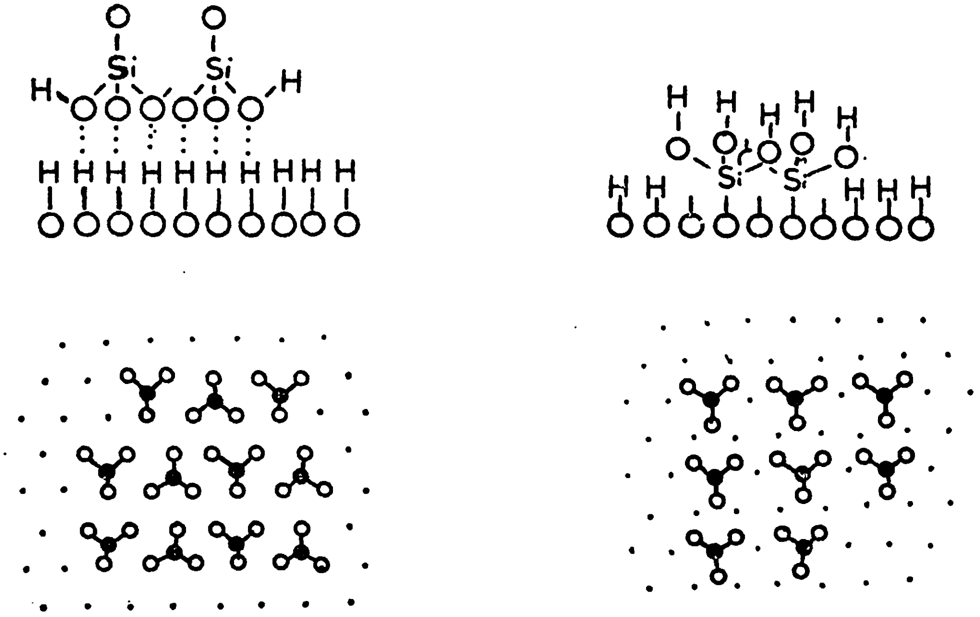
$$\text{where ppm } SiO_2 \text{ uptake} = (\text{added } SiO_2 \text{ concentration} - \text{free } SiO_2 \text{ concentration})$$

Since Mg^{2+} is virtually totally precipitated at the pH of the above experiment, and other experiments where the ratio was calculated, the amount of magnesium in the precipitates is equal to the amount added. For the above experiment the SiO_2/MgO ratio was 0.5 at saturation uptake. The variation of the SiO_2/MgO ratio with pH is given in curve 3, figure 2. In the region of maximum uptake i.e. pH 10-11, the average ratio is 0.51.

The most stable hydrogen bonded configuration should be the triple hydrogen bond adsorption, figure 7a, since, apart from having the greatest number of bonds, the lone pairs on the oxygens attached to silicon are in direct line with the O-H bonds on brucite. By covering both sides of brucite with triple bonded silicic acid the maximum SiO_2/MgO ratio is 0.67, since 2 silicon atoms will be equivalent to 6 hydroxyls on silicic acid molecules

Figure 7.

Two modes of fixation of silica on brucite.



a) b)

· OH on brucite

o O on silicons

● silicon.

and 6 hydroxyls on brucite will be equivalent to 3 magnesium atoms, giving a SiO_2/MgO ratio of 0.67. The O-O distance in brucite is 3.22 Å while the O-O distance in silicic acid is 2.55 Å. This bonding will therefore tend to cause the brucite layers to curve inwards towards the silicic acid molecules. If the surface were covered with Si-O-Mg bonds as shown in figure 7b, then the ratio would also be 0.67 since each oxygen bonded to a silicon atom would be surrounded by 6 oxygens not bonded to silicon atoms due to packing interactions of the silicic acid molecules. This means that one third of the oxygens on one side of brucite are bonded to silicon atoms giving a ratio of two thirds or 0.67 for two sides of brucite.

The ratio of 0.5 indicates that silicic acid has not only covered the outer surfaces of brucite but has penetrated into the interlayers of the crystals as well.

Both types of bonding would provide a suitable 'store' for up to a ratio of SiO_2/MgO of 0.67. This ratio gives rise to the possibility of two layer clay formation, for example the serpentine minerals which have a SiO_2/MgO ratio of 0.67/1.0. Clay formation would invalue the fixation of silica on the surface of brucite by forming extensive regions of Si-O-Mg bonding followed by the polymerisation of silica to give Si-O-Si bonds. Experiments designed to test this possibility will be described at a later point.

If reversible, or physical adsorption such as hydrogen bonding or the ionic type described above, is occurring then the results obtained from the saturation experiment should fit Freundlitch's expression for physical adsorption from solution which has the form

$$\frac{x}{m} = k\, c^{\frac{1}{n}}$$

where x and m are the masses of the substance adsorbed and the adsorbent respectively; c is the concentration of the solution when equilibrium is reached, and n is an empirical constant usually greater than unity. This equation implies that if log $^{x}/m$ is plotted against log c, a straight line will be obtained with slope $^{1}/n$. The data required for this plot, calculated from the saturation experiment results, is given in table 2 and is shown graphically in fig. 8.

The linear curve obtained indicates that a reversible adsorption process is occurring. The empirical constant, n, was found to be 5.9 and k was 0.069.

TABLE 2.

Silica adsorption on $Mg(OH)_2$ at pH 10.8.

Calculated from the saturation experiment results.

$\frac{x}{m}$	$\frac{x}{m}$	log $^x/m$	c	log c
$^{94}/100$	0.94	-0.03	6	0.78
$^{118}/100$	1.18	0.07	32	1.51
$^{130}/100$	1.30	0.11	45	1.65
$^{136}/100$	1.36	0.13	64	1.81

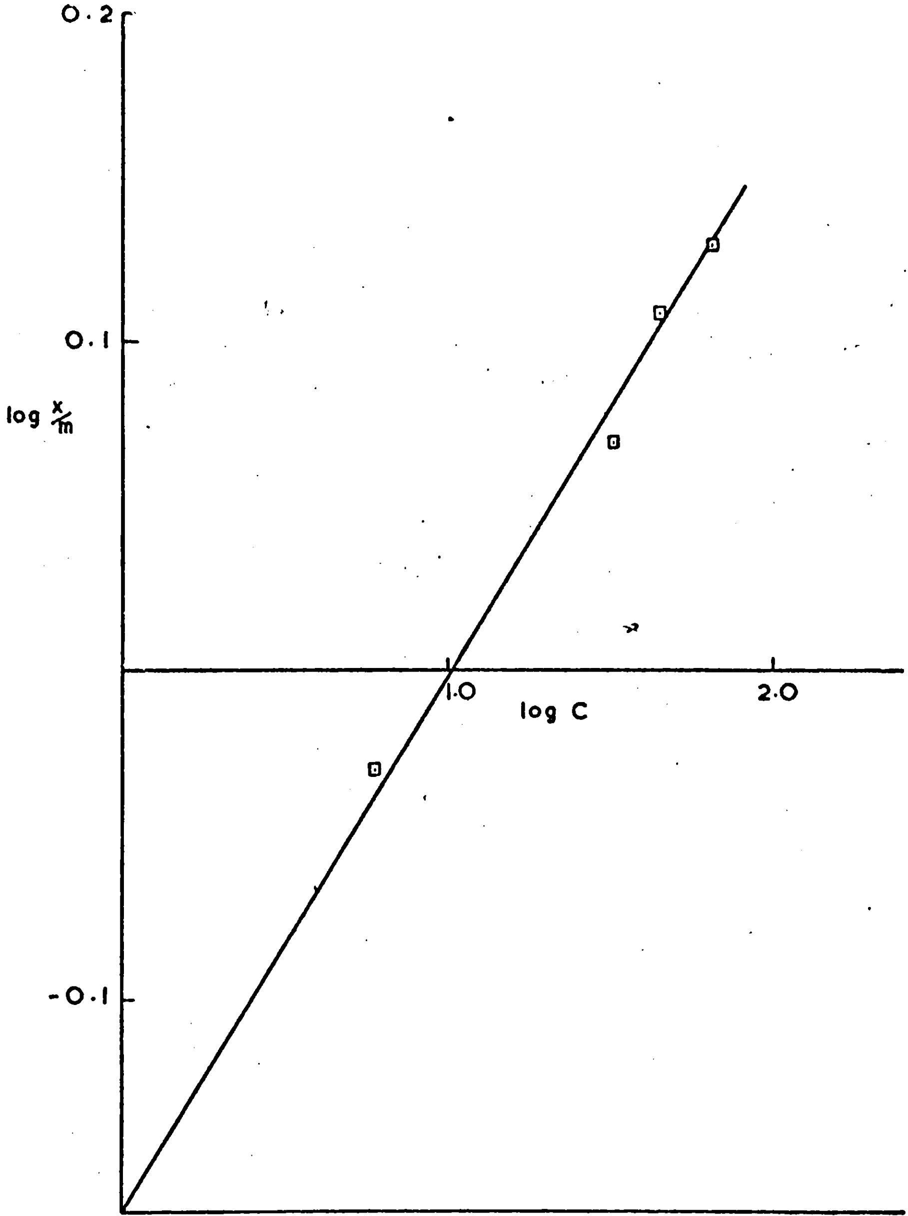


FIG.8. FREUNDLITCH'S PLOT FROM RESULTS OF SATURATION EXPERIMENT.

Ageing processes in the SiO_2/MgO precipitates.

Silica has been shown to be adsorbed onto brucite by, it is proposed, a mainly reversible adsorption process. Ageing processes, as already indicated, might involve at least three types of reaction leading to clay layer formation. The first could be the fixation of silica onto the brucite surface to form Si-O-Mg bonds. This process is shown in figure 9.

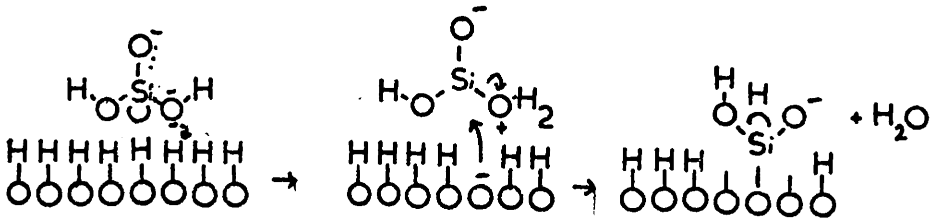


Figure 9. Postulated formation of Si-O-Mg bonds by an S_N2 type reaction.

The mechanism envisaged the transfer of a proton from the brucite to the silicic acid : this will be encouraged by the increase in negative charge on oxygen of the accepting hydroxyl group. The elimination of a water molecule and the formation of a Si-O-Mg bond may be achieved by an S_N2 type reaction. The transient + ve charge of the silicon atom will be stabilised by the partially ionic character of the Si-O-H bond (38% ionic) and the - ve charge on the molecule.

This type of bond would be formed already where singly ionised silicic acid molecules had neutralised + ve sites on the brucite surface (Figure 4).

The second process would involve the linking together of silicic acid monomers to form Si-O-Si bonds in silica tetrahedra bonded to the brucite surface. The process envisaged is shown in Figure 10.

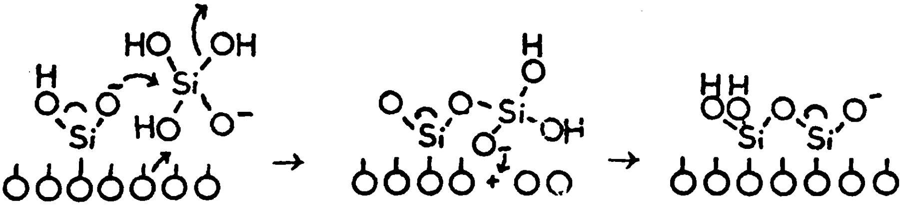
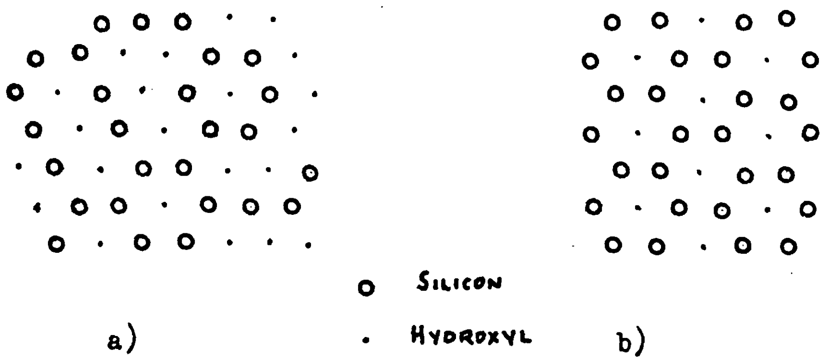


Figure 10. Postulated formation of silica tetrahedral layer.

Two silicic acid molecules polymerise initially, with one of them already bonded to the brucite surface. This linked molecule could then become bonded to the surface by filling a + ve hole. The chances of two such linked molecules leaving the surface by the reversible process outlined in Figure 4 are now much reduced. Alternatively the second molecule could become bonded to the surface by the S_N2 process shown in Figure 9. This would constitute the third process.

Packing restrictions make it virtually impossible for this second molecule to be bonded to the surface in the required position prior to polymerisation. By polymerising first this restriction no longer applies.

There appears to be no strong directing force to cause the bonding of the silica molecules in a clay like hexagonal arrangement as in Figure 11b. Random bonding to the surface will cause lines of linked silica tetrahedra to run for arbitrary lengths across the brucite surface, the only restriction being that they run at 120° to each other and no three tetrahedra can share three adjacent sites (Figure 11a).



a) b)

Figure 11. Possible structures of silica tetrahedral layer.

The structure shown in a) will have similar properties to b) such as solubility in acid but will not show the same degree of crystallinity as defined by its ability to diffract X-Rays due to the random ordering from layer to layer.

Ageing processes will have the effect of making the precipitate less soluble in acid. Experiments were conducted to determine the solubility of the products formed by the above method with time of ageing.

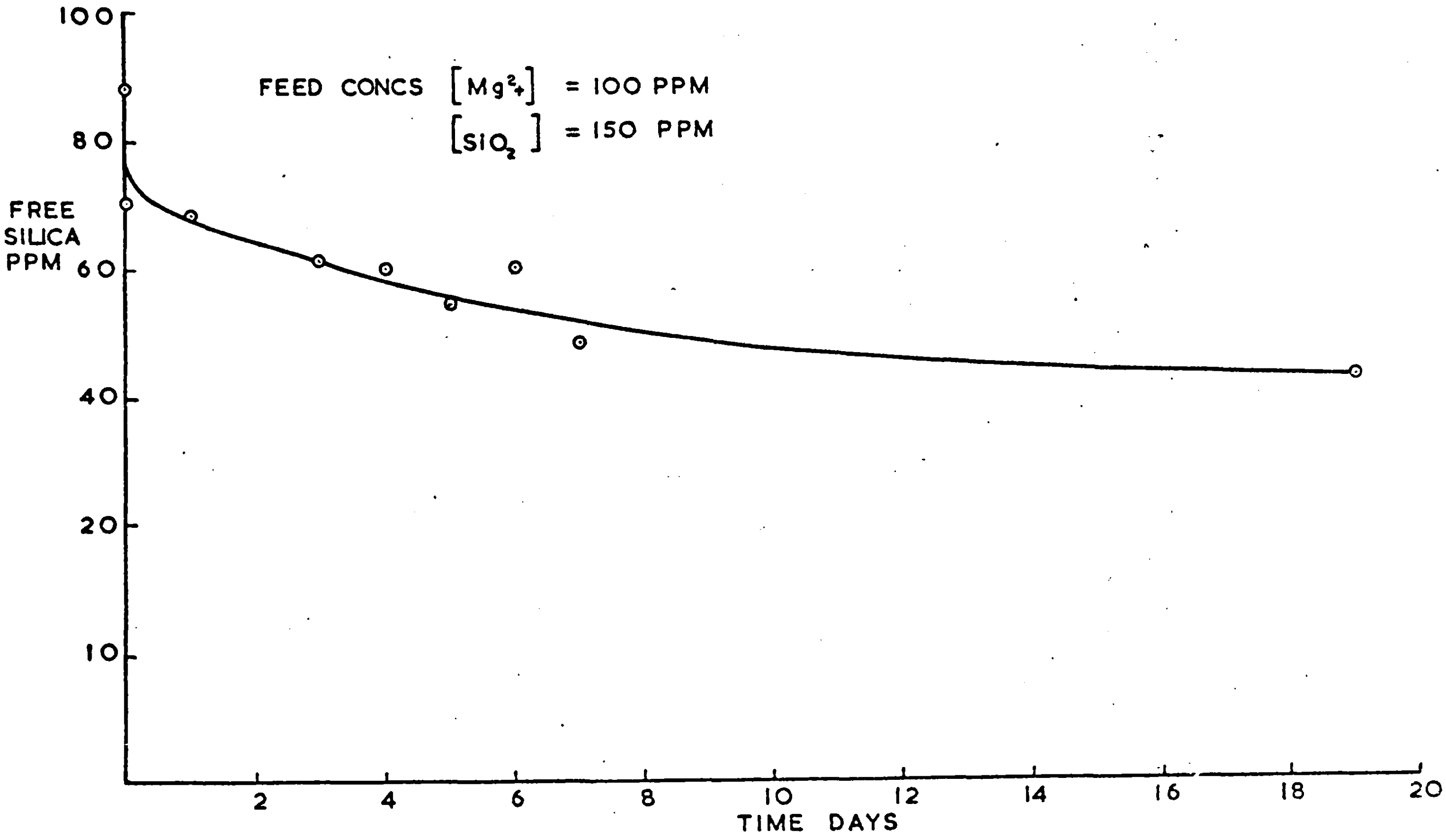
Experimental.

A 250 ml solution of Na_2SiO_3, containing 150 ppm SiO_2 and 100 ppm Mg^{2+} at pH 11.1, was magnetically stirred in a covered polythene beaker. 25 ml samples were withdrawn at intervals up to 19 days. Dilute HCl was added to give a pH of 5.2 and after allowing the solutions to equilibrate to constant pH (about one day) a sample of this solution was centrifuged and the free silica concentration determined.

Results and Discussion.

The results are shown graphically in Figure 12. The precipitate becomes increasingly insoluble in acid with time. At pH 5 $Mg(OH)_2$ would completely dissolve : if silica simply remained hydrogen bonded to brucite throughout this time, then acid treatment would release this silica by dissolving the $Mg(OH)_2$. The drop in free silica cannot be due to polymerisation since the solutions are undersaturated with respect to silica at pH 5. Silica then is becoming increasingly bound in these silicates to form more strongly bonded structures. This effect could be due to the formation of Si-O-Mg bonds from hydrogen bonded molecules or to an increase with

FIG. 12 FREE SiO_2 IN SOLUTION AGAINST TIME OF AGEING SAMPLES TREATED WITH ACID.



time of silicic acid molecules adsorbed by neutralising + ve sites on brucite with some polymerisation or a combination of both of these possibilities.

The evidence for the products ageing to the extent of clay formation will be described in Part 2.

PART 2.

Electron Microscopy study of silica magnesium precipitates.

The silica uptake experiments described in Part 1 showed that silica is adsorbed rapidly from dilute, alkaline magnesium solutions at room temperature and the subsequent ageing process makes the formation of a layer silicate possible. Attempts to detect layer silicate formation from these solutions using electron microscopy, especially electron diffraction, will be described here. For the description of the electron microscopy methods used the reader is referred to the Experimental Appendix.

Experimental.

The stock silica and magnesium solutions were prepared as in Part 1. The reaction mixtures (10 mls) were shaken in polythene vessels (15 mls) for the required time. Samples for electron microscopy were prepared by centrifuging aliquots (2 mls) in a microcentrifuge washing with distilled water and dispersing the precipitate in water prior to mounting.

Two arrays of samples were prepared with concentrations, given in Table 3, at pH 11.0.

The range of SiO_2 concentrations was chosen to investigate the effect of increasing amounts of SiO_2 on the precipitates.

TABLE 3.

Concentrations of SiO_2 and Mg^{2+} in solutions.

Mg^{2+} ppm.	SiO_2	Molecular ratio SiO_2/MgO in solution
50	0	0
50	12.3	0.1
50	245.0	2.0
50	1230.0	10.0

In one series the Mg^{2+} solution was added to the SiO_2 solution and this was called the coprecipitated series. Samples were withdrawn half an hour, three days and eight days after mixing. In the other series the Mg^{2+} solutions were allowed to age for three days at pH 11.0 before the SiO_2 solution was added, and this was termed the aged series. Samples were withdrawn immediately after the addition of SiO_2 and after eight days. A solution containing Mg^{2+} alone was sampled simultaneously with the coprecipitated series to study any changes in $Mg(OH)_2$ with time.

The time period of eight days was chosen since Figure 12 shows that the ageing process has passed its most rapid phase at this time.

Results.

A selected area diffraction pattern for the eight day $Mg(OH)_2$ alone sample gave spacings shown in Table 4. The earlier samples were similar. The spacings show good correlation with those of brucite. The comparison of intensities is not so good since the ASTM index records intensity data from X-Rays not from electron diffraction.

Table 4.

d Å	Brucite (ASTM 7-239) $Mg(OH)_2$ d Å	hkl.
2.71 m	2.73 w	100
2.37 s	2.37 v.s	101
1.58 m	1.58 m	110
1.49 s	1.49	111
1.31 m	1.31 m	201
1.01 w	1.09 w	104
0.91 m	0.91 w	300
0.89 w	0.89 w	301
0.78 w	0.78 w	220
0.77 w	-	-
0.73 w	-	-

The changes in the appearance of $Mg(OH)_2$ with time are shown in Plates 1 to 3 . In general the $Mg(OH)_2$ was composed of platelets (arrow 1, Plate 1), but in the half hour sample (Plate 1) more dense elongated shapes are seen (arrow 2), with about the same length as the diameter of the platelets : they were taken to be rolled up platelets. In time this tube like morphology disappears, probably due to the tubes unrolling, to give a more uniform plate like appearance seen in Plate 3 . The other possibility is that these elongated forms are platelets standing on edge, but since there are no intermediate forms this seems less likely.

Coprecipitated Series.

This series corresponds to the experimental conditions of Part 1. The solution with the molecular feed ratio of SiO_2/MgO = 2.0/1.0 is similar to those studied in that part.

Plates 4 to 12 show each of the ratios with time intervals of half an hour, three days and eight days.

Nearly all the precipitates proved to be amorphous to electron diffraction. Any diffractions observed were very faint or diffuse and corresponded to brucite.

With the ratio 0.1/1.0 the particles are about half the size of a brucite platelet and have a rougher and more crumpled texture. Other areas as shown in the eight day sample appear to be largely unaffected by SiO_2.

Increasing the SiO_2 ratio to 2.0/1.0 gave a more widespread decrease in size with the same roughening and crimping of the brucite platelets.

After eight days the 10.0/1.0 ratio samples showed about the same particle sizes as the 2.0/1.0 run. Plate 12 shows these particles held together by thick strands of material (arrowed). This lace like morphology is due to excess SiO_2 remaining after washing and polymerises during the drying down stage of sample preparation.

The general decrease in particle size with increasing SiO_2 concentration can be attributed to the fact that as soon as brucite crystallises out of solution it will be prevented from growing any larger by the adsorption of silicic acid. Also the distortion of the brucite platelets by this adsorption producing crumpled forms will reduce the overall size.

The aged series.

The effects of silica added to three day old brucite are shown in Plates 13 to 18.

The diffraction data for these samples is given in Table 5. The spacings correlate with those of brucite.

The 0.1/1.0 ratio shows $Mg(OH)_2$ hardly affected by SiO_2. The 2.0/1.0 specimens show crumpled platelets while the 10.0/1.0 ratio shows the lace like appearance due to the excess of silica added. No detectable changes can be observed with ageing, from electron diffraction.

TABLE 5.

Brucite dÅ	SiO_2/MgO 0.1/1.0 Time 8 days Plate 14 dÅ	2.0/1.0 8 days Plate 16 dÅ	10.0/1.0 3 days Plate 18 dÅ
2.71	2.68	2.69	
2.37	2.41	2.38	2.39
1.58	1.58	1.59	1.58
1.31	1.31	1.30	-
1.01	1.01	-	-
0.91	-	-	-
0.89	-	-	-
0.78	-	-	-
0.77	-	-	-
0.73	-	-	-

Conclusions.

The coprecipitated series gave mainly amorphous material, corresponding to the conditions of the uptake experiments. The ageing experiments showed that these products became more insoluble with time : this amorphous material could then correspond to the type of ageing described in Figure 10, that is the formation of X-O-X bonds where X is either Si or Mg, to the extent shown in

Figure 10 or even to that shown in Figure 11a. This would make the product more insoluble than $Mg(OH)_2$ but would destroy the ability of $Mg(OH)_2$ to diffract; the aged material would be insufficiently crystalline to diffract. This type of bonding would cause distortions of the brucite lattice and cause the material to have a crumpled platelet appearance.

Wey and Siffert (1961) claim to have synthesised a trioctohedral mineral, probably a montmorillonite, under similar conditions, after twelve hours of mixing. Repeated attempts here failed to produce any crystalline material with a clay like diffraction.

With the aged series the $Mg(OH)_2$ has had three days in which to improve its crystallinity which seems to enable it to retain a little of its ability to diffract even after five days in contact with a 10.0/1.0 ratio of SiO_2/MgO. A disadvantage of using aged $Mg(OH)_2$ will be that the ageing time will enable Cl^- ions to become adsorbed on + ve sites in the brucite lattice making the adsorption of SiO_2 more difficult. The adsorption which has taken place has been sufficient to give rise to a similar crumpled sheet appearance.

It was concluded that room temperature conditions were sufficient to remove silica from dilute alkaline magnesium solutions and produce distortions in the brucite platelets, but were not vigorous enough to produce a significant phase change within about one week.

It was found that by ageing the coprecipitated solutions for one month two broad clay like diffractions of 1.56 Å and 2.56 Å could be observed from X-Ray diffractinn. This indicates that prolonged ageing can produce some clay like material with regions probably corresponding to those shown in Figure 11 b.

PART 3.

Reflux of dilute silica, magnesium solutions.

It was hoped that by raising the temperature of the mother solutions from room temperature to at or near 100°C the crystallinity of the precipitates would be improved.

Experiments were carried out using glass vessels and with plastic apparatus as a check on possible contamination of the products from the glass.

Method A. Reactions in glass vessels.

Experimental.

25 ml solutions containing 150 ppm SiO_2 and 60 ppm Mg^{2+} at pH 11.2 were refluxed in Pyrex flasks fitted with water condensers. The experiments were carried out in duplicate to check for possible contamination from the flasks. A sand bath was used as a convenient heat source. 5 mls samples were withdrawn at various intervals up to ten days, centrifuged and washed trice before preparation for electron microscopy examination.

Results and Discussion.

The one day and ten day products gave a faint diffraction ring pattern which faded within ten seconds leaving only two weak rings which gave clay spacings of 2.53 Å and 1.51 Å. This is consistent with a poorly crystalline hydrated magnesium silicate which looses structural water due to the heat created in the sample by theelectron beam. Antigorite with a SiO_2/MgO ratio of 0.67/1.0 would fit fairly closely with the uptake SiO_2/MgO ratio of about 0.5/1.0 for this system.

Plates 20 to 23 show micrographs of the product one day and ten days after reflux. For comparison Plate 19 shows the appearance of the product before reflux. Before refluxing the product has a similar appearance to the room temperature precipitates described in Part 2. After refluxing for one day the appearance changes to one of highly crumpled sheets with a spikey texture shown in Plates 20 and 21 at low and high magnification respectively. This could be modelled on sheets rolled up from two or three directions to produce a criss-cross pattern of small tubes which would have a spikey texture. This is similar to a synthetic Si/Mg product made by Caillere, Oberlin and Henin (1954) which they described as having an 'aspect d'asterisque'.

It was thought that the morphology of these products might be considerably affected during the drying down stage of specimen preparation and Si specimens were prepared using an aerosol spray technique. This technique atomises the sample so that the specimen is deposited onto the sample grid practically free of water. It was found that drying down effects are negligible with these samples.

After ten days the product shows finger like protrusions in Plates 22 and 23. An explanation of this morphology is given in Method B.

Conclusions.

It was concluded that these conditions give poorly crystalline hydrated magnesium silicates with antigorite as the likely product.

Prolonged refluxing of the mother solutions was considered to improve the crystallinity of the products but this would cause dissolution of the glass vessel and uncertainty with regard to the silica content of the solutions. This problem will be discussed in Chapter III.

Method B. Reactions in plastic vessels.

To eliminate the possibility of contamination from glass vessels used in Method A, the experiments were repeated using plastic vessels.

Experimental.

High density polythene vessels of 15 mls capacity were used in this method. These vessels were not supplied with matching water condensers and so rubber seals were used. The sealed vessels were secured in a metal sheet which acted as a cover for a steam chest. The metal sheet was moved backwards and forwards by mechanical links to an electric motor to agitate the samples. Samples with SiO_2/MgO feed ratios varying from 0.2/1.0 to 4.0/1.0 at pH 11.2 were treated at steam temperatures, 95°C - 100°C, for ten days and samples prepared for electron microscopy in the usual way.

Results and Discussion.

Samples with ratios of SiO_2/MgO up to and including 0.6 were amorphous to electron diffraction. The SiO_2/MgO ratio of 1.0/1.0 gave lattice spacings compared with those of antigorite as shown in Table 6. (Brindley, 1951)

TABLE 6.

Antigorite d Å	SiO_2/MgO = 1.0/1.0 d Å
7.16	-
4.66	-
3.96	-
3.59	-
3.48	3.48
2.80	2.78
2.52	2.56
2.40	2.36
2.15	-
1.99	1.98
1.85	-
1.81	-
1.72	-
1.70	1.69
1.56	-
1.54	-
1.53	-
1.51	-
1.48	1.49

With an excess of silica SiO_2/MgO = 4.0/1.0 similar but very diffuse diffractions were obtained.

The change in morphology with increasing SiO_2 present in solution is shown in Plates 24 to 29. Up to a ratio of 0.6/1.0 the products have a folded and crumpled sheet appearance.

The higher ratios 1.0/1.0 and 4.0/1.0 have a similar 'finger' like appearance to products made by Method A (Plates 22 and 23).

The folded and tubular appearance will arise from the known misfit of the tetrahedral silica layer and the octahedral brucite layer. The dimensions of the octahedral layer are too great for a perfect superposition of the tetrahedral layer so that any attempt to fit two such layers together will cause the structure to curve (Figure13). Chrysotile has a fibrous appearance which could have developed from structures such as these. Indeed a fibrous like antigorite exists called picrolite which is taken to be a transitional stage to chrysotile.

Chrysotile fibres are made up of spiral and concentric tubes, the diameter of the smallest tubes being about 100Å.

High magnification of material in Plate 28 shows 'finger' like structures in more detal (Plate 29). Measurements from this micrograph gives values of approximately 90Å dimensions measured from the dark centre line of the finger (arrow(1)) to the outside. The finger like appearance could be explained in the following way.

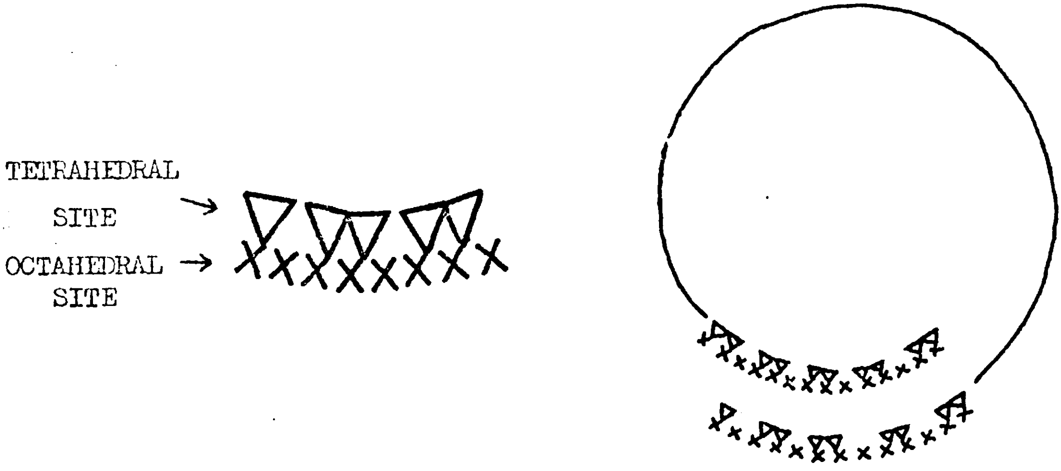
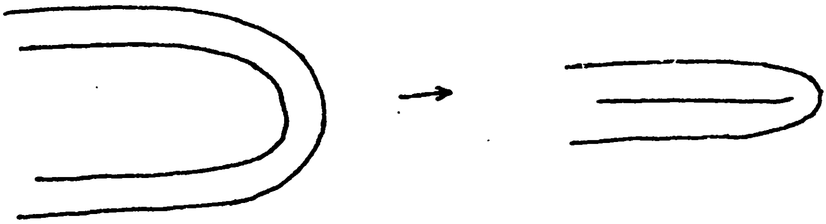
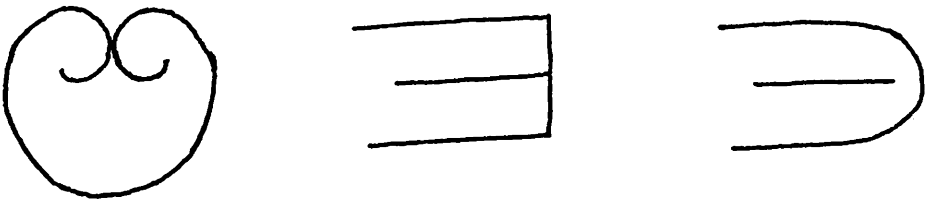


Figure 13. Curved and tubular structures due to misfit of tetrahedral silica layer and octahedral brucite layer.



a) tube folding back on itself.



i) cross section

ii) perpendicular to the electron beam

iii) slightly tilted to electron beam

Figure 14. Folding of sheet structures to give symmetrical finger.

The symmetrical form of the fingers is best explained by tubes folding back on themselves as in a) Figure 14. Highly crystalline chrysotile does not show this morphology but has two or three concentric tubes which will hinder this folding. The above tubes are about one layer thick and not so crystalline and so folding will be more likely. Scheme b) Figure 10 would also give rise to symmetrical finger formation but consistent symmetrical curling is rather unlikely to occur as frequently as is observed. A high magnification micrograph of the SiO_2/MgO ratio 4.0/1.0 product shows the finger like protrusions (arrow (2)).

The more random darker lines may be due to creases in the sheets or by folding effects shown in Figure 15.

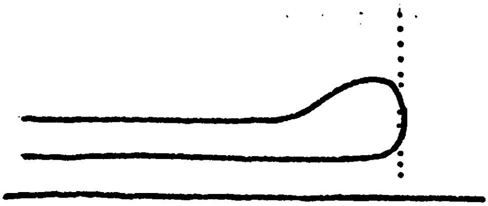


Figure 15.

Conclusions.

It was concluded that equimolar alkaline solutions, pH 11.2, of silica and magnesium produce clay like material analogous to antigonites and chrysotile with a greater degree of crystallinity when treated at or near 100°C.

Part 4.

Additional techniques in the study of silica magnesium solutions.

A) Alternating alkali and acid conditions.

Although clay like material was not detected in experiments conducted at room temperatures it was thought that due to the ageing process found in Part 1, very small quantities of clay material could be formed together with amorphous material. By neutralising the alkali solution the amorphous material could be dissolved leaving the more insoluble material, which could be clay like, to act as nuclei for further growth when the solution was replenished with silica and magnesium and made alkaline again.

A solution containing 150 ppm SiO_2 and 100 ppm Mg^{2+} at pH 11.1 was agitated for one day and then neutralised with HCl. The bulk of the precipitate was dissolved in this way, the remainder was centrifuged down and a small sample prepared for electron microscopy. The precipitate was then dispersed in water, the solution replenished with SiO_2 and Mg^{2+} and the pH adjusted to 11.1. This daily cycle was repeated six times but the material examined remained amorphous to electron diffraction. A weekly cycle, which allowed a longer ageing process, performed for one month gave the same result.

It was concluded that any clay formed would be poorly crystalline and not capable of acting as efficient nuclei. (Assuming that clay can act as nuclei for growth). Another drawback was that the precipitation process on making the solution alkaline would probably entrain clay nuclei with $Mg(OH)_2$ which would restrict the supply of silica to the nuclei.

B) pH gradients.

Systems were devised to provide mediums which would support pH gradients to further attempts at producing clays at room temperature from dilute solutions.

By slowly siphoning an alkaline solution of sodium metasilicate to the bottom of a beaker containing 3 litres of acidic magnesium chloride containing Universal Indicator an alkaline silica rich pool was created with a very sharp pH gradient at the interface of the two solutions. Precipitates formed in this system however were found to be amorphous.

To produce a more even gradient trial experiments were carried out with solid support such as alumina, acid washed sand and powdered cellulose. The latter proved to be the most satisfactory.

A glass trough was filled with a cellulose paste to depth of 15 cms, and tubes inserted to a depth of 5 cms into the bed at regular intervals along its length. Solutions of pH ranging from 2 to 13 were poured into the tubes and the levels maintained by siphoning arrangements, the excess surface liquid being withdrawn by suction. Universal Indicator added to the bed in trials showed that about a week was required to establish a stable gradient. Neutral mixtures of dilute magnesium and silica solutions were injected into the medium. After two weeks plugs of the medium were taken, the fluid and any precipitates washed out by dispersing the plugs in water and passing them down columns with cotton wool filters. Any precipitates formed were found to be amorphous up to four weeks of sampling after which the support medium became unstable.

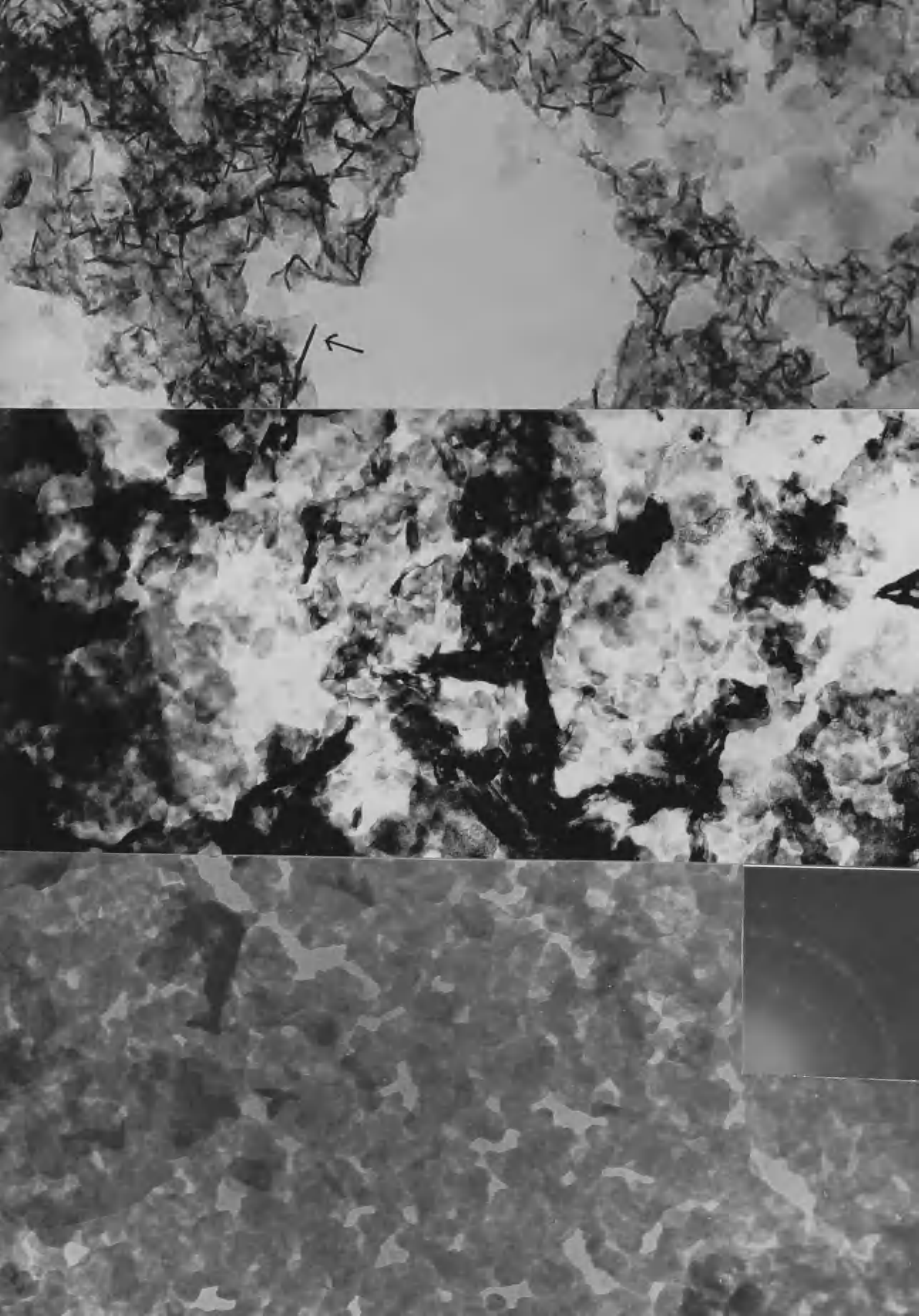
A similar technique on a smaller scale using agar gels as the support medium also gave unsatisfactory results and so further development of these systems was not undertaken.

Plate 1. $Mg(OH)_2$ after half an hour Mag. x 60K

Shows plate-like morphology.
Arrows indicate possible tube like
form of rolled up plates.

Plate 2. $Mg(OH)_2$ after three days Mag. x 60K

Plate 3. $Mg(OH)_2$ after eight days Mag. x 60K



SiO_2/MgO Coprecipitates $SiO_2/MgO = 0.1/1.0$

Plate 4. Half an hour Mag. x 60K

Shows platelets with curled edges.

Plate 5. Three days Mag. x 60K

Plate 6. Eight days Mag. x 60K

SiO_2/MgO Coprecipitates

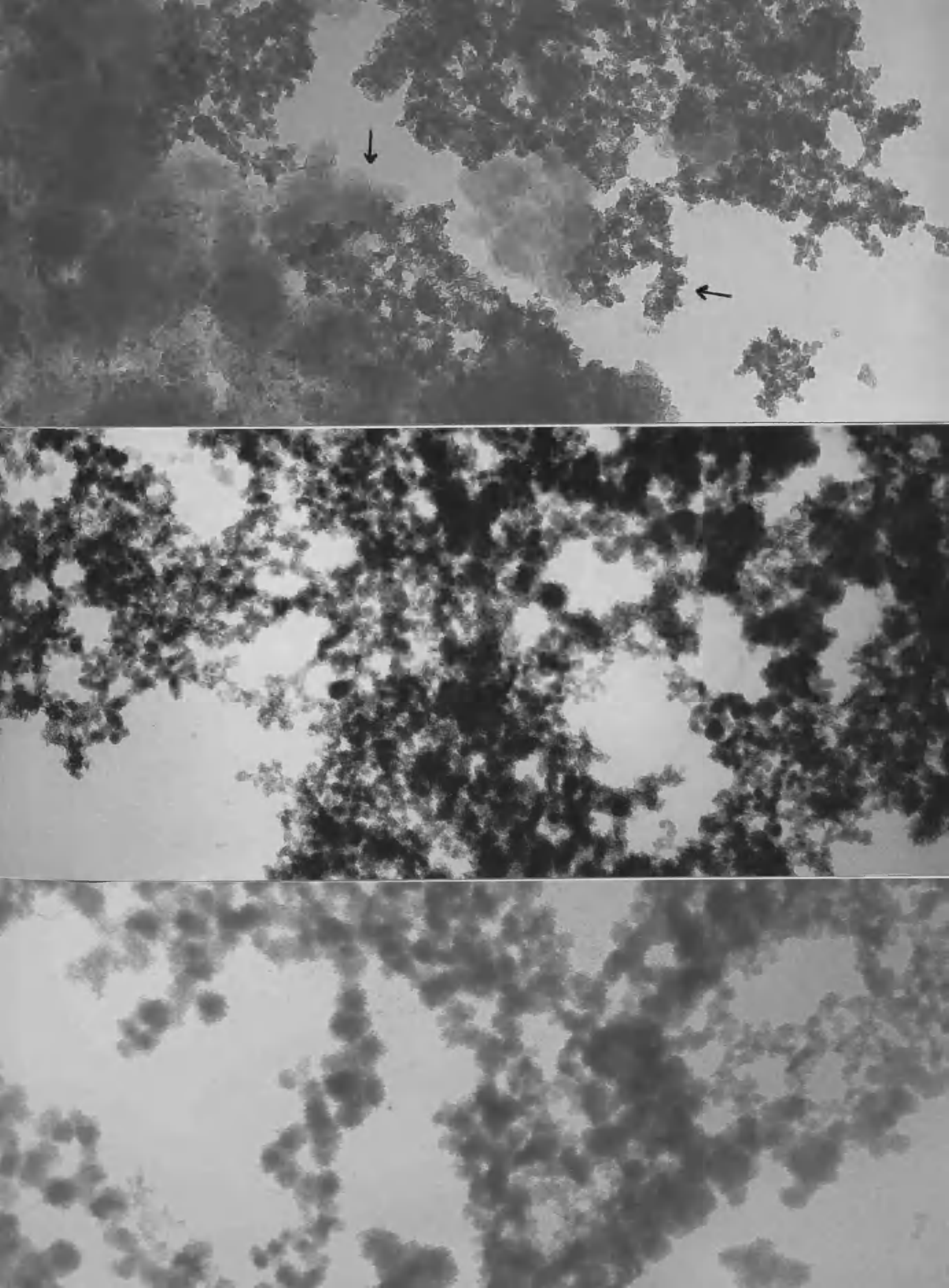
$SiO_2/MgO = 2.0/1.0$

Plate 7. Half an hour Mag. x 60K

Arrows show plates with curled edges.

Plate 8. Three days Mag. x 60K

Plate 9. Eight days Mag. x 60K



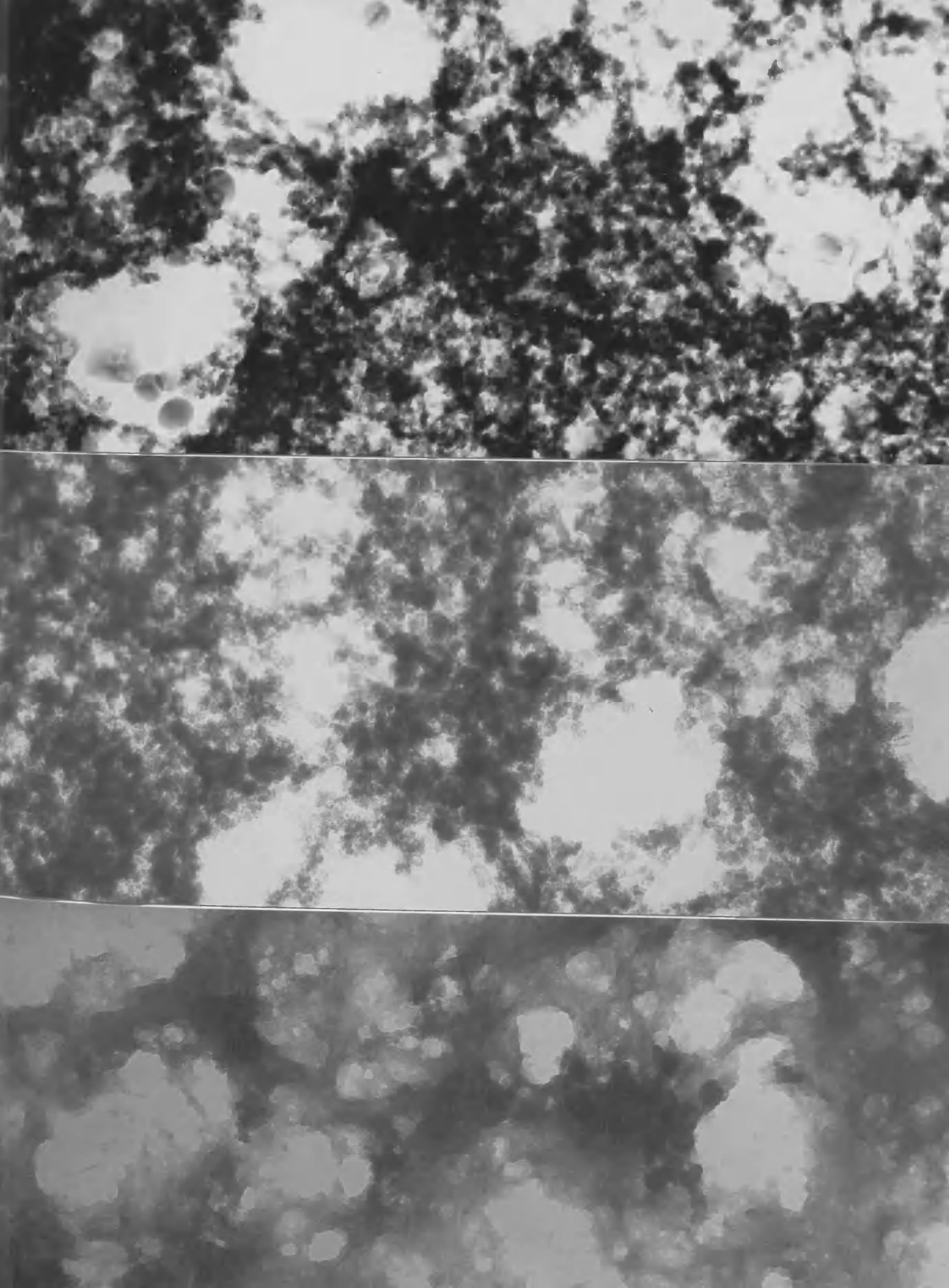
SiO_2/MgO Coprecipitates

$SiO_2/MgO = 10.0/1.0$

Plate 10. Half an hour Mag. x 60K

Plate 11. Three days Mag. x 60K

Plate 12. Eight days Mag. x 60K



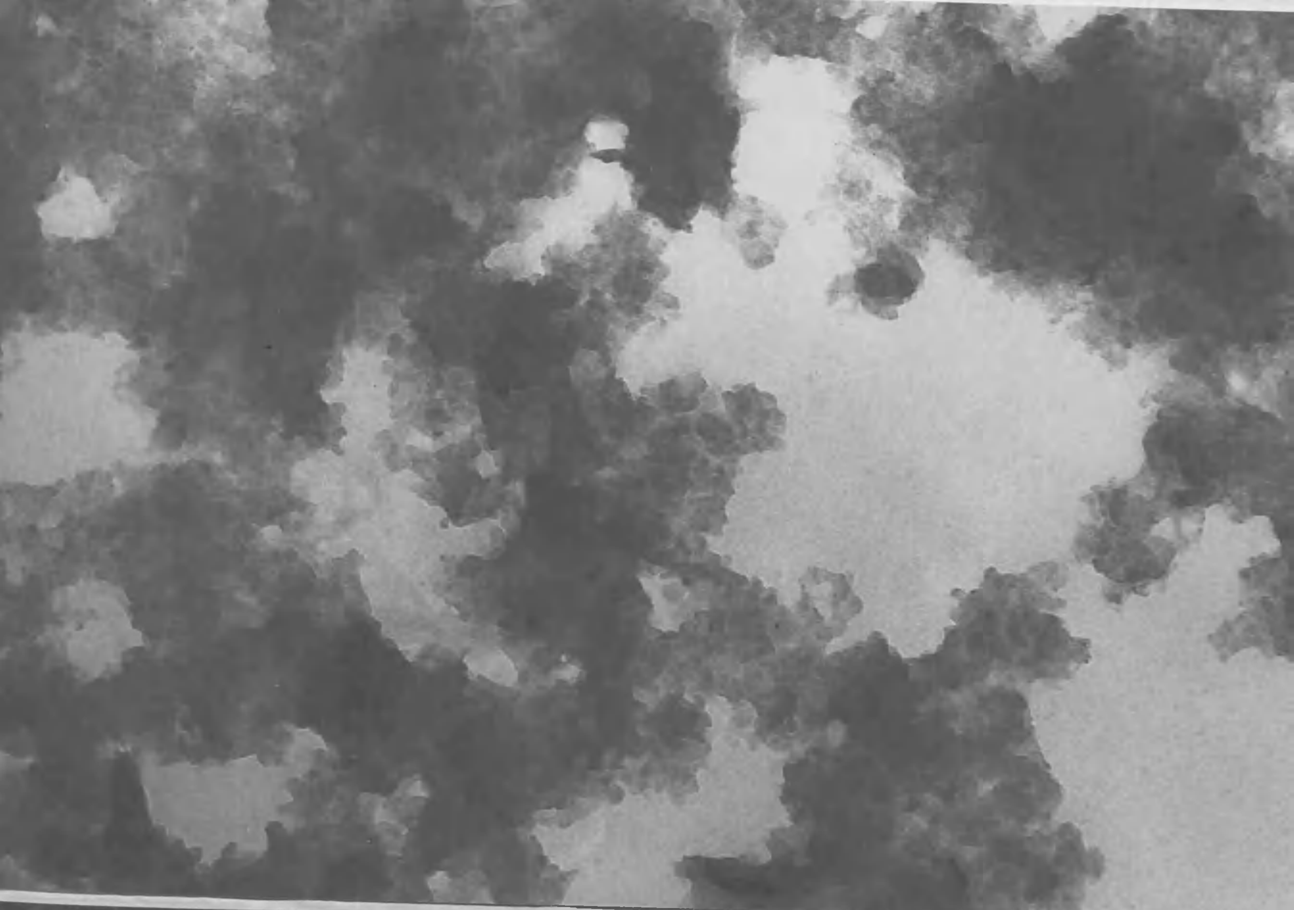
SiO_2 added to three day old $Mg(OH)_2$

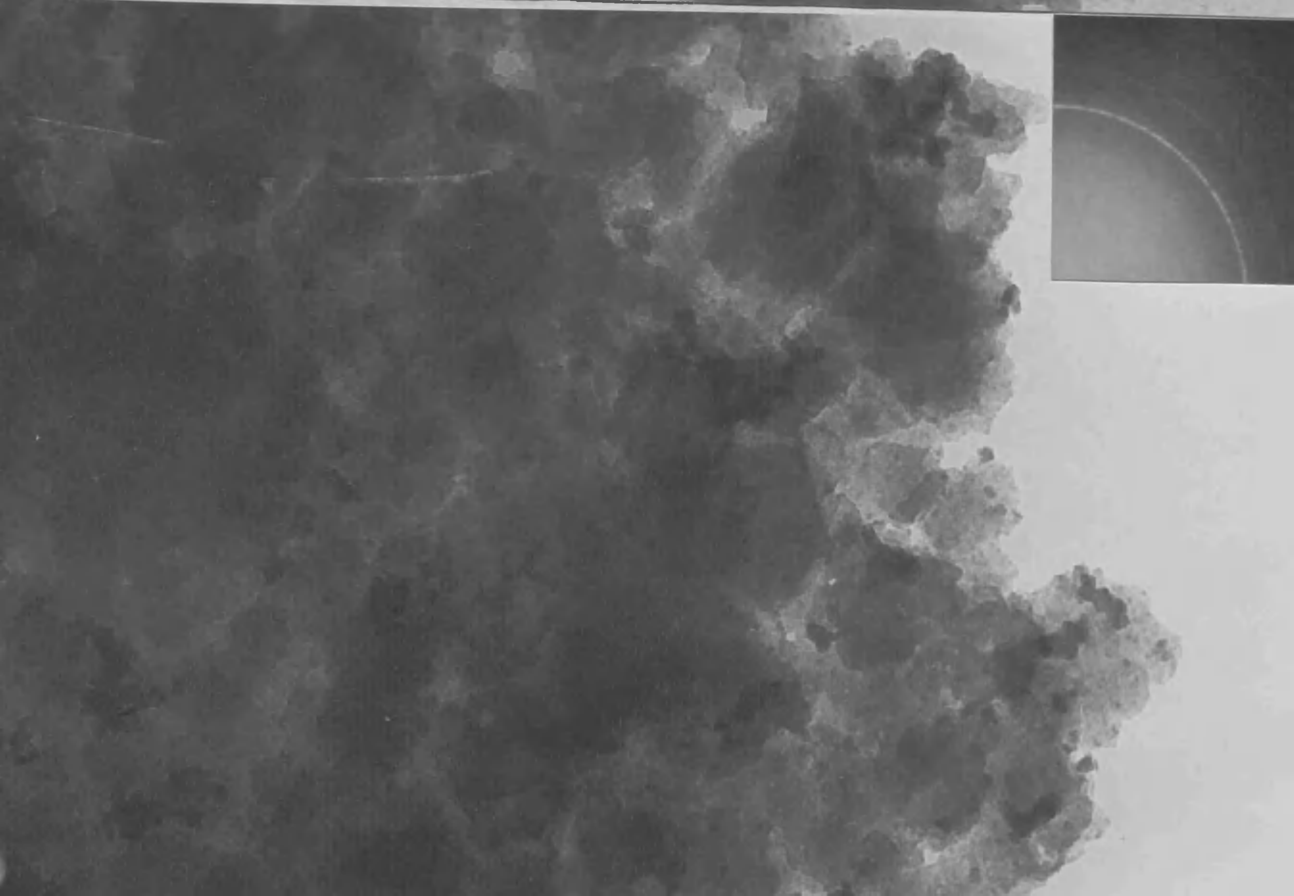
$SiO_2/MgO = 0.1/1.0$

Plate 13. Three days Mag. x 60K

Brucite hardly affected by silica.

Plate 14. Eight days Mag. x 60K





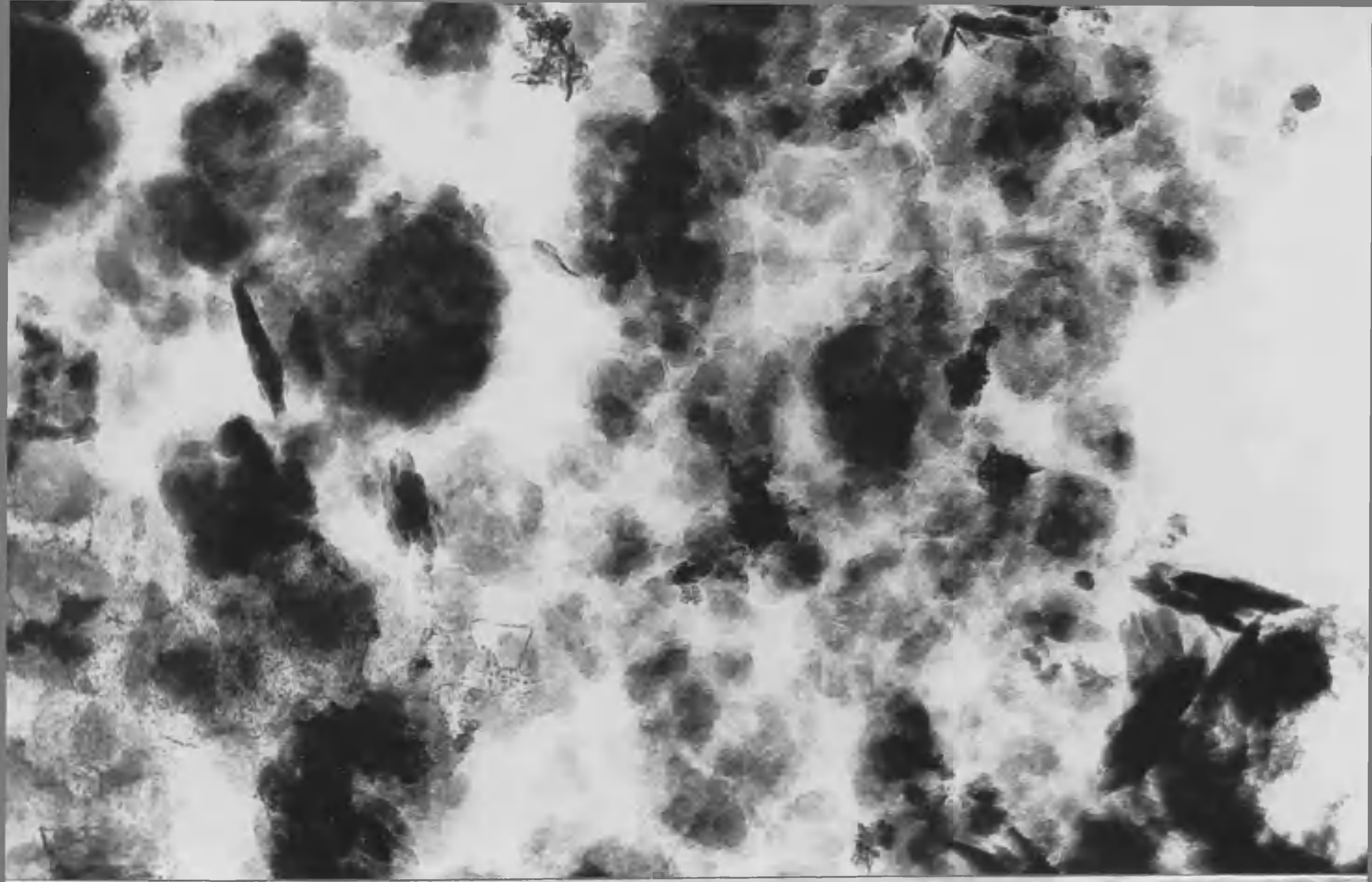
SiO_2 added to three day old $Mg(OH)_2$

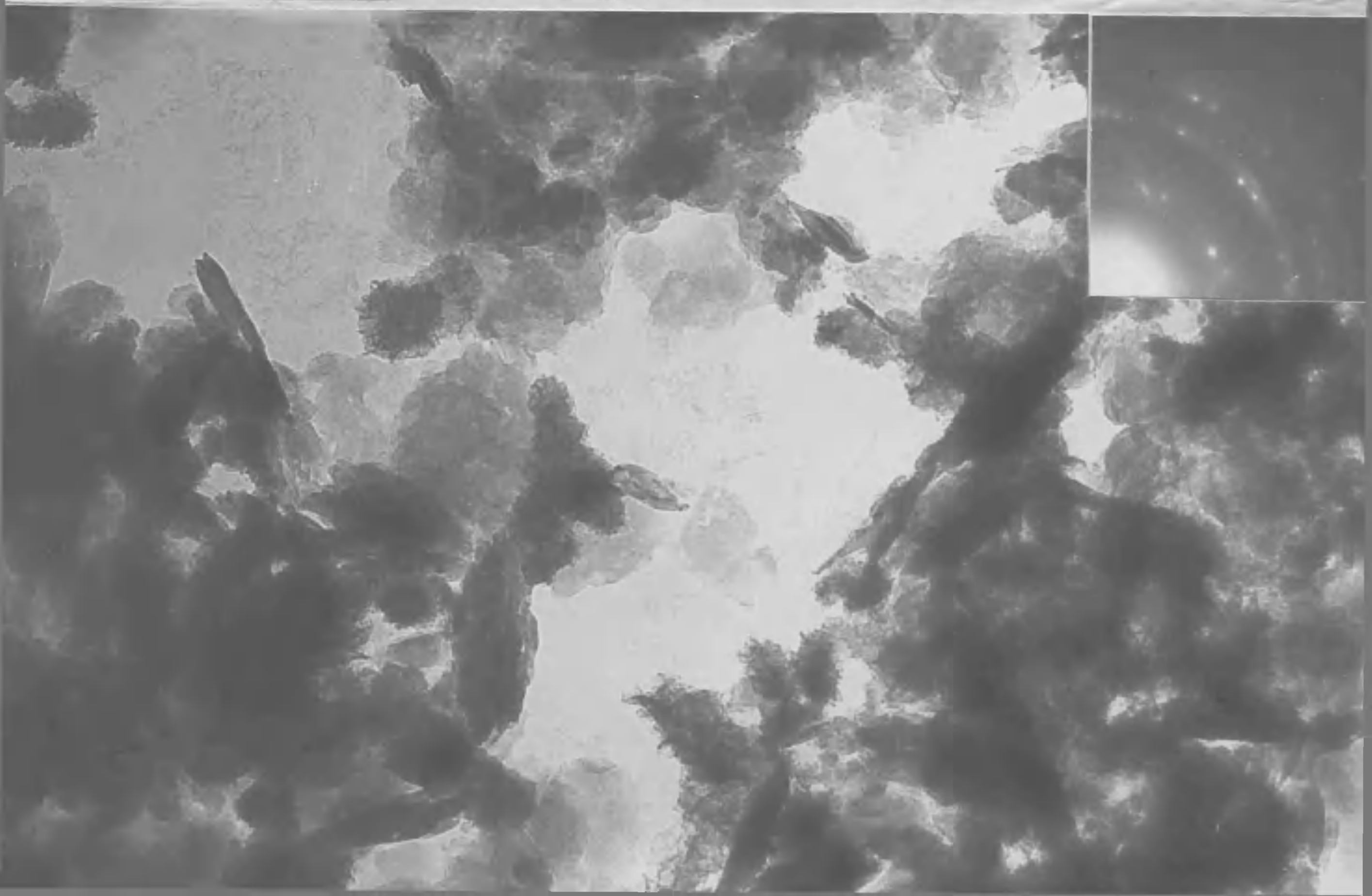
$SiO_2/MgO = 2.0/1.0$

Plate 15. Three days Mag. x 60K

Plate 16. Eight days Mag. x 60K

Platelets show greater degree of attack by silica.





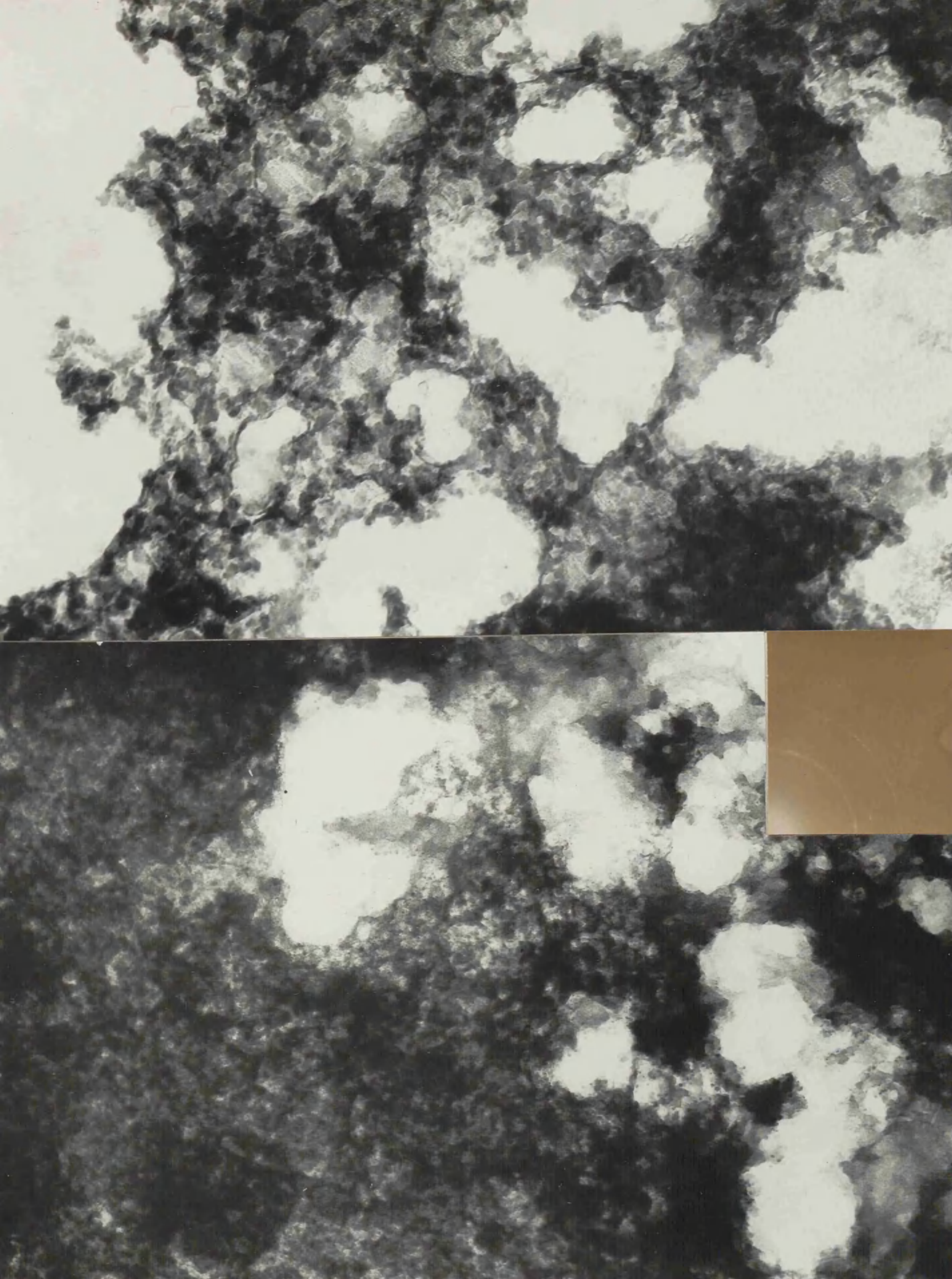
SiO_2 added to three day old $Mg(OH)_2$

$SiO_2/MgO = 10.0/1.0$

Plate 17. Three days Mag. x 60K

Webb-like structure due possibly to excess silica polymerising.

Plate 18. Eight days Mag. x 60K



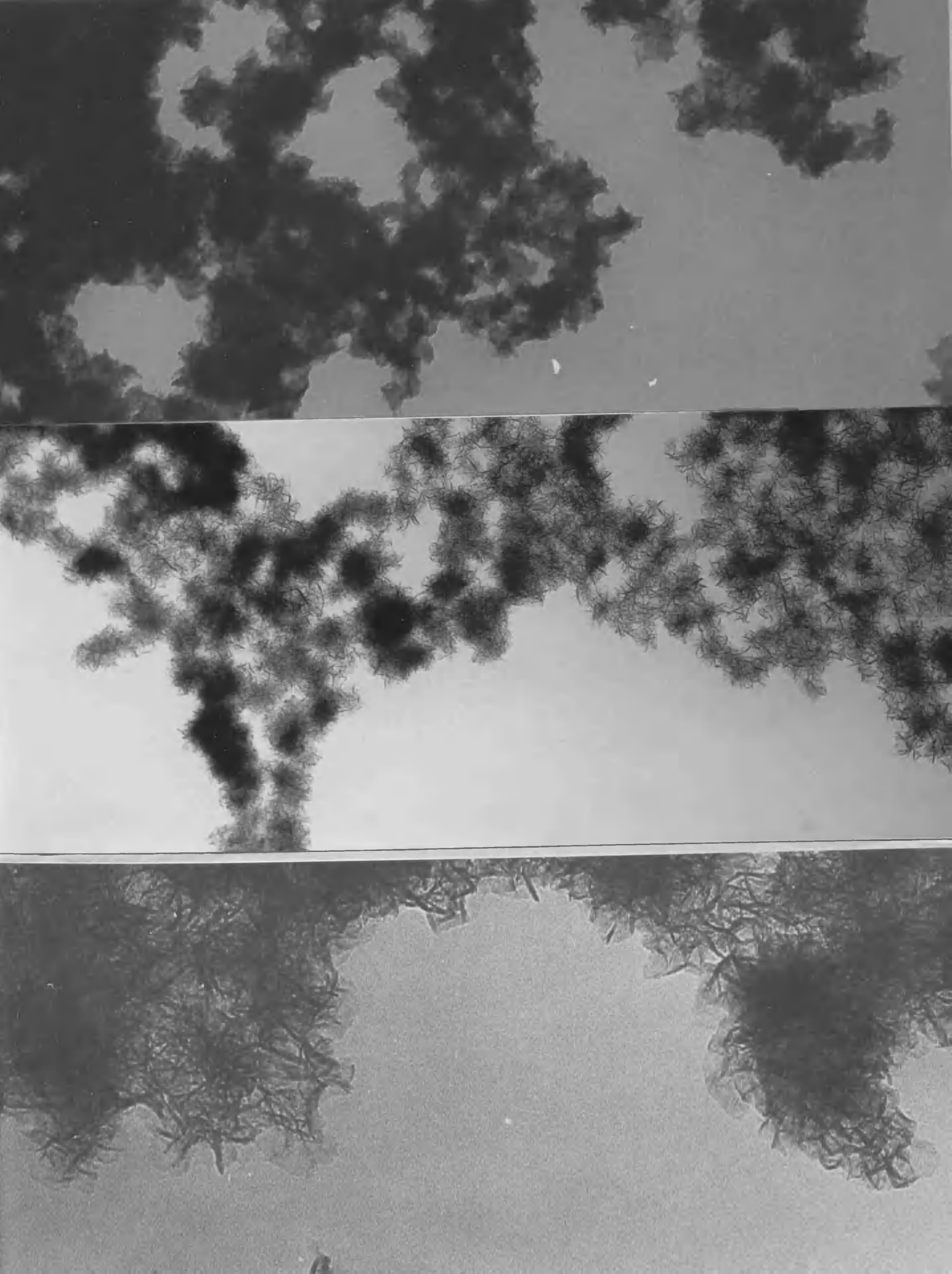
Reflux of SiO_2/MgO solutions in glass vessels

Plate 19. Before reflux Mag. x 60K

Plate 20. One day Mag. x 60K

Shows 'spikey' morphology.

Plate 21. One day Mag. x 160K

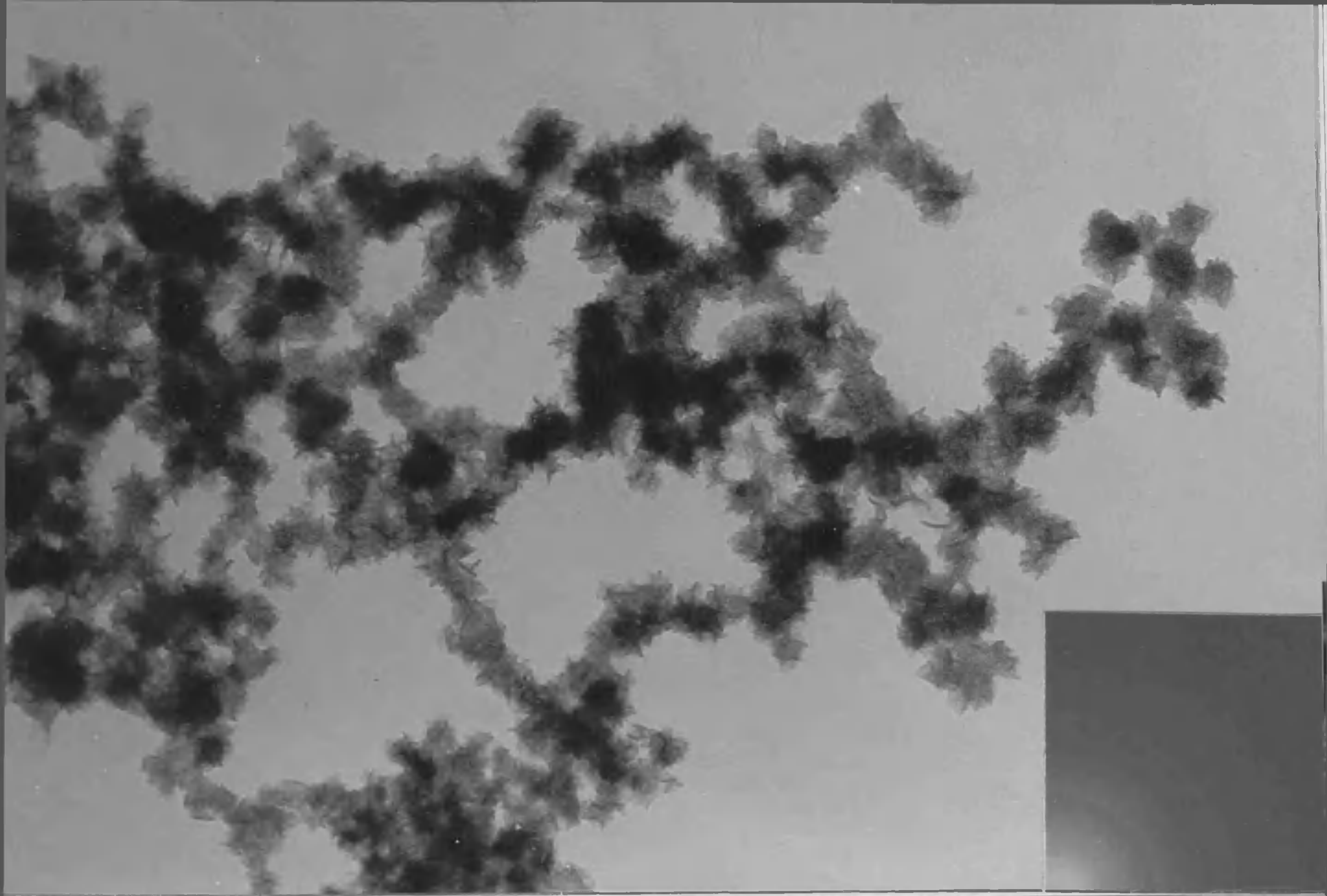


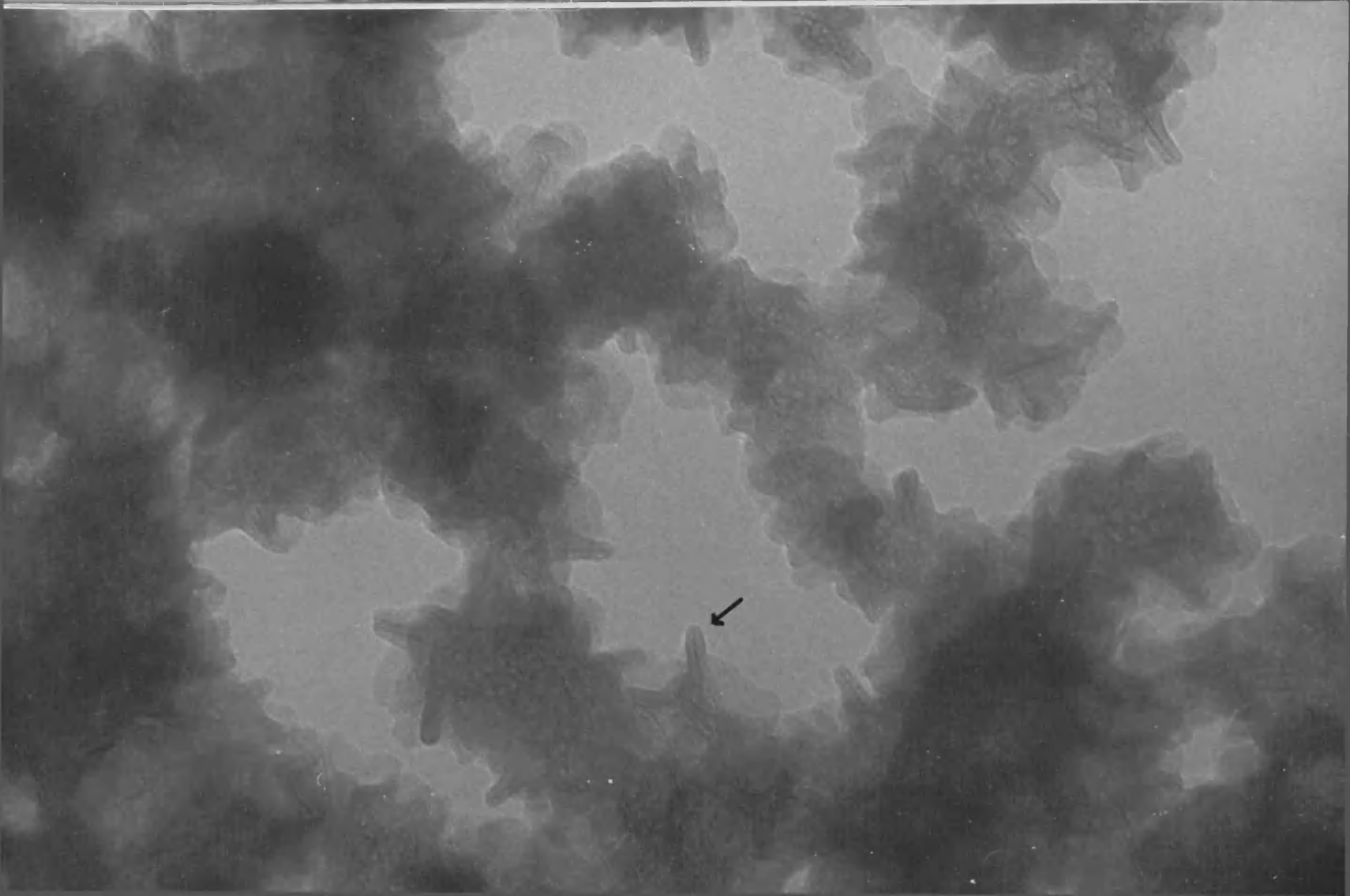
Reflux of SiO_2/MgO solutions in glass vessels

Plate 22. Ten days (aerosol sprayed) Mag. x 60K

Plate 23. Ten days Mag. x 160K

Shows 'finger' morphology.



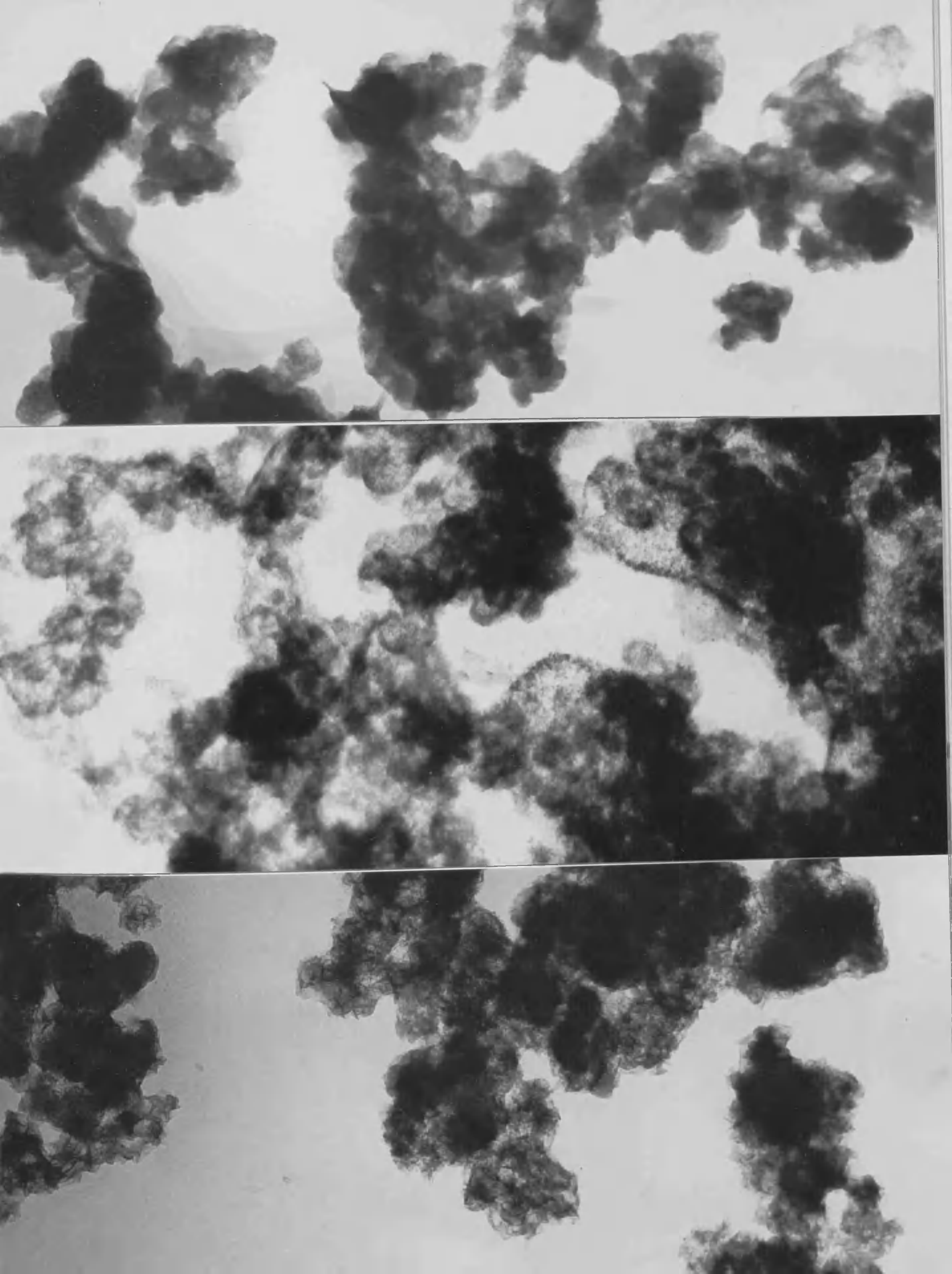


SiO_2/MgO solutions heated in plastic vessels

Plate 24. $SiO_2/MgO = 0.2/1.0$ Mag. x 60K

Plate 25. $SiO_2/MgO = 0.4/1.0$ Mag. x 60K

Plate 26. $SiO_2/MgO = 0.6/1.0$ Mag. x 60K



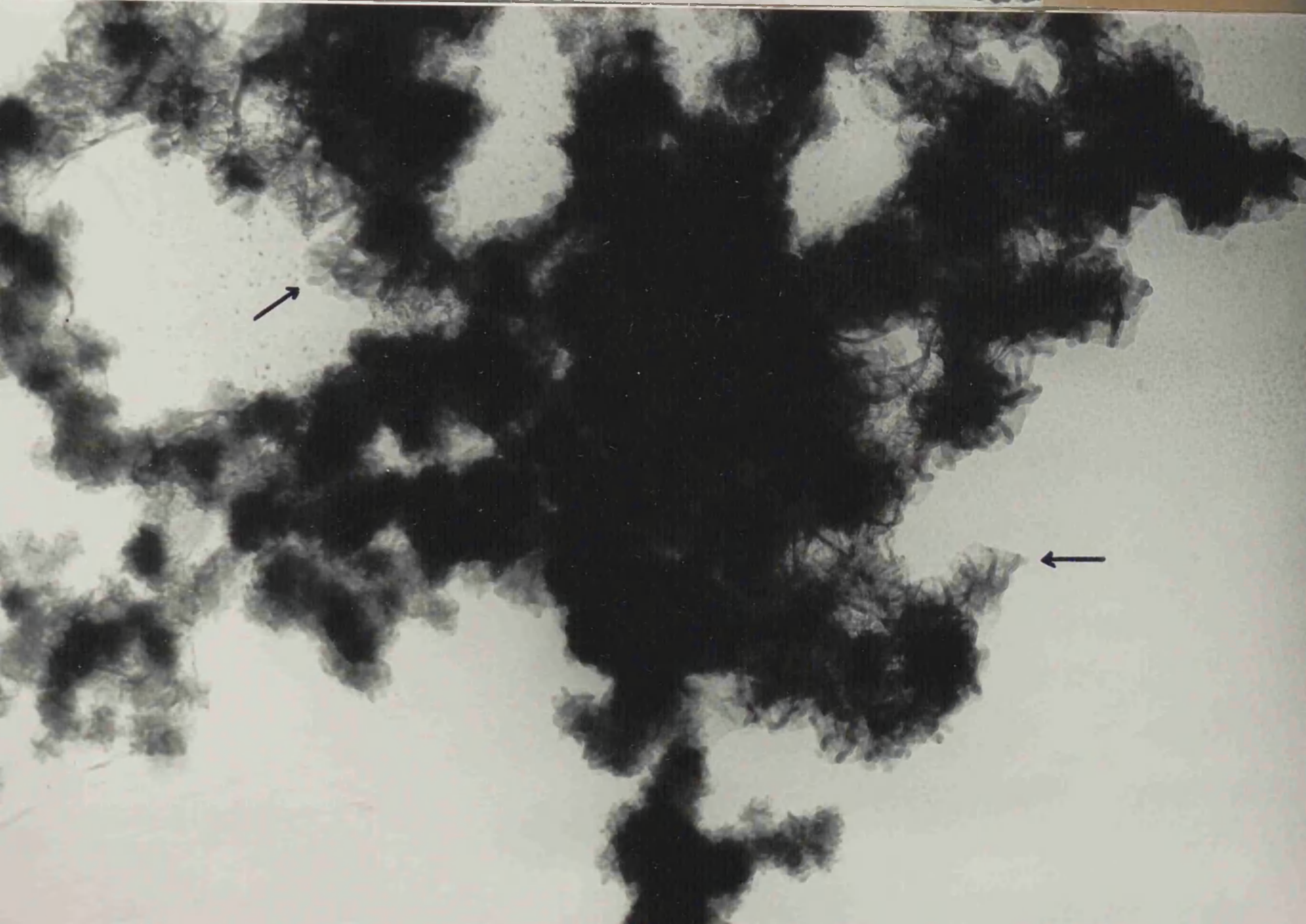
SiO_2/MgO solutions heated in plastic vessels

Plate 27. $SiO_2/MgO = 1.0/1.0$ Mag. x 60K

Shows appearance of finger shapes.

Plate 28. $SiO_2/MgO = 4.0/1.0$ Mag. x 60K

Again finger like material is present.



SiO_2/MgO solutions heated in plastic vessels

Plate 29. $SiO_2/MgO = 4.0/1.0.$ Mag. x 120KX

High magnification of fingers.

PLATE II.

[illegible]

CHAPTER II.

Dilute solution studies on the SiO_2/Al^{3+} system.

Studies were conducted on the silica uptake from dilute solutions of aluminium at pH 8.5, with magnesium and aluminium present in one series.

The possibilities of (Si, Al) clays being formed at reflux temperatures and at 80°C in the presence of organic compounds and inorganic salts were also investigated.

PART 1.

Silica uptake from dilute magnesium and aluminium solutions at 25°C.

Introduction.

Wey and Siffert (1961) have studied the uptake of SiO_2 from dilute solutions of Al^{3+} at various pHs and found that maximum uptake occurred between pH 8 and 10. Their solutions contained about 150 ppm SiO_2 and 40 ppm Al^{3+}. The following experiments were carried out in the region of pH 8.5 with more dilute solutions i.e. SiO_2 contents up to 30 ppm and Al^{3+} up to 30 ppm.

Experimental.

The stock solutions of silica and magnesium were prepared as described in Part 1, Chapter I. The aluminium solutions were prepared from aluminium sulphate, $Al_2(SO_4)_3.17H_2O$, Analor reagent quality supplied by British Drug Houses Ltd. Normally a stock solution containing 1000 ppm Al^{3+} was made for use in these experiments.

The cation solutions were added to the silica solutions and the pH adjusted with HCl or NaOH using glass electrodes to record the pH. The pH of the solutions was stabilised during the silica uptake experiments with a barbiturate buffer made from diethylbarbituric acid and its sodium salt.

The free silica concentration was determined as described in Part 1 of Chapter I.

SiO_2 uptake experiments.

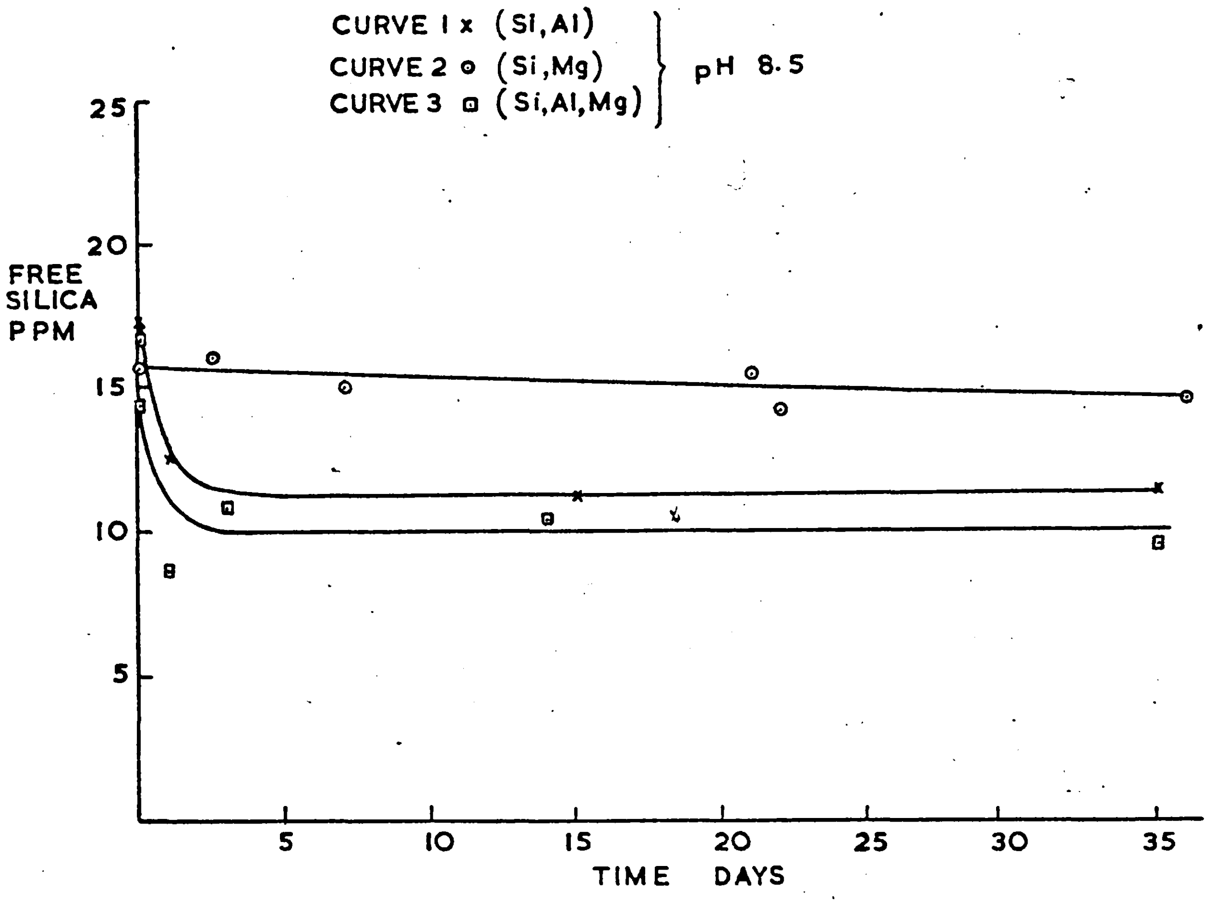
100 ml solutions were made up using the barbiturate buffer as solvent containing 18 ppm SiO_2 and 7.2 ppm aluminium at Al^{3+}, giving a SiO_2/Al_2O_3 ratio of 2.2.

Duplicate mixtures were shaken in polythene containers for about one month and samples withdrawn at various intervals to determine the free silica concentration, and the average of the two results used to plot the curves.

Results and Discussion.

The results are shown in Curve 1 (Figure 1). The free SiO_2 content falls to about 13 ppm after one day and to about 11 ppm after 35 days. It was generally found that the silica level fell

FIG. 1. FREE SILICA CONCENTRATIONS IN SiO/Al^{3+} SOLUTIONS



more slowly compared with the magnesium experiments to give a more colloidal solution. Indeed the 35 day precipitate proved to be amorphous to electron diffraction. Under these conditions the trihydrate of alumina, bayerite, $Al(OH)_3$, or $Al_2O_3.3H_2O$, would be expected to be present.

Experiments with Mg^{2+} present.

The reactions were repeated in the presence of 8.5 ppm Mg^{2+}. The silica uptake shown in Curve 3 (Figure 1) is slightly greater compared with (Si, Al) alone. A parallel run, Curve 2, with (Si, Mg) alone showed virtually no uptake.

The increased uptake was not considered large enough to propose any distinct cooperative effect although some form of mixed oxide lattice of aluminium and magnesium could be formed similar to that in octohedral layers of smectites which would enhance silica uptake. The products however were again found to be amorphous.

It was proposed to study the (Si, Al) system alone at higher temperatures with the possibility of increasing crystallinity of any products formed.

PART 2.

Reflux of dilute silica, aluminium solutions.

Large volumes of dilute solutions were used to provide larger yields of precipitates. It was proposed to add the Al^{3+} solution slowly to prevent the precipitations of boehmite, AlO(OH) and gel formation with random Si-O-Al, Al-O-Al bond formation. It was hoped to synthesise clay like products purely from solution, rather than through an intermediate solid hydroxide phase. Lithium fluoride was added as a potential catalyst.

Experimental.

2.5 litres of a sodium metasilicate solution containing 100 ppm SiO_2 and 0.024 g (1 mmole) LiF with a barbiturate buffer was held in a 5 litre three necked flask fitted with a water condenser. A dropping funnel held 250 mls of the Al^{3+} solution, prepared from $Al_2SO_4.17H_2O$ containing 1,500 ppm Al^{3+}. The Al^{3+} solution was added dropwise to the boiling silica solution over a period of nineteen days during which the solution maintained a pH of between 7.0 and 8.0. Samples for electron microscopy examination were taken after seven, twelve and nineteen days.

Results.

The seven and twelve day samples were mainly amorphous. The nineteen day sample gave spacings corresponding to those of bayerite, $Al(OH)_3$.

TABLE 1.

Bayerite (ASTM 12-457) dÅ	19 day sample dÅ
4.72	4.71
2.34	2.36
2.06	2.08
1.63	1.63
1.55	1.54
1.28	1.28
1.26	1.26
-	1.04
-	0.82
-	0.79

The total addition of the Al^{3+} solution gave a final SiO_2/Al_2O_3 ratio of 2.0/1.0, the kaolinite group formula, but no clay diffractions were observed.

PART 3.

Silica and aluminium solutions with organic and inorganic additives at 80°C.

It was proposed to chelate mildly the Al^{3+} ions in solution with organic compounds to either promote the formation of the more insoluble Si-O-Al layer structures or to slow down its precipitation as a hydroxide to improve its crystallinity and so perhaps encourage greater silica uptake.

Oxalic acid has been used by Wey and Siffert (1961) to promote the synthesis of a poorly crystalline kaolin at room temperature and so it was selected for this experiment.

Phenols retain Al^{3+} in basic solutions by providing phenolate anions and so two water soluble phenols were chosen. Lithium fluoride was used again here as a possible catalyst.

The addition of KCl to the solutions gave the possibility of mica formation.

Experimental.

Solutions of sodium metasilicate $Na_2SiO_3.8H_2O$ and aluminium sulphate, $Al_2(SO_4)_3.17H_2O$ were prepared containing 100 ppm. Al^{3+} and concentrations of SiO_2 so as to give four ratios of SiO_2/Al_2O_3, namely, 20.0/1.0, 8.0/1.0, 2.0/1.0, and 0.2/1.0. Additions to each of these solutions were made to give a 1/1 molecular, to g. ion ratio to Al^{3+}. The additives are given in Table 2.

TABLE 2.

Additives to SiO_2/Al^{3+} solutions.

A. none (Si,Al) alone

B. oxalic acid

C. p-nitro phenol

D. m-amino phenol

E. lithium fluoride

F. potassium chloride

G. 1/1 mixture of LiF and KCl.

The organic additives were recrystallised from water prior to use. A series with (Si,Al) alone was conducted as a blank.

2 ml solutions of each mixture were held in sealed polythene containers : the pH was adjusted to about 8.5 with HCl and NaOH. Four batches of seven containers each were clamped between alloy sheets and suspended in water baths maintained at 80°C. After fourteen days the contents were microcentrifuged, washed twice and mounted for electron microscopy examination.

Results and Discussion.

In general the precipitate formed under these conditions gave rise to more crystalline material. The spacings derived from the diffraction patterns are given in Tables 3 to 7 for the corresponding micrographs contained in Plates 1 to 10. A summary of the phases indentified is given in Table 8.

With solutions containing a SiO_2/Al_2O_3 ratio of 20.0/1.0, the additives had little effect compared with (Si,Al) alone. Precipitates were similar to Plate 1, the product obtained with p-nitro phenol the lattice spacing relating to bayerite. The solution containing LiF and KCl gave a product similar to dickite with some amorphous material present. The crystals are held together in a lace like structure caused partly by the presence of amorphous material and partly by the excess silica forming a gel like material.

From the series with a SiO_2/Al_2O_3 ratio of 8.0/1.0 (Si,Al) alone gave a mixture of amorphous material with the morphology of allophane, x Al_2O_3, y SiO_2, x H_2O (Plate 3) and dickite (Plate 4). The solution containing oxalic acid gave amorphous material (Plate 5). With LiF, norstandite was obtained, an aluminium hydroxide which can contain up to 4% SiO_2.

The solutions with a SiO_2/Al_2O_3 ratio of 2.0/1.0 gave bayerite with m-aminophenol (Plate 7) and with KCl a form of harmotome, an alumina silicate framework structure. The spacing data shown in Table 6 is for the sodium form, but it is probable that the lattice contains both K^+ and Na^+ as counter ions.

Solutions with a SiO_2/Al_2O_3 ratio of 0.2/1.0 gave mainly bayerite. With LiF present, a precipitate containing boehmite was formed, (Plate 10).

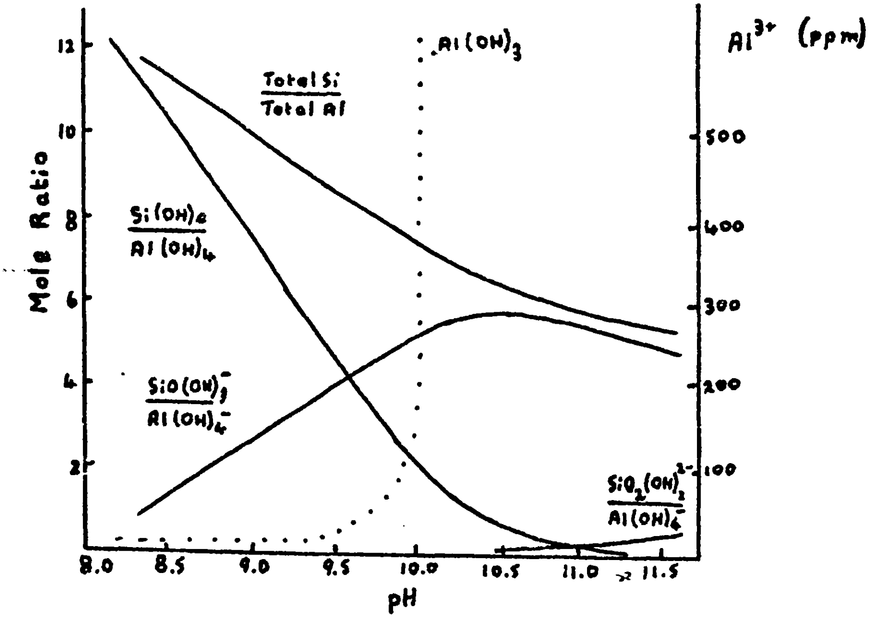


Figure 2. Mole ratio of total silica to total alumina and the various silica species in solution to the alumina species in solution as a function of pH. The dotted curve shows the solubility of $Al(OH)_3$. (After Mason (1966) and Mariner and Surdam (1970)).

At pH 8.5 Al^{3+} is virtually totally precipitated as $Al(OH)_3$ (Figure 9). The silica is almost totally present as monosilic acid $Si(OH)_4$. The silica uptake shown in Figure 1 will probably be due to the adsorption of monosilicic acid onto the hydroxide layers of $Al(OH)_3$. From the work of Mariner and Surdam (Figure 2) the formation of alumino silicate gels is favoured at higher pHs where aluminium is present as $Al(OH)_4^-$. On ageing these alkaline gels at 80°C for two weeks framework structures, that is, zeolites crystallise out. This result could account for the poorly crystalline harmotome formed in some of the above reactions. The formation of layer silicate structures is then restricted to lower pHs and indeed dickite has been synthesed in the above experiments.

Under these conditions bayerite was the major phase : discussion of this result will be deferred to Chapter IV.

TABLE 3.

Bayerite (ASTM 12-457) $Al(OH)_3$ dÅ	1C dÅ	3D dÅ	4C dÅ
4.72	4.68	-	-
2.69	-	2.63	-
2.45	-	-	2.47
2.21	-	-	2.20
2.06	2.01	2.08	-
1.97	-	1.98	-
1.83	-	-	1.85
1.71	1.72	-	-
1.59	-	1.62	-
1.55	-	-	1.54
1.45	-	-	1.45
1.26	1.27	1.25	1.23
1.18	1.17	1.13	1.19

TABLE 4.

Boehmite (ASTM 5-0190) AlO(OH) dÅ	4E dÅ
3.16	3.26
2.35	2.35
1.86	1.88
1.45	1.45
1.31	1.32
1.14	1.14

TABLE 5.

Dickite (ASTM 10-430)		
$Al_2Si_2O_5(OH)_4$ dÅ	1G dÅ	2A dÅ
3.78	3.79	-
3.58	-	3.58
3.43	3.44	-
2.79	2.79	-
2.56	2.58	-
2.21	2.18	2.21
1.86	1.86	-
1.79	-	1.79
1.72	1.72	-
1.65	-	1.65
1.49	1.49	-
1.39	-	1.37

TABLE 6.

Norstandite (ASTM 15-141)	
$Al(OH)_3$, 4% SiO_2 dÅ	2E dÅ
4.79	4.79
3.89	3.91
3.60	3.60
2.85	2.85
2.39	2.39
2.03	2.02
1.65	1.65
1.43	1.43

TABLE 7.

A Harmotome (ASTM 12-687) $(Na,K)Al_2Si_6O_{16}.6H_2O$ dÅ	3F dÅ
4.08	4.08
3.65	3.65
2.94	2.94

TABLE 8.

Additives \ $\frac{SiO_2}{Al_2O_3}$	1 20.0/1.0	2 8.0/1.0	3 2.0/1.0	4 0.2/1.0
A. (Si,Al) alone		(dickite (norstandite		
B. oxalic acid			(bayerite (harmotome	
C. p-nitrophenol	bayerite		bayerite	bayerite
D. m-aminophenol	bayerite	(bayerite (norstandite	bayerite	bayerite
E. LiF		norstandite	(bayerite (norstandite	boehmite
F. KCl	boehmite		harmotome	bayerite
G. 1/1 LiF/KCl	dickite	norstandite	harmotome	

SiO_2/Al_2O_3 solutions heated at 80°C

Plate 1. 1C[*] Bayerite Mag. x 60K

Plate 2. 1G Dickite Mag. x 60K

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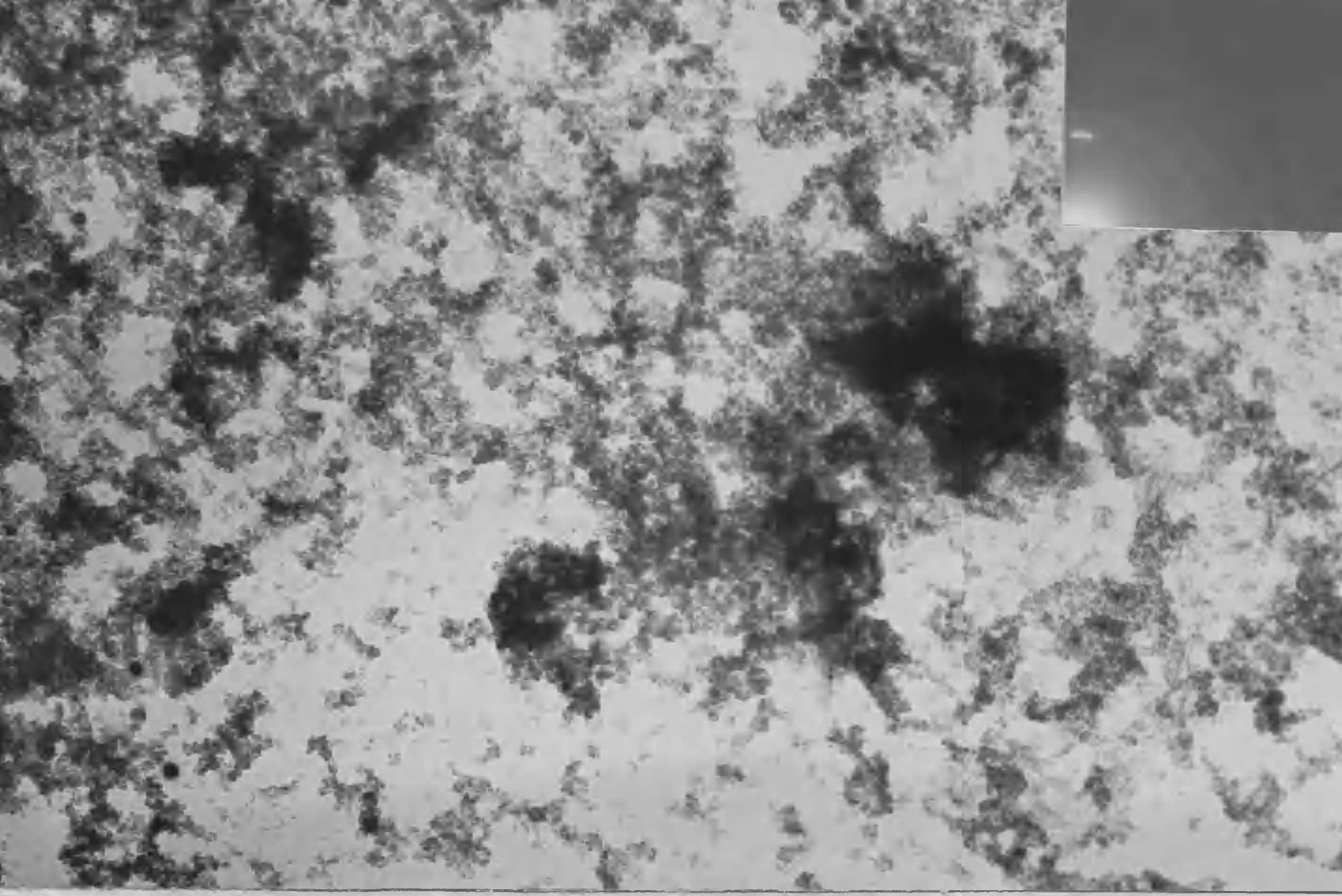
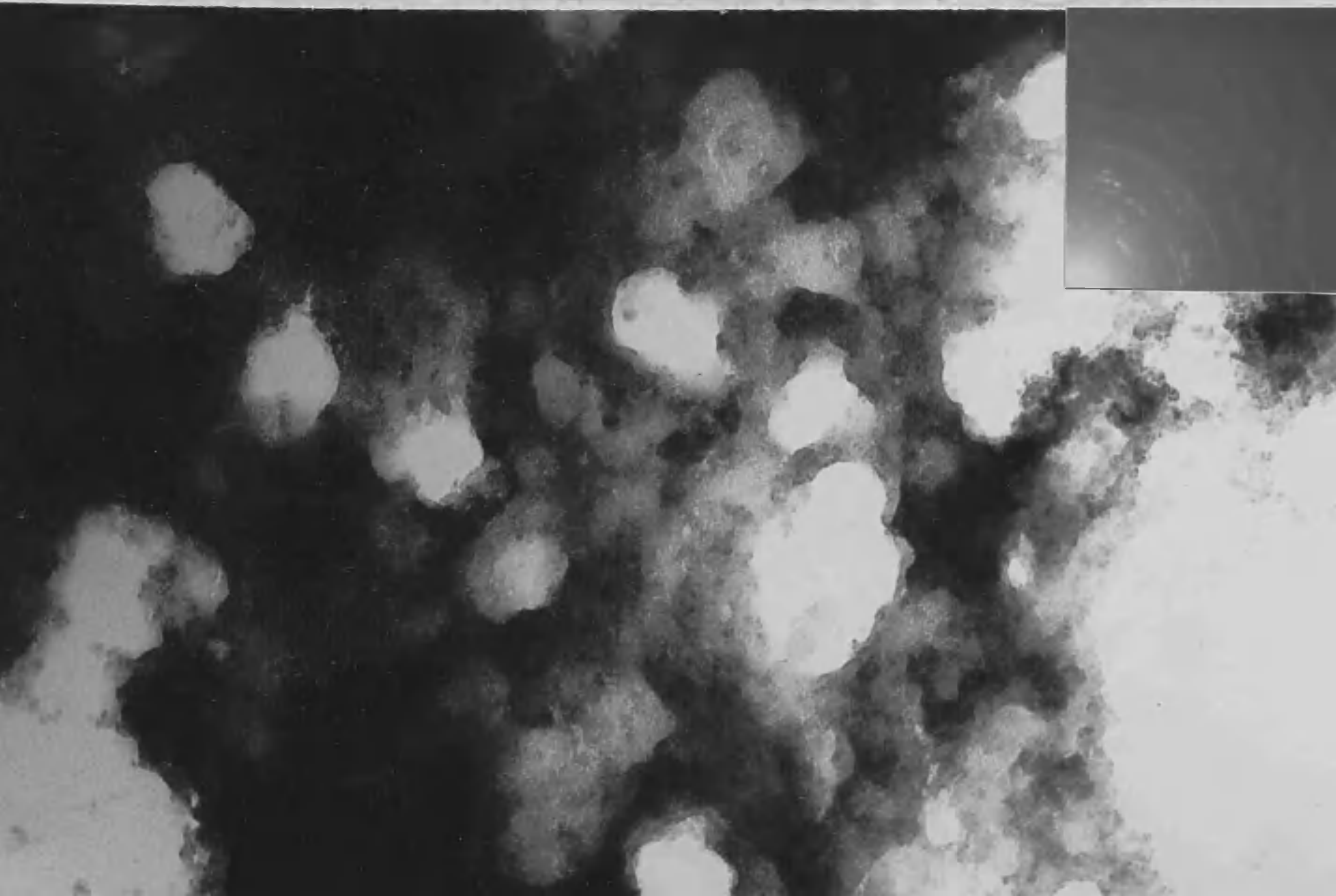
[*] The number and letter refer to the additives in the solutions - see Table 8.

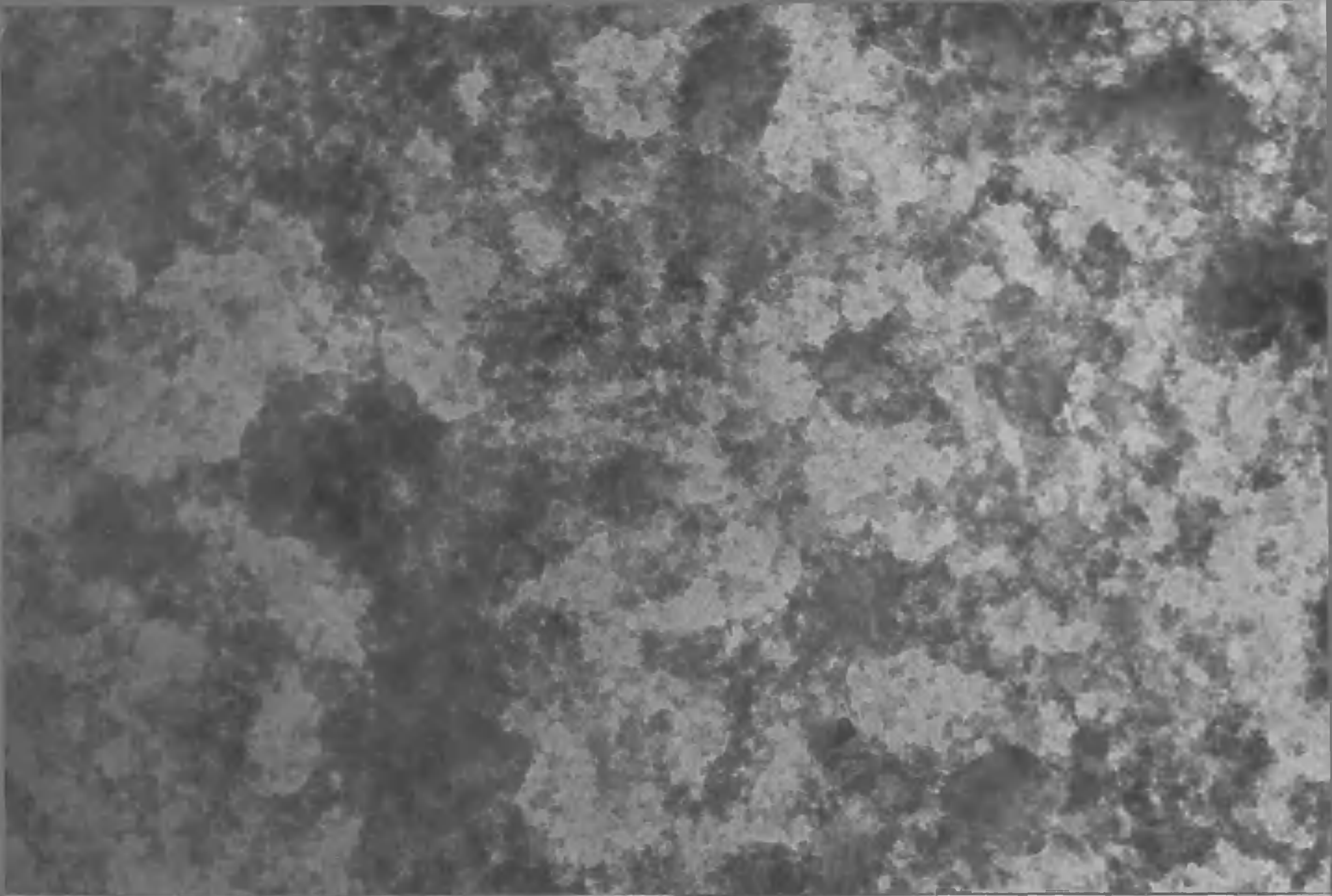


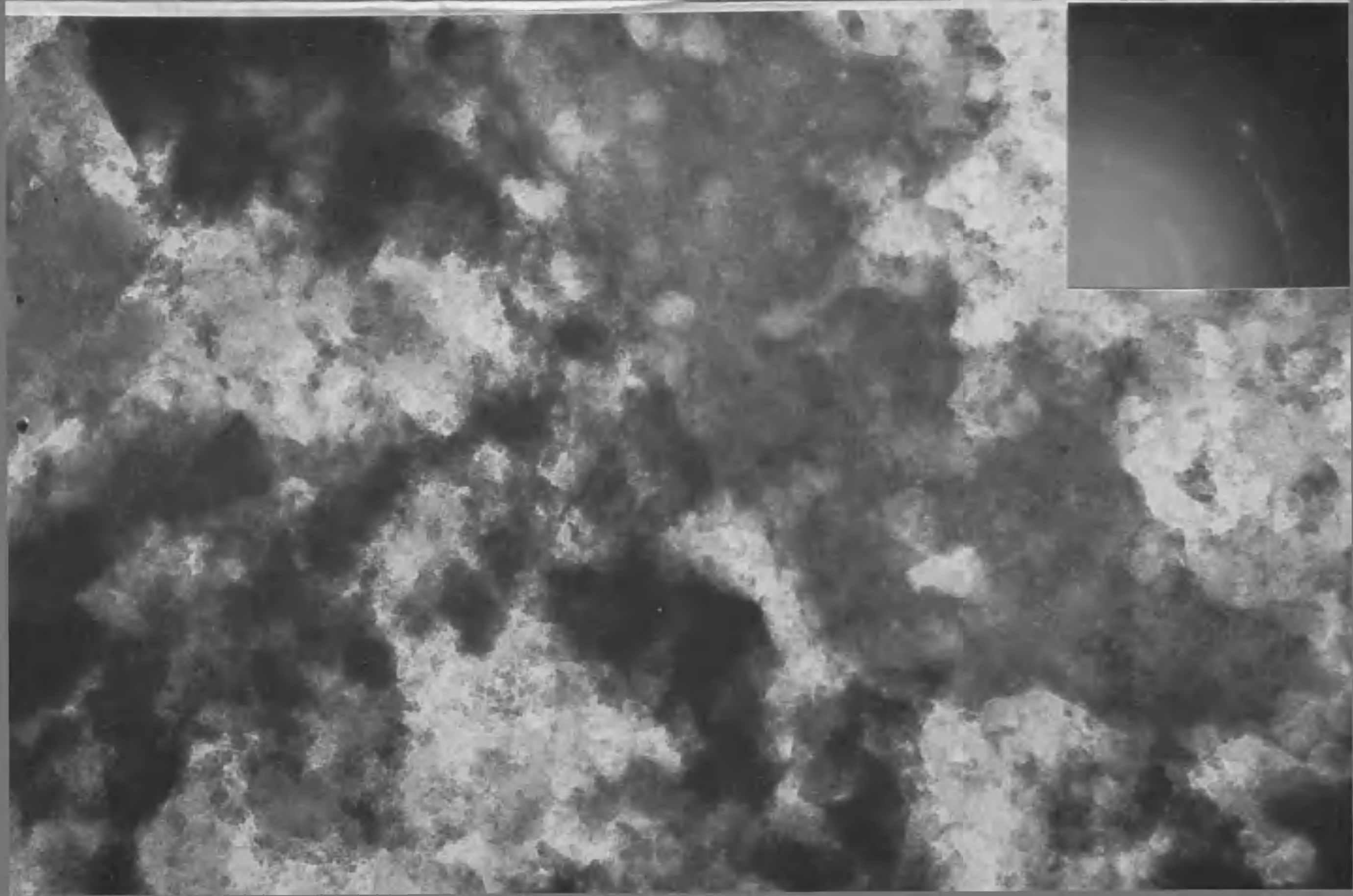


SiO_2/Al_2O_3 solutions heated at 80°C

Plate 3. 2A Allophane like material Mag. x 60K

Plate 4. 2A Dickite and amorphous material Mag. x 60K

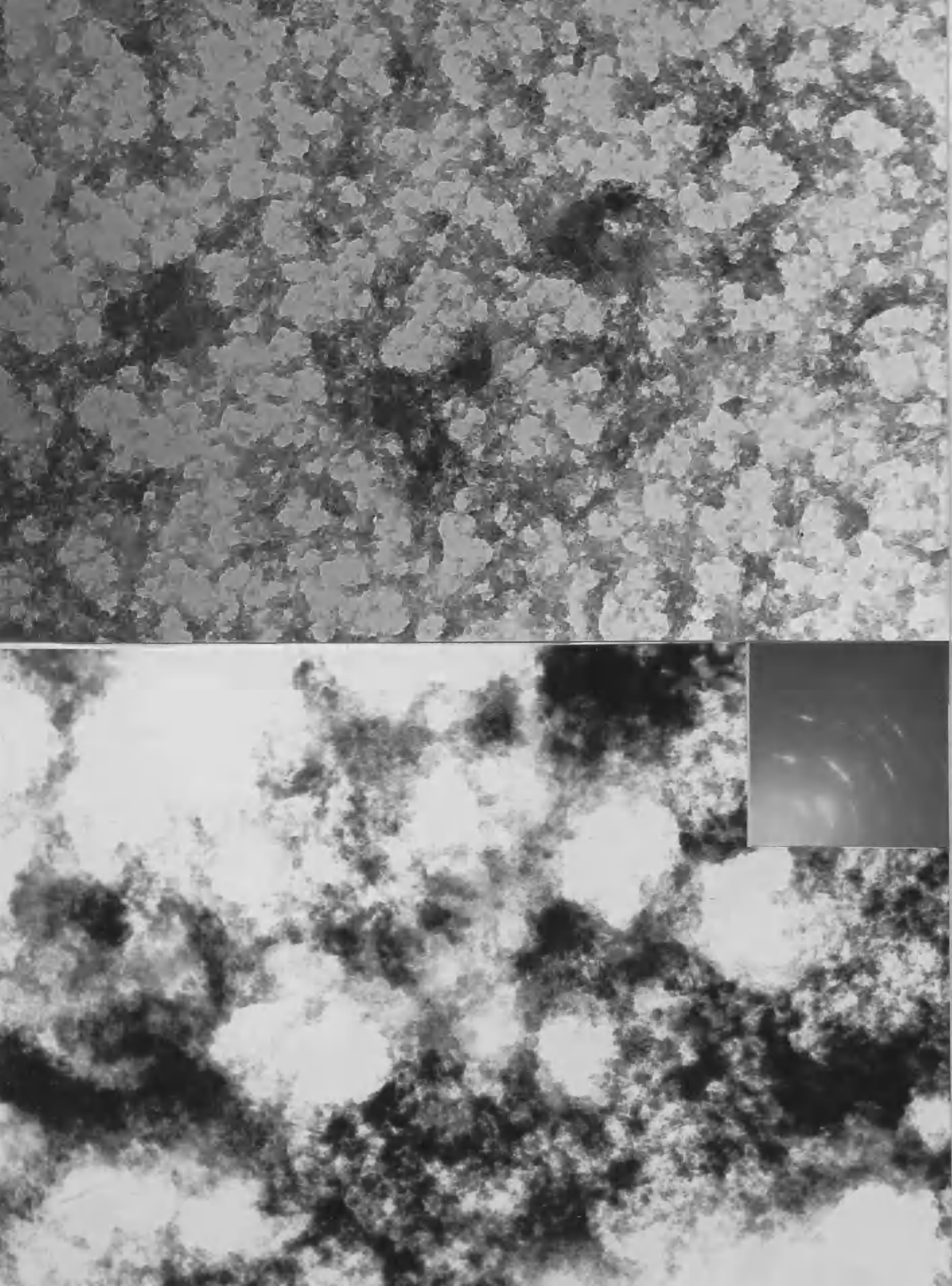




SiO_2/Al_2O_3 solutions heated at 80°C

Plate 5. 2B Allophane like material Mag. x 60K

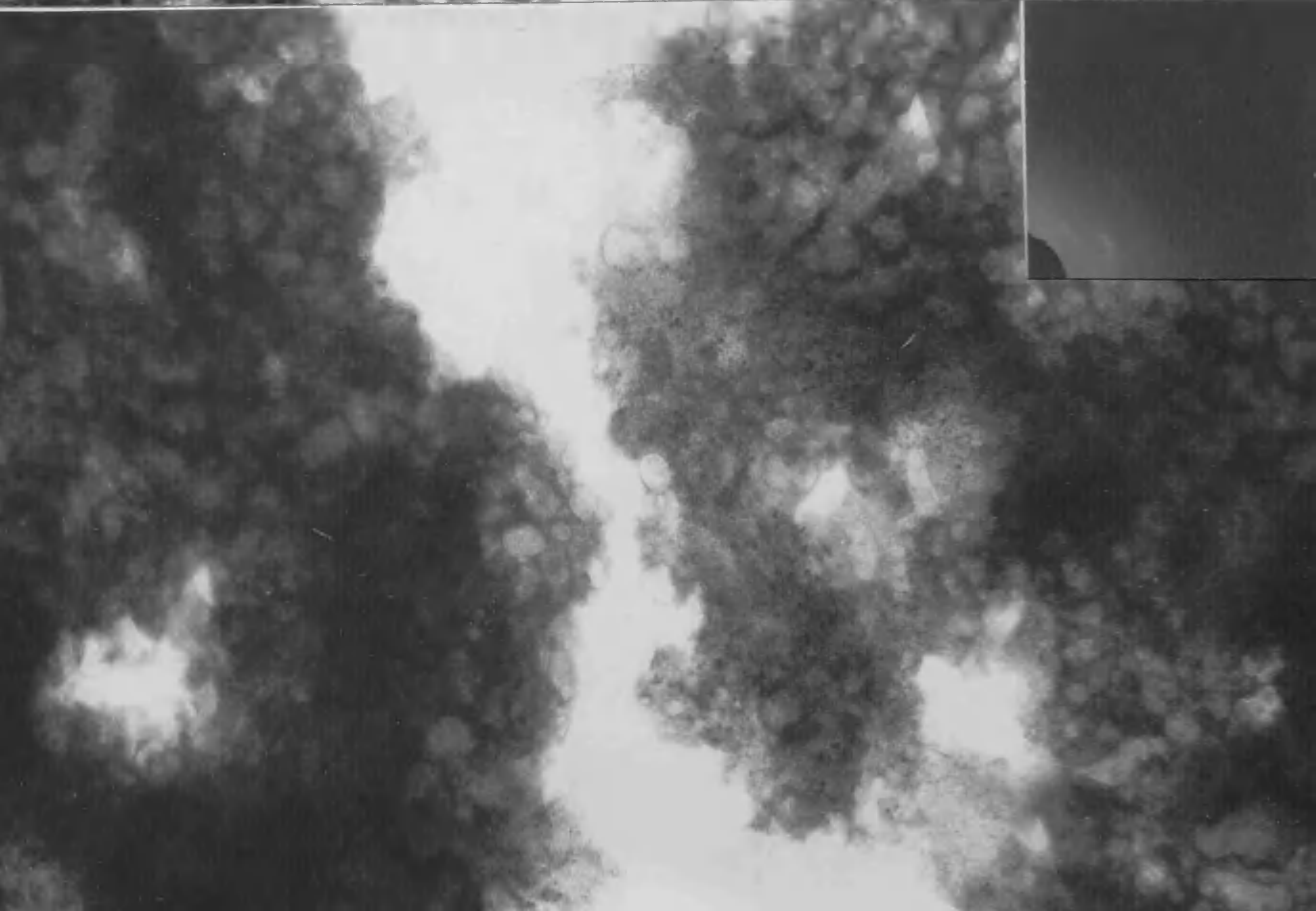
Plate 6. 2E Norstandite Mag. x 60K



SiO_2/Al_2O_3 solutions heated at 80°C

Plate 7. 3D Bayerite Mag. x 60K

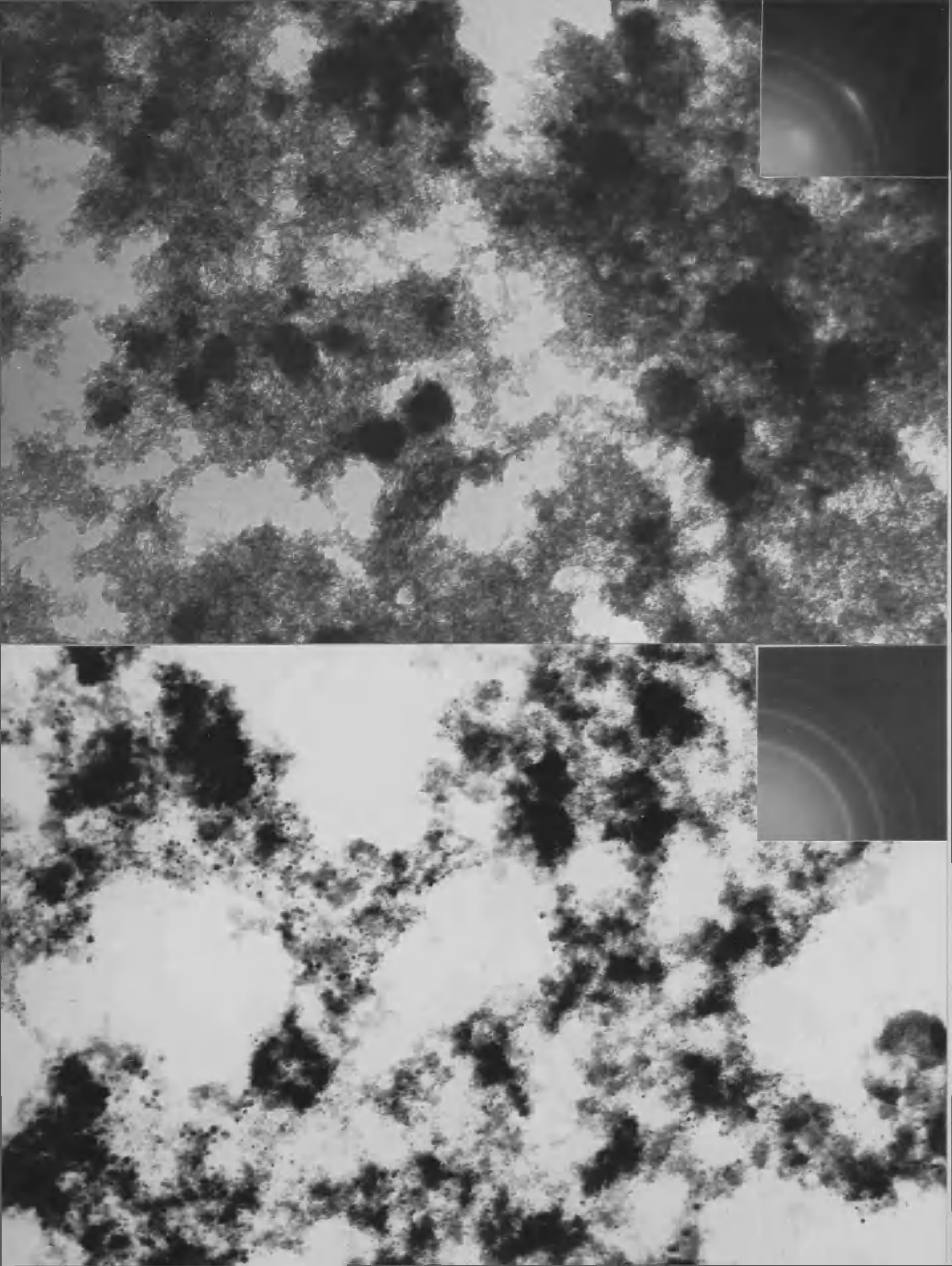
Plate 8. 3F Harmotome Mag. x 60K



SiO_2/Al_2O_3 solutions heated at 80°C

Plate 9. 4C Bayerite Mag. x 60K

Plate 10. 4E Boehmite Mag. x 60K



CHAPTER III.

Slurry Reactions in the SiO_2/MgO System.

Attention was turned to systems capable of yielding clays at atmospheric pressure in greater quantities and more reproducibly than described in the preceding chapters so that a more detailed study could be made of the clay formation process. Initial studies by Granquist and Pollack (1960) show that hectorite can be synthesised by refluxing slurries of silica gel and magnesium hydroxide containing Na^+ or Li and/or F^- for a period of seven days. The system with $SiO_2/MgO/LiF$ gave a product most closely resembling that of natural hectorite with X-Ray diffraction and D.T.A. as the main criteria. Advantages of this system compared with dilute solution methods include shorter reaction times and syntheses can be performed with the choice of adding other ions; dilute solutions necessarily contain counter ions such as Na^+, Cl^- and SO_4^{2-}.

The composition of hectorite is taken as being, after Granquist and Pollack :

$$Li_xMg_{6-x}\ Si_8O_{20}\ F_y(OH)_{4-z}\ ^{(x+y)-}.xM^+.$$

In this formula, Li^+ partially replaces Mg^{2+} in the octahedral layer and F^- replaces some of the hydroxyls.

An electron microscopy study was made of the changes occurring in the slurry during hectorite synthesis both with time and by varying the SiO_2 content of the feed mixtures.

The products were also examined by X-Ray diffraction using a diffractometer and by Differential Thermal Analysis (D.T.A.). The equipment and techniques are described in the Experimental Appendix.

Additional identification techniques were used and these are described in Part 3.

The reactions of slurries containing ions in addition to $SiO_2/MgO/LiF$ are contained in Part 4.

Experimental.

The method involved hydrothermal treatment of aqueous slurries containing about 10% solids comprising silicic acid, magnesium hydroxide and lithium fluoride. The silicic acid source was powdered silicic acid, $SiO_2.xH_2O$, supplied by Mallinckrodt (100 U.S. mesh, analytical grade) which contained about 85% SiO_2. Magnesium hydroxide was prepared by precipitation from a 25% magnesium chloride solution (made from $MgCl_2.6H_2O$ 'Analar' reagent supplied by British Drug Houses Ltd.) with 10 M ammonia. The magnesium hydroxide was filtered off under suction and thoroughly washed to remove traces of NH_3 and NH_4Cl. It was then homogenised in a blender and stored in polythene bottles. The weight of $Mg(OH)_2$ per ml for each batch was determined so that the slurry could be handled volumetrically.

A typical feed mixture for a ratio of $SiO_2/MgO/LiF$ = 1.33/1.0/0.25 contained 2.09 g silicic acid, 1.25 g $Mg(OH)_2$, 0.14 g LiF

('Analar' reagent, B.D.H.) in 50 mls of distilled water. The slurries were vigorously shaken and then treated hydrothermally by refluxing in a Pyrex glass vessel fitted with a water condenser. Plastic vessels were used for some of the experiments to eliminate contamination from glass vessels.

The above quantities gave sufficient material for examination from 10 ml aliquots. The samples were normally washed twice and then dried in air at 70°C or 100°C.

PART 1.

Ratio Experiments.

These experiments were aimed at determining the critical amount of SiO_2 required to achieve the synthesis of hectorite.

Experimental.

Slurries were prepared containing SiO_2/MgO/LiF in ratios from 0.1/1.0/0.25 to 2.0/1.0/0.25 and were refluxed in Pyrex vessels for six days. Samples were examined by X-Ray diffraction and electron microscopy.

Results and Discussion.

The electron diffraction patterns obtained from SiO_2/MgO ratios of 0.1, 0.2, 0.4, 0.7 and 2.0 (the LiF proportion being kept constant at 0.25) are shown in Plates 3 to 7. This suggests that hectorite is present even in the 0.1 sample. The definition of the pattern improves with increasing SiO_2 content. The spacings from the 2.0/1.0 sample are given in Table 1 compared with those of natural hectorite.

TABLE 1.

Natural hectorite (after Granquist & Pollack) dÅ	SiO_2/MgO/LiF = 2.0/1.0/0.25. dÅ
4.51	4.50
2.58	2.60
1.72	1.71
1.51	→ 1.52
1.31	1.31
1.26	1.27
0.99	0.98
0.88	0.87

The 001 spacings measured from X-Ray diffractometer traces are shown in Table 2.

TABLE 2.

SiO_2/MgO	001 spacing Å. 70°C oven dry basis.
0.1/1.0	9.0
0.2/1.0	8.5
0.4/1.0	14.7
0.7/1.0	15.5
2.0/1.0	14.0 (dried at 110°C:12.8Å)

The 001 spacings for the ratios 0.1 and 0.2 are 8-9 Å which suggests that these structures are not able to adsorb interlayer water due to the low crystallinity of the products. At 0.4/1.0 the 001 spacing increases to 14.7 Å and the hectorite diffractions become sharper. The basal spacing from the 2.0/1.0 product dried at 70°C was 14.0 Å and contracted on drying at 110°C to 12.8 Å corresponding to the loss of interlayer water. This is typical of the behaviour of three layer expanding smectites.

Micrographs of this series are shown in Plates 8 to 14. For comparison the micrograph of unreacted $Mg(OH)_2$ starting material is shown in Plate 1 which reveals its plate like appearance. The more dense elongated particles are platelets standing on edge to the electron beam. The spacings for this material, derived from the diffraction pattern shown in Plate 2, are shown in Table 3 to correspond to those of brucite.

TABLE 3.

Brucite $Mg(OH)_2$ dÅ	$Mg(OH)_2$ starting material dÅ
2.73	2.72
2.37	2.36
1.58	1.58
1.49	1.47
1.31	1.30
1.09	1.08
0.91	0.90
0.89	0.89
0.78	0.78
-	0.78
-	0.72

The morphology of the 0.1/1.0 product shown in Plate 8 resembles sheets highly folded at the edges with ring like forms within the platelets. This folded appearance and ring form is more evident in ratios 0.2/1.0 to 0.7/1.0 (Plates 9 to 12). These ring like forms were called 'doughnuts' and their significance in the hectorite synthesis will be discussed in the kinetic experiments in Part 2. The ratio 2.0/1.0 (Plates 13 and 14) shows larger, more smoothly folded sheets typical of smectites. Natural hectorite from Hector California has a lath like form. This synthetic hectorite is more like the natural hectorite found at Cadouin, France or Ghossoul, Morocco (Atlas of Electron Microscopy and their Admixtures 1968).

Weight losses were however detected from the glass vessels which varied with the initial amounts of silicic acid added. The lower the amounts added, the more the glass dissolved. Blanks reactions were carried out with $Mg(OH)_2$ and LiF alone. On average 1.64 g of glass dissolved in a slurry of 1.25 g $Mg(OH)_2$ and 0.14 g LiF. No detectable loss occurred when 1.74 g SiO_2 were added to an otherwise identical slurry. Indeed with no silica added a poorly crystalline hectorite was synthesised (Plates 15 and 16), the diffraction pattern shows that $Mg(OH)_2$ was still present. By refluxing $Mg(OH)_2$ and LiF hectorite was formed (Plates 17 and 18). Further tests showed that so long as the feed mixtures contained a ratio SiO_2/MgO 1 no loss could be detected from the glass.

Experiments were performed with very small additions of SiO_2, which in the light of these findings it would be expected that the product would tend towards higher silica products because of the dissolution of the glass. The results of these experiments are exemplified in the six day reflux of a slurry containing

$SiO_2/MgO/LiF$ = 0.01/1.0/0.25 shown in Plate 19. The product is seen to have a rosette like structure suggesting that the edges of the platelets have curled back so far and then the reaction has not been able to progress. The 001 spacing was not detected in X-Rays but from the high magnification micrograph (Plate 20) the lattice spacing was found to be 10 Å. This can be rationalised by considering the relative rate of solution of the two sources of silica. The powdered silicic acid will dissolve more rapidly than the glass. The added silicic acid would then penetrate the brucite platelets first and become bound to the brucite surface to give hectorite fringes which would block the further penetration of the SiO_2 from the glass. This gave the first indication, together with the above experiments, that the brucite platelets, compared with Mg^{2+} ions in solution, have considerable influence on the course of this reaction.

<u>Reaction in plastic vessels</u>.

To eliminate contamination of the slurry by the dissolution of glass with feed mixtures of $SiO_2MgO < 1$, the above experiments were repeated using polypropylene flasks which could withstand heat sources of up to 145°C.

<u>Experimental</u>.

Slurries were prepared containing ratios $SiO_2/MgO/LiF$ of (0.01-2.0)/1.0/0.25. The necks of the flasks were sealed with polythene sleeves which expanded to relieve the pressure in the flasks.

The flasks were heated on a sand bath for seven days at 140°C, to give internal temperatures of 90-95°C. The slurries were then allowed to dry down at 70°C. They were not washed so that the amounts of $Mg(OH)_2$ could be determined without loss of Mg^{2+} ions.

Results.

Typical D.T.A. traces are shown in Figure 1. From this data SiO_2/MgO ratios $\geqslant$ 1.6 appear to give products most closely resembling natural hectorite.

With the low ratios, inspection of the electron diffraction data, Table 4 from Plates 21 to 30 shows that $Mg(OH)_2$ is present up to SiO_2/MgO = 1.0/1.0, with the hectorite spacings appearing at about 0.4/1.0. This is confirmed in Table 5 which also shows the 001 spacings present in from the 0.4/1.0 sample onwards.

Table 6 gives the comparison between hectorites made in glass and polypropylene with a ratio of $SiO_2/MgO/LiF$ of 2.0/1.0/0.25 compared with the results for natural hectorite and the synthetic hectorite of Granquist and Pollack. This shows that with feed mixtures of high ratios, the products are indistinguishable when formed by the two methods.

Figure 1. D.T.A. traces of ratio products.

SiO_2/MgO (LiF proportion constant at 0.25)

A. 0.4/1.0

B. 0.8/1.0

C. 1.2/1.0

D. 1.6/1.0

E. 2.0/1.0

F. Natural hectorite.

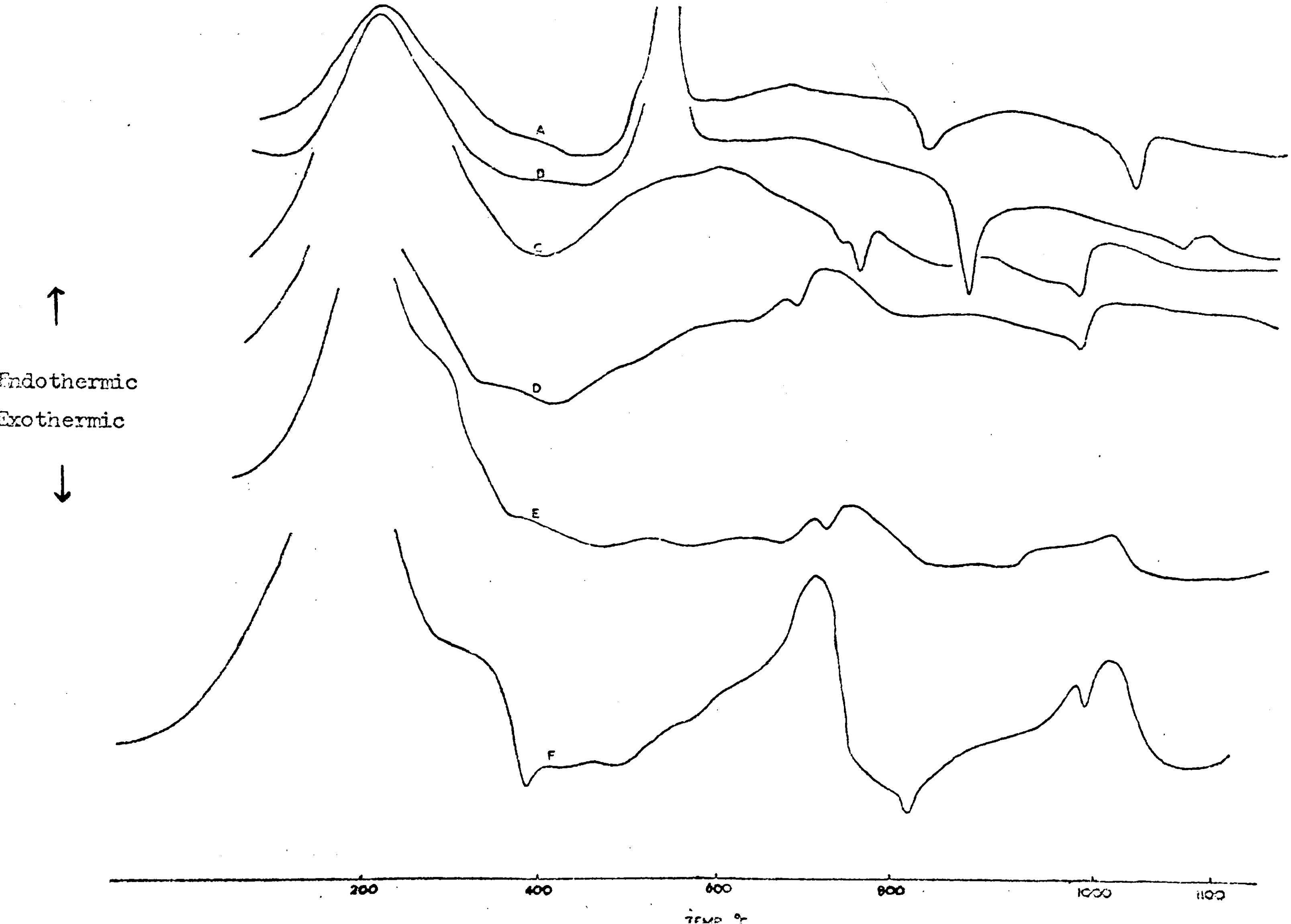

Endothermic
Exothermic
A
B
C
D
E
F
200
400
600
800
1000
1100
Temp °C

TABLE 4.

Brucite $Mg(OH)_2$	SiO_2/MgO 0.2/1.0		0.4/1.0		0.6/1.0		0.8/1.0		1.0/1.0		1.2/1.0		1.4/1.0		1.6/1.0		2.0/1.0	Hectorite
2.37	-	4.56		4.59	2.38	4.56	-	4.56	-	4.56		4.58		4.56		4.56	4.56	4.51
1.58	1.58	2.61		2.62	1.58	2.62	-	2.62	-	2.61		2.66		2.62		2.62	2.61	2.58
1.49	-	-		1.74	-	1.74	1.49	-	1.49	1.71		1.77		1.74		1.74	1.74	1.72
1.31	1.32	-		1.53	-	1.53	-	1.53	-	1.52		1.56		1.53		1.55	1.53	1.51
1.09	1.10	-		-	-	-	-	1.32	-	1.31		1.36		1.32		1.32	1.32	1.31
														1.28			1.28	1.26
																	0.99	0.99
																	0.89	0.88

TABLE 5. 001 spacings. Samples dried at 70°C.
The presence of $Mg(OH)_2$ is also indicated. (X- Rays)

SiO_2/MgO	001 spacing d Å	I mm	Relative Intensity	
0.2/1.0	-	-	-	$Mg(OH)_2$ present.
0.4/1.0	14.0	11	0.15	$Mg(OH)_2$ present.
0.6/1.0	14.5	18	0.24	$Mg(OH)_2$ present.
0.8/1.0	14.0	33	0.45	$Mg(OH)_2$ present.
1.0/1.0	13.6	39	0.53	$Mg(OH)_2$ present.
1.2/1.0	13.8	35	0.47	
1.4/1.0	13.6	72^{+}	1	
1.6/1.0	13.4	78^{+}	-	
2.0/1.0	13.6	72^{+}	-	
	$^{+}$Av. 74			

TABLE 6.

Diffraction data from natural and synthetic Hectorite *

	X-ray diffraction (diffractometer)				Electron diffraction	
			Synthetic Hectorite (present study)		Synthetic Hectorite (present study)	
Indices	Natural Hectorite Hofman (1941)	Synthetic Hectorite Granquist and Pollack (1959)	Pyrex Vessel	Poly-propylene Vessel	Pyrex Vessel	Poly-propylene Vessel
11,02	4·51 s	4.5 s	4.55 s	4.54 s	4.54 s	4.56 s
13,20	2.58 s	2.6 s	2.60 s	2.59 s	2.59 s	2.61 s
22,04	2.25 vw	2.25 vw	2.26 vw	2.25 vw	-	-
31,15,24	1.72 mw	1.74 m	1.71 m	1.72 w	1.71 m	1.74 m
33,06	1.51 s	1.53 s	1.52 s	1.52 s	1.52 s	1.53 s
26,40	1.31 m	1.31 m	1.31 m	1.31 m	1.31 s	1.31 s
35,17,42	1.26 w	1.28 w	1.27 w	1.26 w	1.26 m	1.28 m
08,44	1.15 vvw	1.18 w	-	-	-	-
37,28,51	1.05 vvw	1.04 w	-	-	-	-
19,53,46	0.99 mw	0.98 m	0.98 w	0.97 w	0.98 w	0.99 w
39,60	0.88 m	0.88 m	0.87 w	0.88 w	0.87 w	0.89 w

* after Baird, Cairns-Smith, MacKenzie, Snell (1971).

Typical X-Ray diffractometer traces are shown in Figure 1A. Here SiO_2/MgO ratios $\geqslant 1.2$ appear to give hectorite.

The relative amounts of hectorite and brucite were calculated from the (02), (06) and (101), (001) peaks respectively, as shown in Table 7. The integrated intensities were calculated by multiplying the width at half the peak height by the intensity above background. The integrated intensity of $Mg(OH)_2$ with no SiO_2 added was found by plotting the log of known intensities against the SiO_2/MgO ratio. The straight line obtained was extrapolated to zero to find the required intensity.

These results are plotted in Figure 2. Curves 4 and 5 give the theoretical amounts of hectorite and $Mg(OH)_2$ respectively that should be found for each ratio assuming the SiO_2/MgO ratio to be 1.33/1.00 in hectorite. Curves 1, 2 and 3 show the actual amounts found.

Curves 2 and 3 show that more $Mg(OH)_2$ is utilised than is required. The slurries were not washed so that the total magnesium content was the same for all the samples. Curve 3 corresponds to the decrease in the (001) intensity and shows a more rapid rate of decrease than the (101) intensity. This may be due to the adsorption of silicic acid between the layers with the formation of islands of tetrahedra as shown in Figure 3. The 001 intensity would tend to decrease faster than the other intensities on this basis.

Figure 1A. X-Ray diffractometer traces of ratio products.

	SiO_2/MgO (LiF = 0.25).
A.	0.4/1.0
B.	0.8/1.0
C.	1.2/1.0
D.	1.6/1.0
E.	2.0/1.0
F.	natural hectorite.

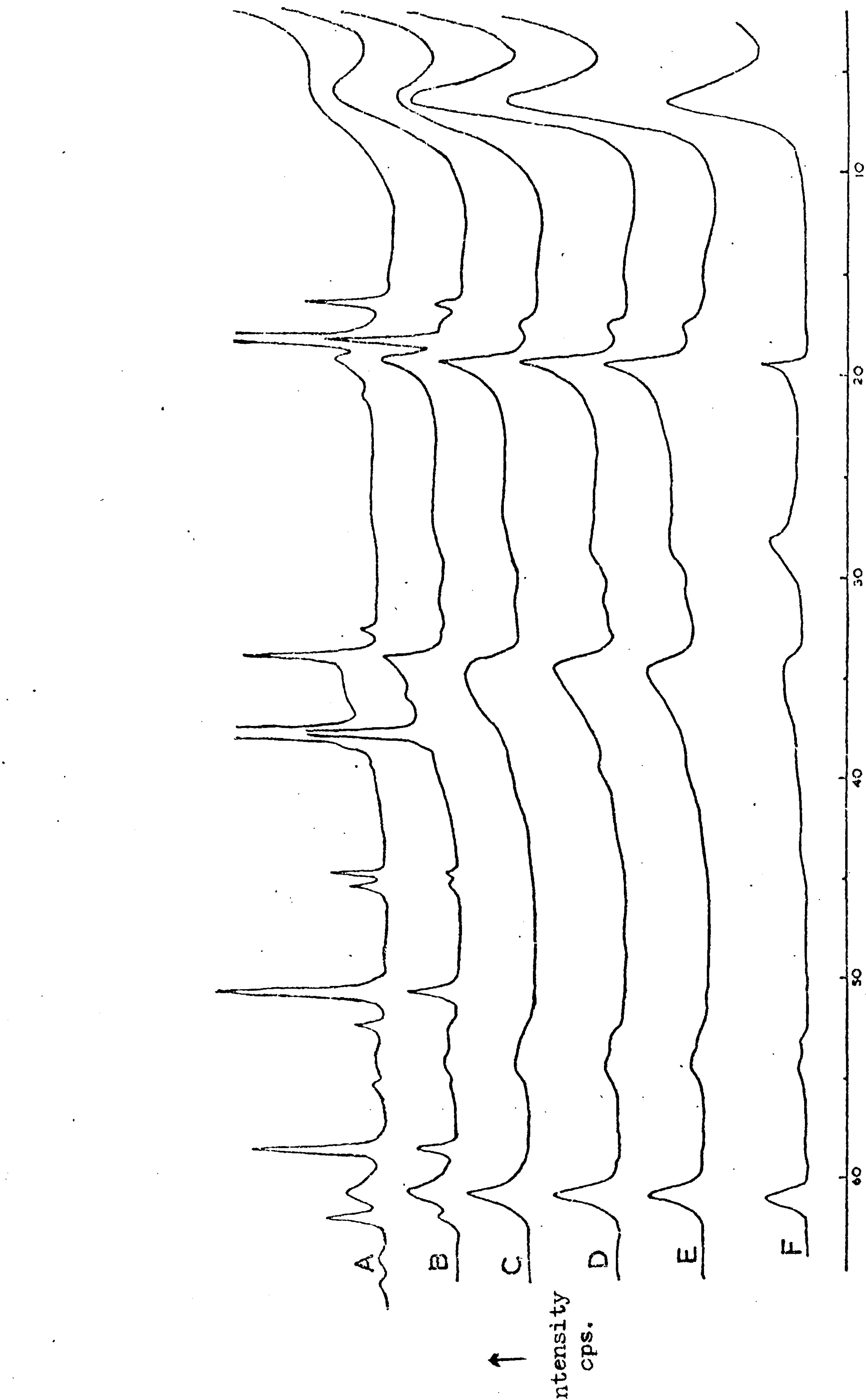

A
B
C
D
E
F
Intensity
cps.
DEG. 2θ
10
20
30
40
50
60

TABLE 7. Relative amounts of $Mg(OH)_2$ and hectorite in ratio experiments.

SiO_2/MgO	Hectorite I(06)mm	Width mm	Integrated Intensity	Relative Intensity	Hectorite I(02)mm	Width mm	Integrated Intensity	Relative Intensity
0.0/1.0	-	-	-	-	-	-	-	-
0.2/1.0	16.0	6.0	96	0.31	-	-	-	-
0.4/1.0	20.0	9.5	190	0.62	28	13.5	378	0.59
0.6/1.0	20.0	11.0	220	0.72	36	13.0	470	0.73
0.8/1.0	25.0	11.0	275	0.90	42	14.0	590	0.91
1.0/1.0	29.0	10.0	290	0.95	48	12.0	576	0.89
1.2/1.0	31.0	10.0	310 *	1.00	52	12.0	624	0.97
1.4/1.0	33.0	9.0	297 *	-	58	11.0	638 *	1.00
1.6/1.0	34.0	9.0	306 *	-	58	11.0	638 *	-
2.0/1.0	32.0	9.6	307 *	-	56	12.0	672 *	-

* Average 305

*Average 649.

TABLE 7.

SiO_2/MgO	$Mg(OH)_2$ I(101)mm	Width mm	Integrated Intensity	Relative Intensity	$Mg(OH)_2$ I(001)mm	Width mm	Integrated Intensity	Relative Intensity
0.0/1.0	-	-	2455 *	1.00	-	-	1905 *	1.00
0.2/1.0	388	4.0	1552	0.63	398	2.8	1114	0.58
0.4/1.0	362	3.0	1086	0.45	186	3.0	558	0.29
0.6/1.0	162	4.0	648	0.26	102	3.5	356	0.19
0.8/1.0	104	4.0	416	0.17	56	3.5	196	0.10
1.0/1.0	50	6.0	300	0.12	14	3.1	44	0.02
1.2/1.0	-	-	-	-	-	-	-	-
1.4/1.0	-	-	-	-	-	-	-	-
1.6/1.0	-	-	-	-	-	-	-	-
2.0/1.0	-	-	-	-	-	-	-	-

* by extrapolation.

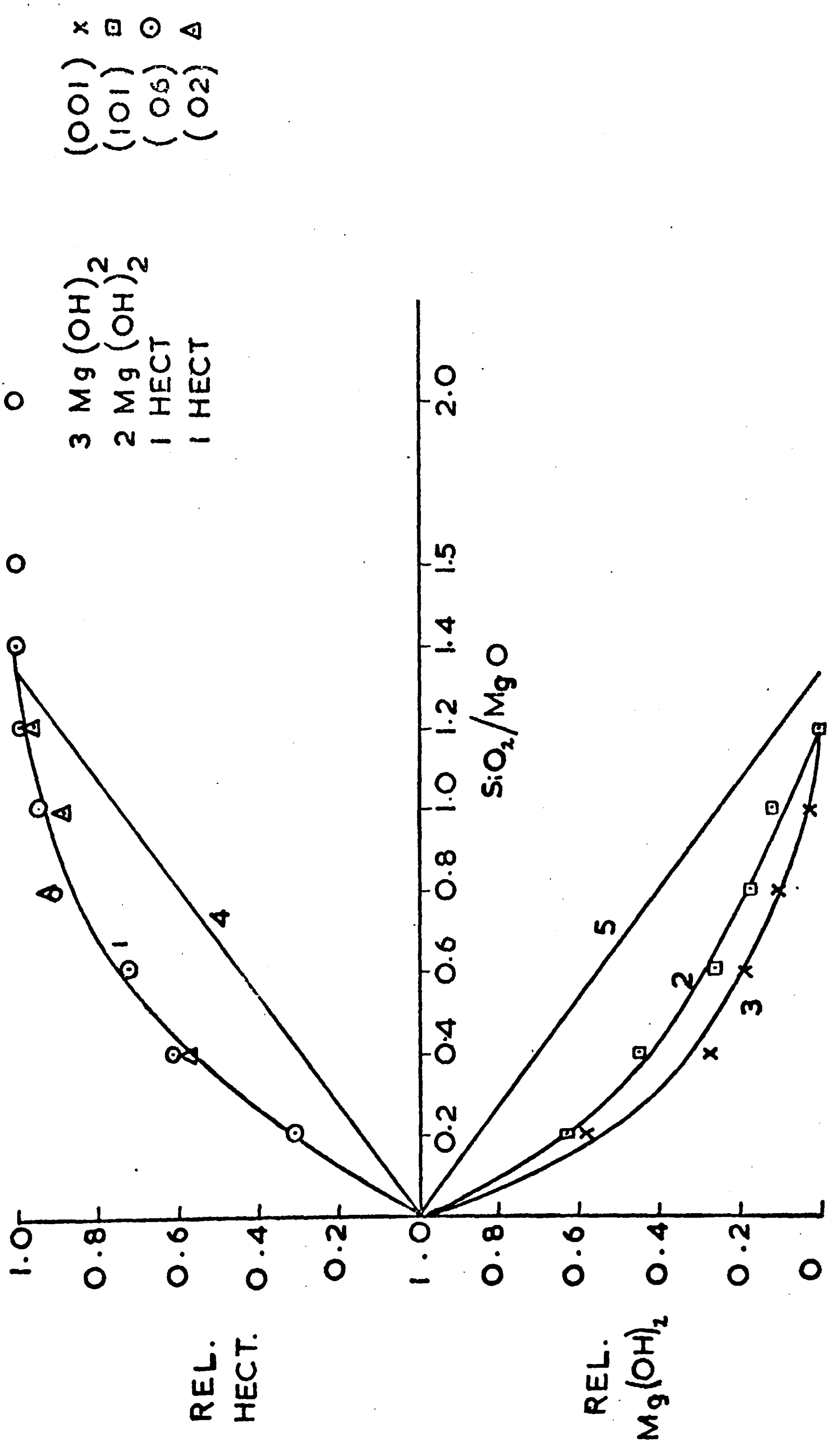

REL. HECT.
REL. $Mg(OH)_2$
1.0
0.8
0.6
0.4
0.2
1.0
0.8
0.6
0.4
0.2
0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.5
2.0
SiO_2/MgO
1
2
3
4
5
3 $Mg(OH)_2$ (001) x
2 $Mg(OH)_2$ (101) ⊡
1 HECT (06) ⊙
1 HECT (02) △

FIGURE 2

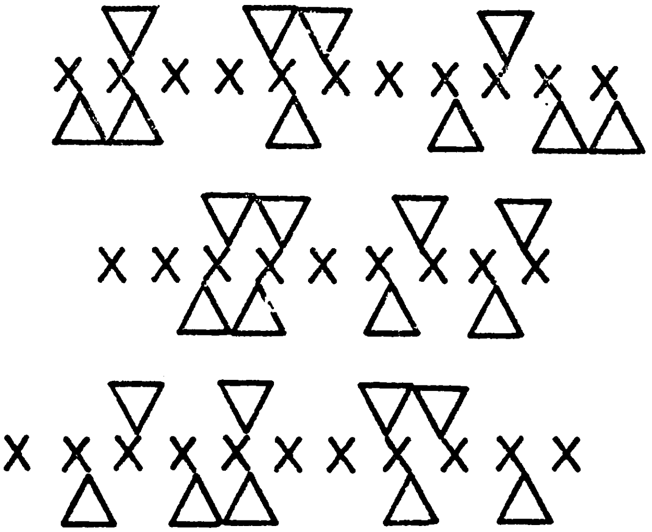


Figure 3. Formation of 'islands' of silica tetrahedra.

This type of structure would lead to a disproportionate decrease in the $Mg(OH)_2$ intensities for a given amount of silica added. This island type of structure will create a 'skeleton' hectorite which will diffract to give higher intensities than the theoretical value for a given amount of silica added.

Thus by postulating that hectorite formation occurs on and within the brucite layers it is possible to account for the excess decrease in the $Mg(OH)_2$ content and the enhanced hectorite levels with the increasing ratio of SiO_2/MgO.

The morphological changes with increasing silica content are shown in Plates 31 to 40. With a silica content of 0.2 (Plate 32), platelets with curled edges can be seen (arrowed). This indicates attack of silica at the edges of the brucite platelets. More extensive folding at edges occurs with 0.4 and 0.6 levels (Plates 33 and 34). Plates 35 and 36 reveal the doughnut type structures seen in Plates 10 and 11. Discussion of these forms will be deferred to Part 2. With ratios $SiO_2/MgO > 1.0$ the morphology increasingly resembles that of a smectite with large folded sheets the predominant feature.

It might have been expected that at ratios near 0.6/1.0 two layer clays would form, for example antigonites. However since the pH of these slurries remained in the region of 8.5 to 9.5 during the course of the syntheses, this would appear to be the controlling factor as opposed to the composition of the feed mixtures. It is conceivable that some chlorite type structures may form with the SiO_2/MgO ratio of 0.6, but they were not detected by the methods used here.

The result that feed mixtures of ratio $SiO_2/MgO \leqslant 1$ still contain $Mg(OH)_2$ explains the dissolution of glass in this range, since SiO_2 will dissolve out of the glass to saturate any remaining $Mg(OH)_2$.

The main conclusion from these ratio experiments was that with ratios $SiO_2/MgO \geqslant 1.2$ the hectorite reaction is complete.

PART 2.

Kinetic experiments with SiO_2/MgO/LiF slurries.

It was proposed to follow the formation of hectorite with time from slurries containing SiO_2/MgO/LiF in an attempt to elucidate the mechanism of the reaction. The process was followed over a period of five days by X-Rays and D.T.A. and up to 24 hours by X-Rays and electron microscopy.

Experimental.

The materials and methods used were the same as for Part 1.

It was decided to use glass for these experiments with a ratio of SiO_2/MgO/LiF of 2.0/1.0/0.25 to ensure negligible contamination from the glass. The temperature of the reaction could be maintained at 100°C by refluxing whereas the temperature of the polypropylene slurries was in the region of 90-95°C.

Results and Discussion.

Changes in the general composition of the slurries with time are shown in the results obtained from D.T.A. measurements (Table 8).

Examples of D.T.A. traces are shown in Figure 4.

This data indicates the appearance of hectorite after one day, with LiF still present up to two days. Poorly crystalline silicates appear after four days; this small peak may be due to silicates precipitating out of solution.

<u>Figure 4</u>. Examples of D.T.A. traces obtained from kinetic experiments.

<u>Time of reflux</u>.

A. Feed mixture ($SiO_2/MgO/LiF = 2.0/1.0/0.25$)

B. 3 hours.

C. 1 day.

D. 2 days.

E. 3 days.

F. 4 days.

G. 5 days.

H. natural hectorite.

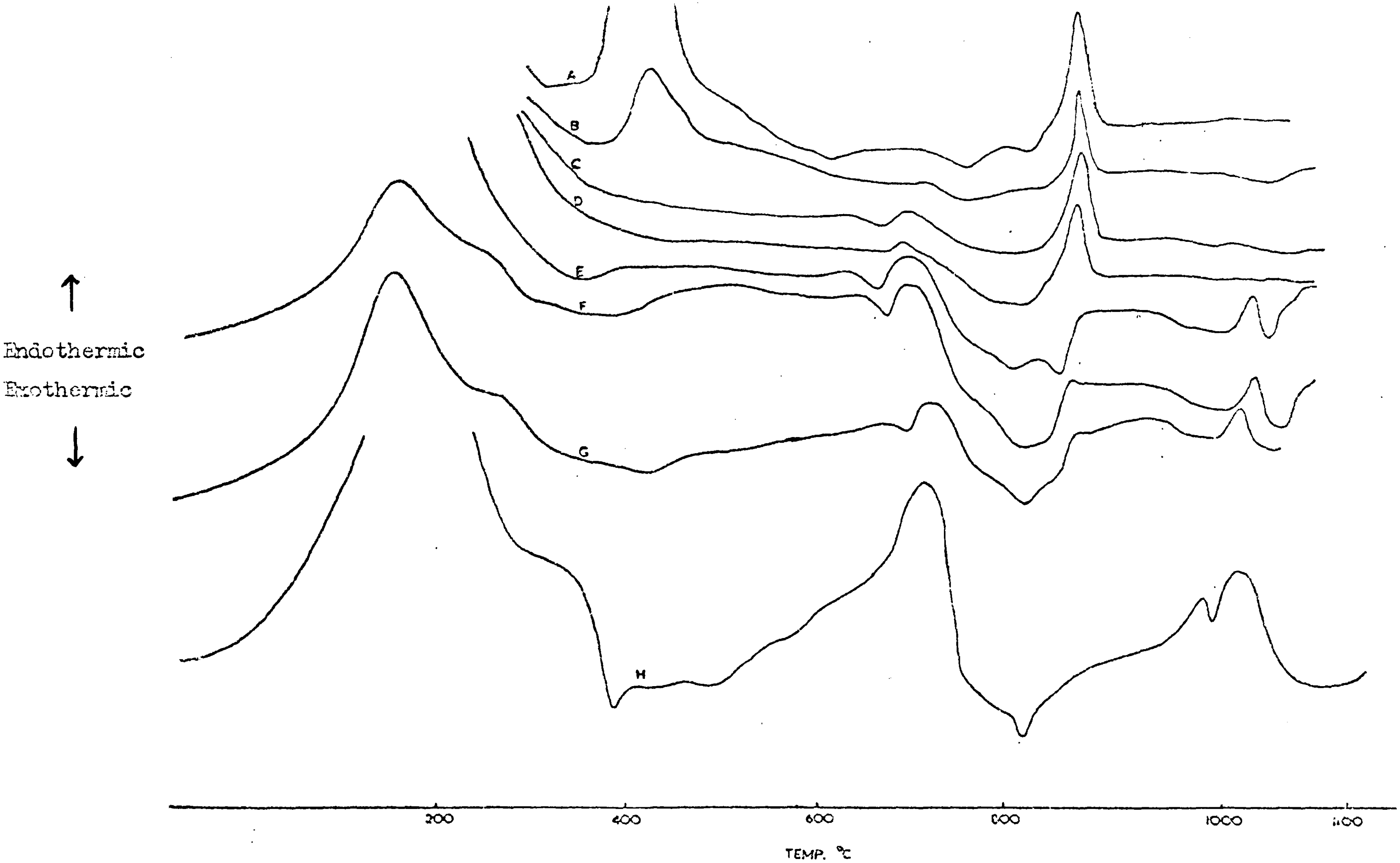

A
B
C
D
E
F
G
H
Endothermic
Exothermic
200
400
600
800
1000
1100
TEMP. °C

TABLE 8.

Time	Peak Temp. °C	t	Phases present	Transition
3 hours	394	endo	$Mg(OH)_2$	$Mg(OH)_2$ $MgO + H_2O$
	863	endo	LiF	2LiF $Li_2O + F_2$
1 day	685	endo	hectorite	
	853	endo	LiF	
2 days	657	endo	hectorite	
	844	endo	LiF	
3 days	692	endo	hectorite	
	1022	endo	hectorite	
4 days	685	endo	hectorite	
	806	exo	poorly crystalline silicates	
	1022	endo	hectorite	
5 days	132	endo	H_2O	loss of surface water
	233	endo	H_2O	loss of interlayer water
	697	endo	hectorite	
	806	exo	poorly crystalline silicates	
	1022	endo	hectorite	

The formation of hectorite was more satisfactorily followed from the appearance of the (06) peak and the change in $Mg(OH)_2$ content from the (001) peak in X-Ray diffraction. The change in relative intensities is shown in Table 9 and plotted in Figure 6. Typical diffraction traces are shown in Figure 5.

It would appear from this X-Ray data that the formation of hectorite is complete after one day. The $Mg(OH)_2$ content decreases faster than the formation of hectorite. This suggests that there is an initial adsorption process of silicic acid on brucite which lowers the brucite content followed by a slower ageing to give a hectorite -like product.

A solution process would be expected to be accelerated by the addition of preformed hectorite, assuming that the growth of hectorite can be seeded. An experiment was carried out in which hectorite 'seeds' from another experiment were added to a similar slurry to the above prior to refluxing. The 'seed' hectorite amounted to 0.1g in 4.53g of slurry, or about 2% by weight. The X-Ray data collected, corrected for this addition, is shown in Table 10 and graphically in Figure 6. From the slopes of the curves the maximum rate difference between the normal and seeded runs occurs after about two to three hours. This suggests that a solution process becomes more important at this time. This result can be correlated with subsequent evidence obtained from the micrographs taken of the slurry products during a kinetic experiment.

Figure 5. X-Ray diffractometer traces from kinetic experiments (Feed mixture $SiO_2/MgO/LiF$ = 2.0/1.0/0.25).

Time of reflux.

A. Room temperature sample.

B. 1 hour

C. 2 hours.

D. 7 hours.

E. 1 day.

F. natural hectorite.

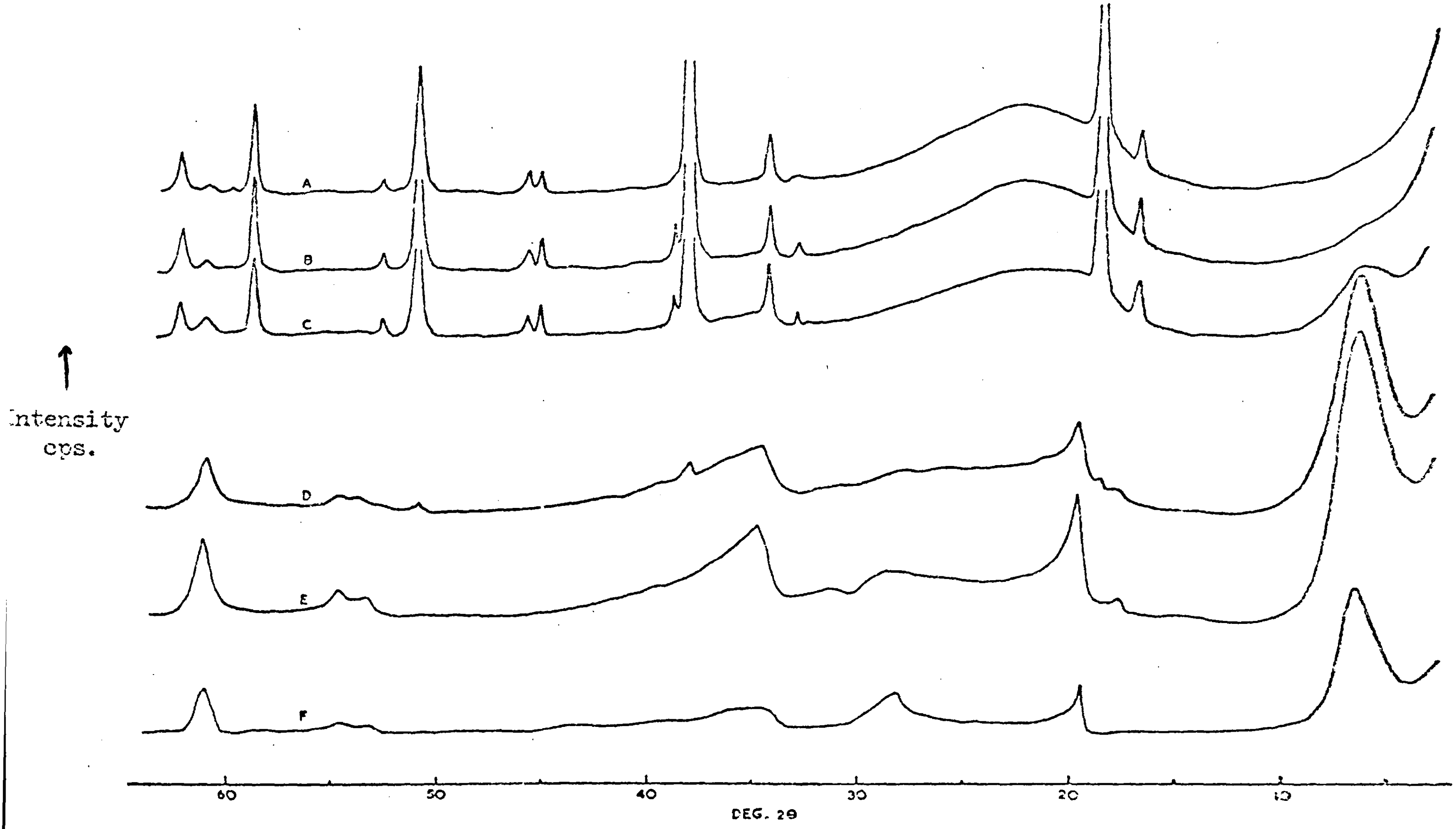

Intensity
cps.
A
B
C
D
E
F
60
50
40
30
20
10
DEG. 2θ

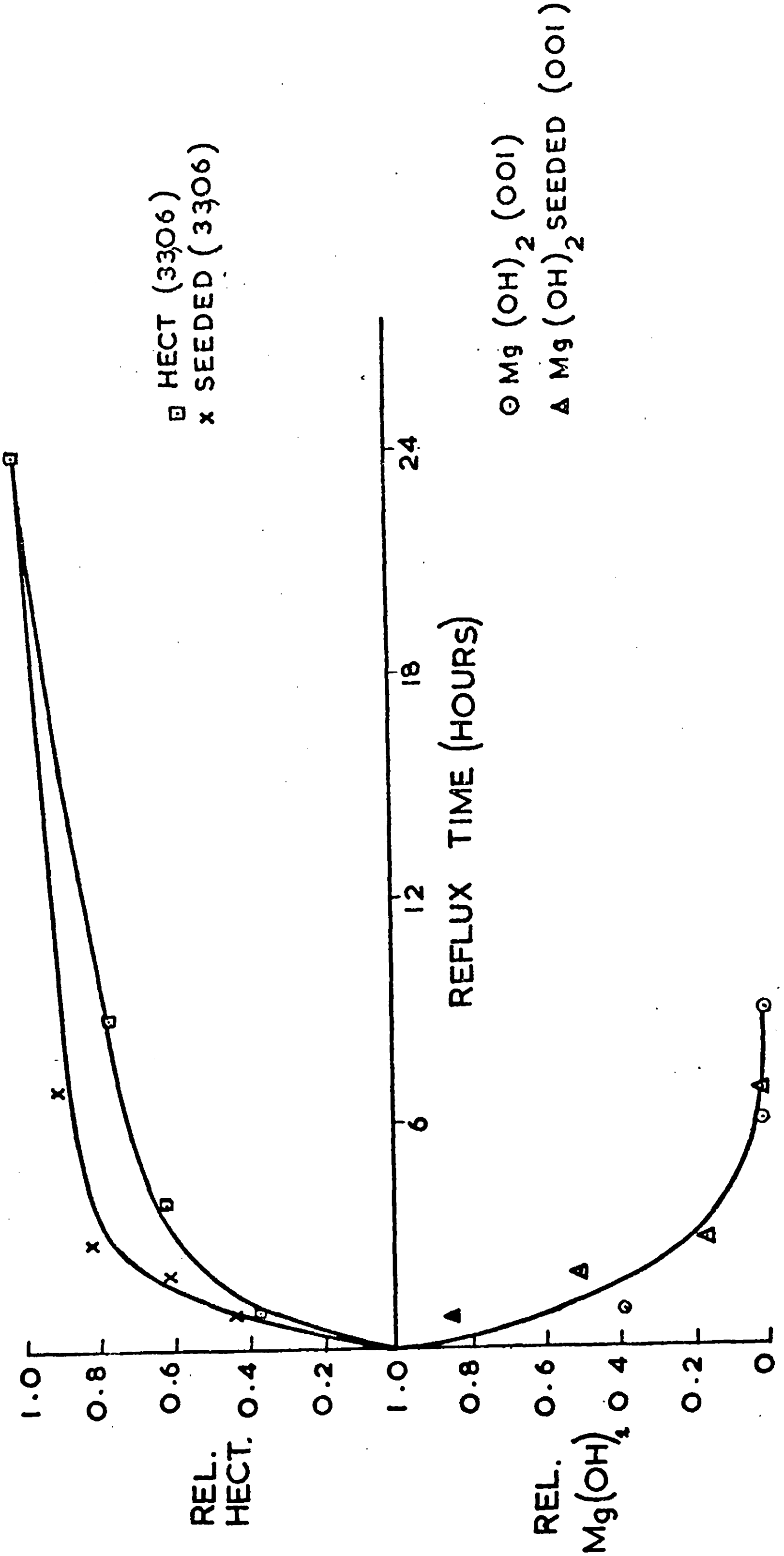
TABLE 9. Relative amounts of $Mg(OH)_2$ and hectorite with reflux time.

Time	$Mg(OH)_2$ I(001)mm	Width mm	Integrated Intensity	Relative Intensity	Hectorite I(06)mm	Width mm	Integrated Intensity	Relative Intensity
0	158	10.0	1580	1.00	-	-	-	-
1 hr.	64	9.6	614	0.39	7.4	14	104	0.38
4 hrs.	10	4.0	40	0.03	17.0	10	170	0.62
9 hrs.	-	-	-	-	19.0	11	209	0.76
24 hrs.	-	-	-	-	29.0	9.5	276	1.00

TABLE 10. Relative amounts of $Mg(OH)_2$ and hectorite from seeded run.

Time	$Mg(OH)_2$ I(001)mm	Width mm	Integrated Intensity	Relative Intensity	Hectorite I(06)mm	Width mm	Integrated Intensity	2% seed Correction	Relative Intensity
0	111	5.5	605	1.00	-	-	-	-	-
1 hr.	97	5.3	514	0.85	13	11.0	143	140	0.44
2 hrs.	61	5.0	305	0.50	17	12.0	204	200	0.61
3 hrs.	26	4.0	104	0.17	25	11.0	275	270	0.82
7 hrs.	3	2.0	6	0.01	30	10.0	300	294	0.89
2 days	-	-	-	-	31	11.0	341	334 *	1.00
5 days	-	-	-	-	35	10.0	330	323 *	-

* Average 329



REL. HECT.
1.0
0.8
0.6
0.4
0.2
REL. Mg(OH)$_2$
1.0
0.8
0.6
0.4
0.2
0
6
12
18
24
REFLUX TIME (HOURS)
⊡ HECT (33O6)
x SEEDED (33O6)
⊙ Mg (OH)$_2$ (OOI)
▲ Mg (OH)$_2$ SEEDED (OOI)

FIGURE 6.

A series of micrographs was taken during the first 24 hours of a synthetic run from samples of a slurry containing $SiO_2/MgO/LiF = 2.0/1.0/0.25$, the same as the above.

Since the reaction is rapid, synthesis may even occur at room temperature or below. As soon as the above slurry was mixed it was cooled to 0°C and a sample prepared for electron microscopy. The slurry was then allowed to equilibrate to room temperature and another sample prepared by freeze drying. The effect of this treatment is shown in Plates 41 and 42 with the corresponding diffractions in Plates 50 and 51. The spacings from the diffraction patterns (Table 11), show that brucite is the only phase detectable in both cases, although the micrographs show a slight degree of attack on the platelets even on warming to room temperature.

Samples were then taken immediately before refluxing and during a period of 24 hours. Specimens for electron microscopy were prepared in the usual way by drying down a drop of the sample suspended in water at 30°C. The change from brucite to hectorite during one day of refluxing is shown in the spacings in Table 11 measured from the diffractions shown in Plates 51 to 56. The micrographs corresponding to these diffractions are shown in Plates 43 to 48.

Comparison of the room temperature samples prepared by freeze drying and by evaporation at 30°C shows that even treatment

TABLE 11.

Brucite $Mg(OH)_2$	$0^{\circ}C$ Freeze Dried		$0^{\circ}C$ Equilibrated To Room Temp. Freeze Dried		Room Temp. Dried At $30^{\circ}C$		1 Hour		1½ Hours		2 Hours		7 Hours		1 Day		Hectorite
2.73	2.73		2.73		2.74	4.48	2.73	4.51	2.73	4.52	2.73	4.53	-	4.54		4.54	4.54
2.37	2.34		2.34		2.34	2.56	2.35	2.58	2.35	2.59	2.36	2.59	-	2.58		2.59	2.58
1.79	1.78		1.78		1.79	-	1.78	-	-	-	-	-	-	1.71		1.71	1.72
1.57	-		1.58		-	1.52	-	1.52	1.58	1.52	1.58	1.53	1.58	1.52		1.50	1.51
1.49	1.49		1.49		1.48	-	1.49	1.30	1.49	-	-	1.30	-	1.30		1.30	1.31
1.37	1.39		1.39		1.39	-	1.38	-	-	-	-	-	-	-		-	1.26
1.31	1.30		1.30		1.31	-	-	-	1.31	-	-	-	-	-		-	0.99
1.18	1.19		1.18		1.16	-	1.17	-	-	-	-	-	-	-		-	0.88
1.01	1.00		1.00		-	-	-	-	-	-	-	-	-	-		-	-
0.95	0.93		0.94		0.95	-	0.94	-	-	-	-	-	-	-		-	-

at $30^{\circ}C$ produced some hectorite material (Plate 43), showing platelets with slightly curled edges surrounded by a low contrast fringe. After refluxing for one hour the brucite platelets have become more disordered and reduced in size (Plate 44) and displaced from the centre of ring like structures, the 'doughnut' forms seen in Plates 9 to 11 and 35 and 36. After 1½ and 2 hours the doughnuts are clearly evident (Plates 45 and 46) and become filled in and enlarged after 7 hours with the appearance of curled edges and folds (Plate 47). The morphological changes are summarised in Figure 7.

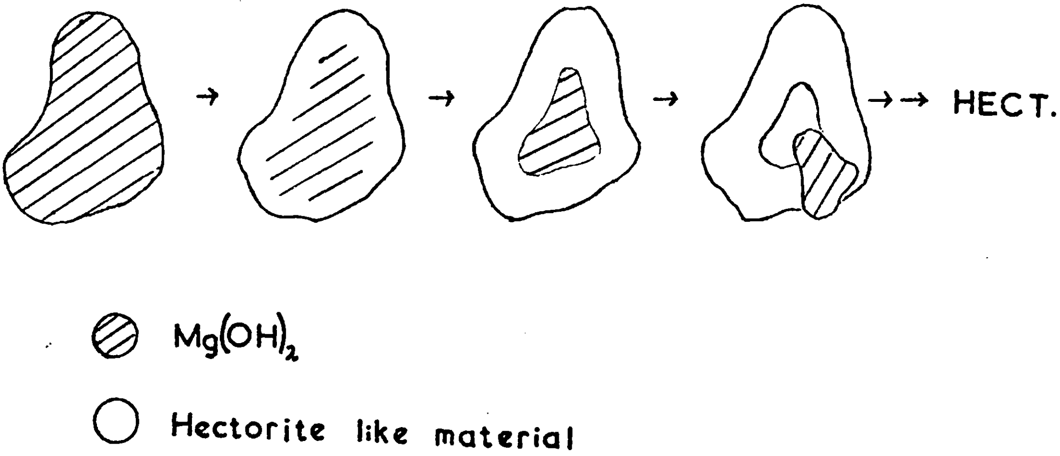


Figure 7. The changes in brucite to hectorite with refluxing.

Viewed at right angles to the c-axis in Figure 8 the process is visualised as the adsorption of silicic acid molecules on and in between the brucite platelets.

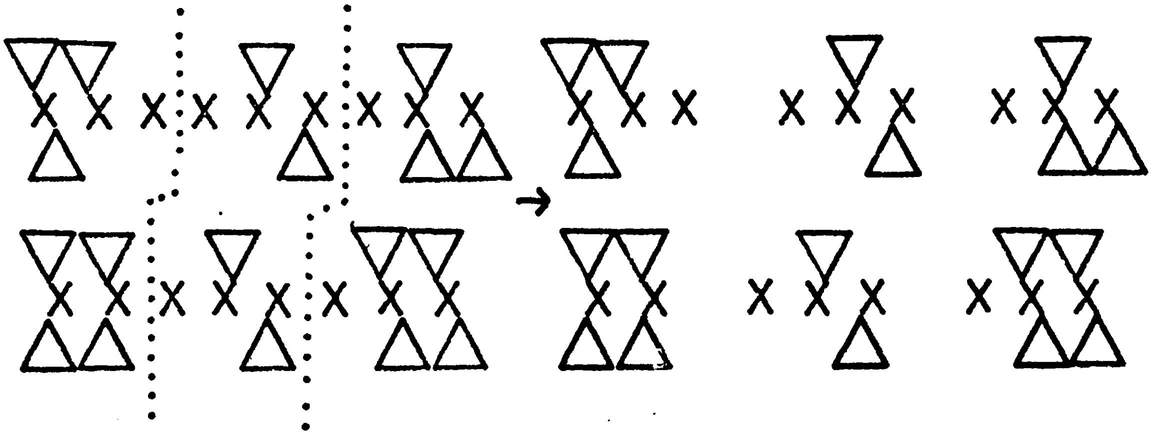


Figure 8. Formation of doughnut structure.

The mechanical strain set up within the brucite crystal at the diffusion front will cause the platelet to rupture thus displacing the centre portion leaving a doughnut structure. Thereafter the process will be a solution one, the Mg^{2+} ions being produced by the remaining brucite centres, to give filled in doughnuts and sheets of hectorite.

Similar structures were found in slurries heated in polypropylene (Plates 35 and 36), this served as a check that the effects were not influenced significantly by glass.

The most direct evidence of a solid phase reaction arises from the arcing patterns seen in Plates 54 and 55 where both $Mg(OH)_2$ and hectorite diffractions are present.

Brucite has hexagonal symmetry and so a single crystal lying at right angles to the electron beam with respect to the ab plane will give rise to a hexagonal spot pattern. Epitaxial growth of a phase on this crystal will give additional diffractions related to the original. If the new phase has planes parallel with approximately the same spacing as the host, the diffraction pattern will have the same orientation. Arcs will be formed instead of spots where the planes are not quite parallel to those of the host (Figure 9): the angle α, subtended by the arc to the centre of the pattern, is the angle of divergence of the planes from parallel alignment.

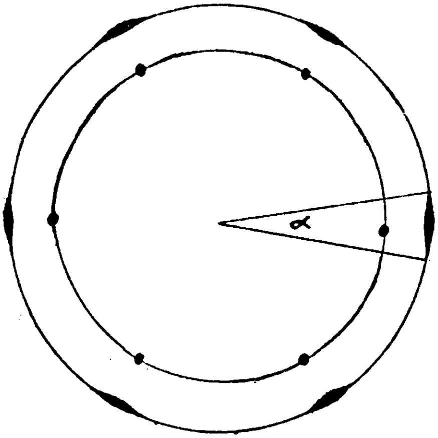


Figure 9. Ideal arcing pattern from hexagonal spot diffraction.

This effect is shown in Plate 57 with hectorite arcs opposite the spots of brucite. The spacings giving rise to the arcing are as follows :

Hectorite dÅ	Index. hexagonal,	orthohexagonal.	Brucite dÅ	hexagonal
1.51	300	33, 06	1.58	110
2.58	110	13, 20	2.71	100

The units cells have been drawn to scale in Figure 10 showing the the unit cell of brucite lies at 30° to that of hectorite. This means that the 110 planes of hectorite are parallel to the 100 planes of brucite, as are the 300 planes of hectorite and the 110 planes of brucite, thus accounting for the arcing effects from these planes. It will be seen that the silicon atoms lie approximately over the oxygens of the brucite layer as would be expected in the growth of the tetrahedral layer in hectorite.

It is not completely clear whether this epitaxy within the doughnut indicates the formation of hectorite as such or an intermediate "silicated magnesium hydroxide". However this analysis does show that silica is bound to the brucite layers in an orderly way.

The rapid rate of this reaction could be attributed to the properties of Li^+ and F^- in relation to silicic acid and brucite.

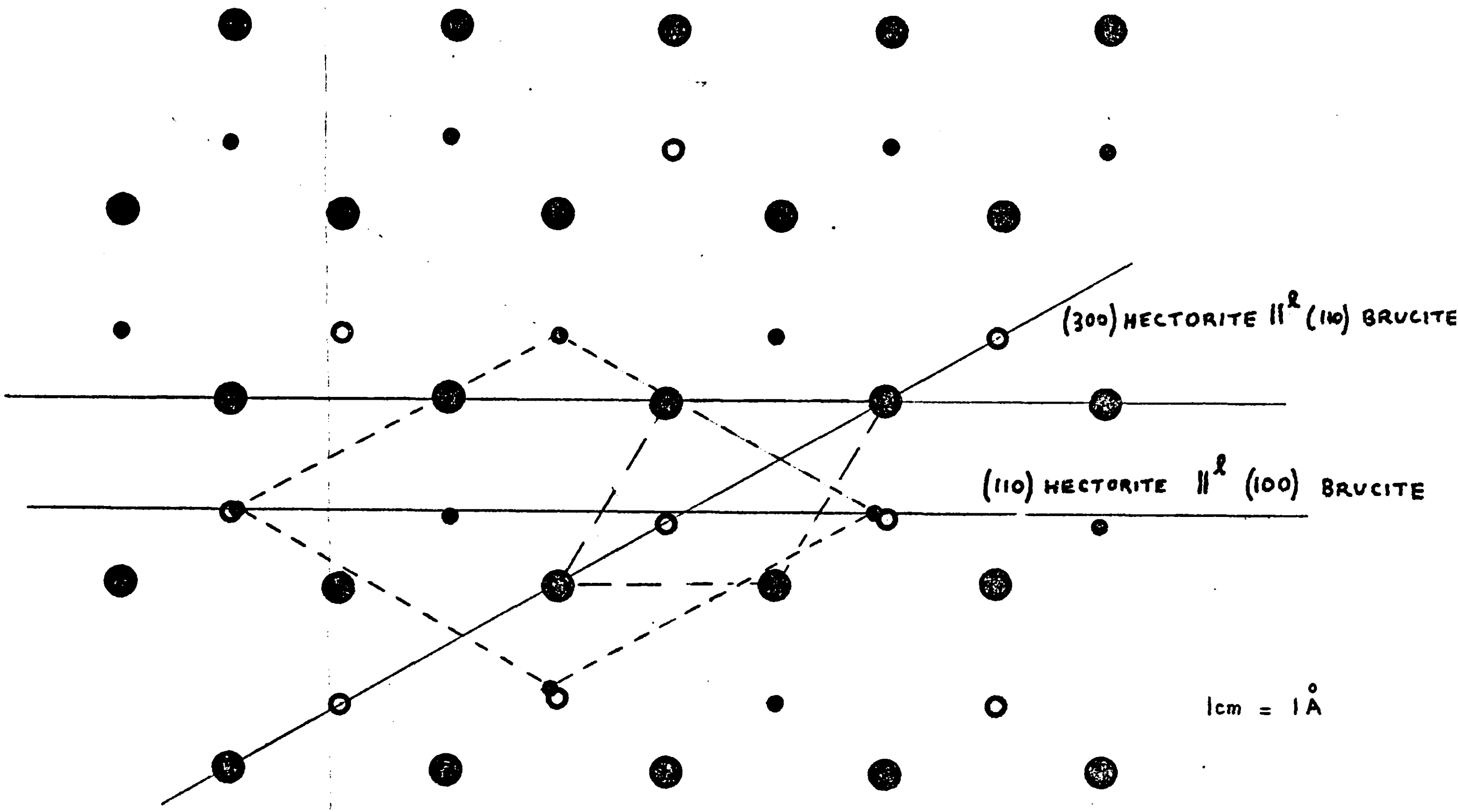


Figure 10. Scale drawing of a silica layer superimposed on the surface of brucite. The unit cells of brucite and hectorite are shown.

● MAGNESIUM
• SILICON
○ OXYGEN

The incorporation of Li^+, ionic radius 0.68 Å, into the brucite lattice, the ionic radius of Mg^{2+} being 0.66 Å, during the solution stage of growth will give a net - ve charge to the brucite layer. The - ve layers would lose OH^- more readily which would encourage the adsorption of $Si(OH)_3O^-$ molecules as shown in Figure 11.

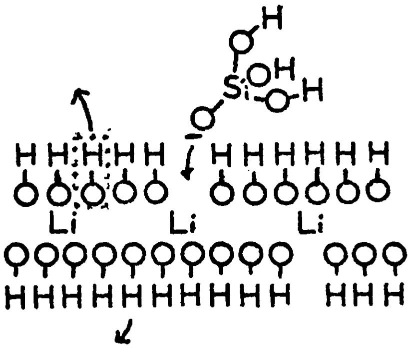


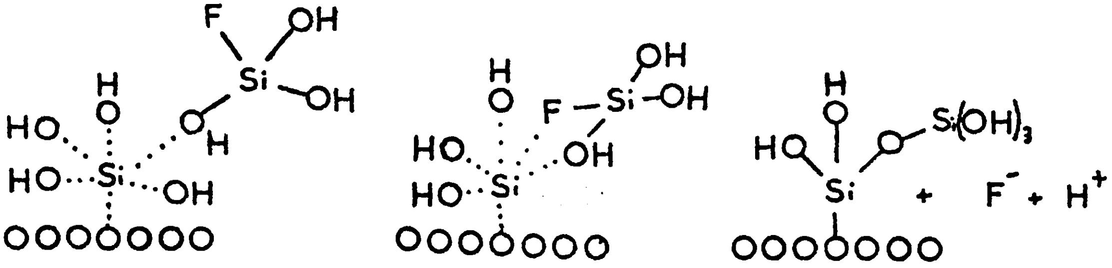
Figure 11. Adsorption of $Si(OH)_3O^-$ on Li^+ substituted brucite.

Indeed Granquist and Pollack have shown that the addition of LiOH to a slurry of SiO_2 and MgO increases the rate of synthesis compared to a slurry containing no LiOH. The net - ve charge will be balanced by Li^+ ions outside the layer.

Li^+ may have another role through its ability to stabilise - ve charges on silica as indicated by Iler. Low SiO_2/Li_2O ratios of 4/1 to 25/1 are sufficient to produce this effect and are of the order of the ratios used in the above experiments. These - ve charges may thus be stabilised prior to the polymerisation of the silicic acid molecules on the surface of brucite.

The F^- ion may act as a catalyst in the polymerisation stage. Iler postulates that an increase in the coordination number of silicon from 4 (in $Si(OH)_4$) to 6 will occur only when an OH^- or F^- ion combine in $Si(OH)_4$.

Along these lines a possible mechanism could be as shown in Figure 12.



Figurè 12. Polymerisation of silica by 6 fold coordination mechanism.

The linked unit would then be able to bond to the surface as in Figure 10 , Chapter I.

F^- ions could also replace OH^- ions in the brucite lattice. F^- is slightly smaller than OH^- (1.36 vs 1.53 Å) and so will be more mobile than the OH^- leading to a more rapid creation of + ve holes available for $Si(OH)O^-$ ions to react with.

The pH of this reaction falls in the range 8.5 to 9.5. The relative rate of polymerisation against pH is shown in Figure 13 (Gimblett F.G.R. 1963).

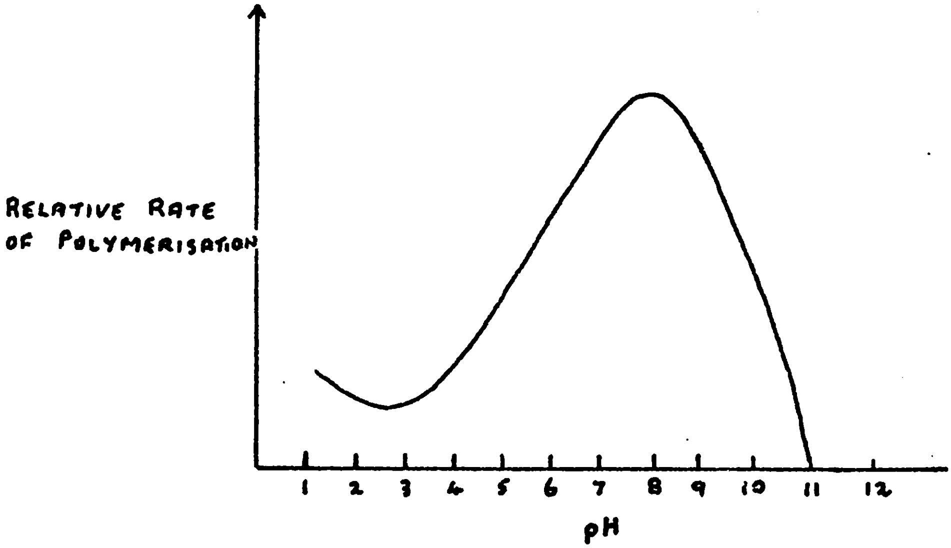


Figure 13. Relative rate of polymerisation with pH.

According to these authors the higher rates of polymerisation are in the range of pHs 8.0 to 10.5, which includes the above range, corresponding to a reasonable concentration of single and undissociated molecules of silicic acid. They visualised the polymerisation occurring with silicon in coordination (Figure 14).

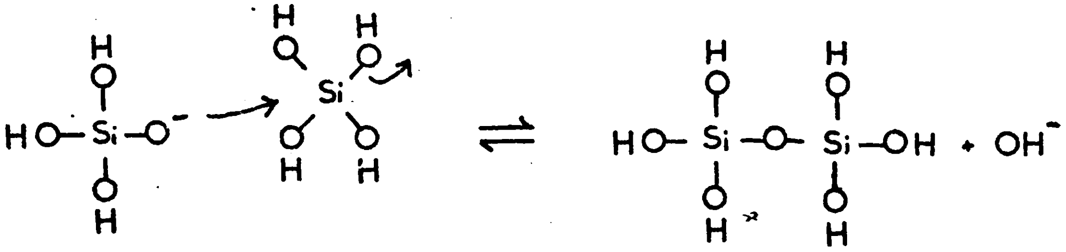


Figure 14. Polymerisation of silica (after Gimblett 1963).

PART 3.

Other Techniques of Identification.

The main analytical techniques used in the above experiments were X-Ray diffraction, electron diffraction and D.T.A. The cation exchange capacity was also determined for the final product in the slurry reaction as a further indication of the nature of the clay formed. Density gradients techniques were investigated both to determine the density of the synthetic hectorite and as a possible means of following the progress of the reaction by separation of the intermediate products.

Cation Exchange Capacity.

A rapid means of determining the cation exchange capacity has been described by Robertson and Ward (1951) using the adsorption of methylene blue.

Experimental.

The product chosen was a synthetic hectorite obtained by refluxing a slurry containing a molecular ratio of $SiO_2/MgO/LiF$ of 2.0/1.0/0.25 in glass.

The product was weighed before and after drying at 110°C for two hours to find the water content. The water content of methylene blue was similarly found.

A suitable weight of clay was transferred to a glass stoppered bottle and shaken with 5 ml of water and left standing overnight. 50 ml of 0.3% dye was added and the suspension shaken for 20 minutes. It was then filtered into a boiling tube, the first light coloured filtrate rejected, and the remaining filtrate shaken well when the bulk of the liquid had been collected. The concentration of the filtrate was found from calibration curves drawn from adsorption values at 665 m . Data for this experiment is shown in Table 12. The cation exchange capacity in milliequivalents per 100 g of dry clay was calculated as follows :

$$\frac{(\%\text{ of dye initially} - \%\text{ dye in filtrate}) \times \%\text{ purity of dye}}{\frac{\text{Equivalent weight of dye}}{1000} \times \frac{100}{\text{volume of dye in ml.}} \times \text{dry weight of clay}}$$

TABLE 12.

Percentage of dye initially = 0.3

Percentage of dye in filtrate = 0.07

Percentage of dye adsorbed = 0.23

Moisture content of dye = 12.3%

Purity of dye taken as = 87.7%

Milliequivalent of dye = 0.3199 g (anhydrous)

Volume of solution used = 50 ml

Weight of clay (moist) = 0.3324 g

Moisture content of clay = 13.8%

Dry weight of clay = 0.332 x 0.862 g

Results.

The ionic capacity is :-

$$\frac{0.23 \times 87.7}{(0.3199 \times 2) \times 0.332 \times 0.862} = 81.7 \text{ milliequivalent/100 g.}$$

Repetition of this determination gave results around 80 milliequivalents/100 g which agrees with results for natural smectites having values of 80-100 milliequivalents/100 g.

The main exchangeable cation in Granquist and Pollack's synthetic hectorite was Li^+. Ionic exchange adsorption proceeds more quickly than physical adsorption: Robertson and Ward (1951) found that shaking at room temperature for 20 minutes was a measure of mainly ion exchange.

Density Gradient Experiments.

One method of determining the density of a pure compound is to float the material in a liquid of higher density and then add a sufficient quantity of a lighter liquid till the material just sinks. By weighing a known volume of this liquid the density of the material can be found. Clays however usually have a range of densities and a more satisfactory technique is to employ density gradient columns.

Experimental.

Trial experiments were carried out with mixtures of sym-tetrabromoethane, $C_2H_2Br_4$ and benzene.

5 mls of $C_2H_2Br_4$, density 2.96, was pipetted into a test tube and a further 5 mls of benzene, density 0.89 carefully added.

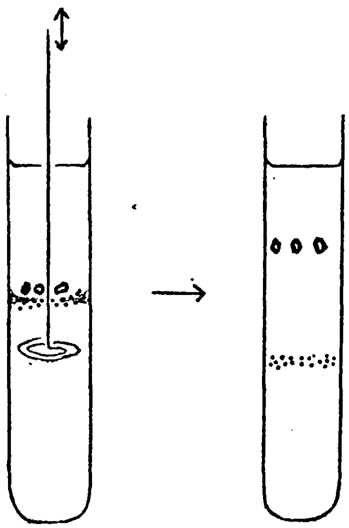


Figure 15.

Slow continuous strokes up and down about the liquid interface with a stirrer (Fig. 15) gave an approximately linear gradient extending for about 2 cms. Columns were initially stored in a water bath maintained at 25°C but it was found that the gradients remained stable for about two weeks when kept at ambient room temperature.

An approximate calibration of the gradients was normally made with silica gel, average density, 2.2 and potassium dichromate, density 2.69. Other standards used were $Mg(OH)_2$ (2.38) and LiF (2.6).

Organic crystals of compounds (of accurately known density) insoluble in either liquid were tried but were found to adsorb the liquids thereby altering their density.

The products were all dried at 110°C for 2-3 hours before use. The maximum amount of material used was 15-20 mgs.

The loaded columns were centrifuged at about 150 g for 10 minutes to accelerating the settling process.

Results.

One difficulty that arose was the tendency of the particles to form clusters of heterogeneous material to give broad bands. Even a sample of a mixture of silicic acid, $Mg(OH)_2$ and LiF gave broad bands: when added in order of decreasing density, sharp bands were obtained. Attempts to break up these clusters by ultrasonicating the samples in the lighter liquid before addition to the column gave no improvement in the results. Acetone was also tried as the lighter liquid with the same result.

However, the change of density in the products obtained from the ratio experiments described in Part 1 can be seen in Figure 16. With low silica content the densities tend to be that of $Mg(OH)_2$. With increasing silica content the densities approach that of natural hectorite.

The change in density of a slurry composed of SiO_2/MgO/LiF in the ratio of 2.0/1.0/0.25 with time is shown in Figure 17.

Figure 16. Density of products obtained from the ratio experiments described in Part 1.

Left to right:-

SiO_2/MgO (LiF constant at 0.25)

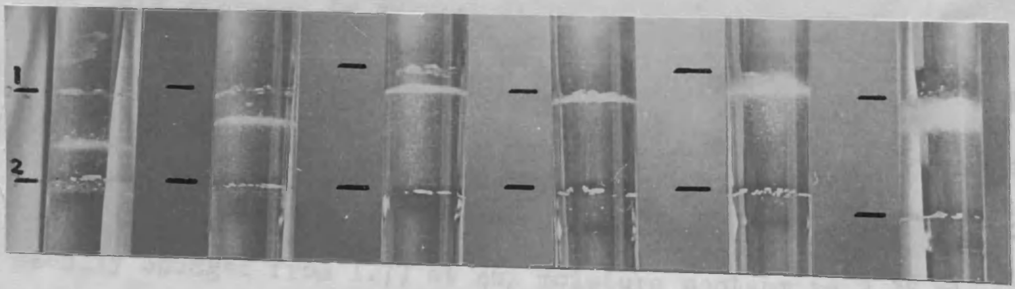
0.2/1.0   0.6/1.0   1.0/1.0   1.4/2.0   2.0/1.0   Hectorite(nat)

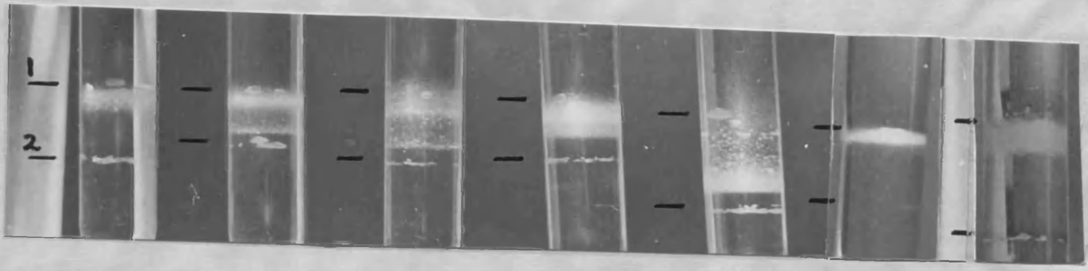
Figure 17. Density of products obtained from kinetic experiments.

Left to right:-

Time of reflux

Room temp.   1hr.   2hrs.   4hrs.   6hrs.   1day   Hectorite.





DENSITY REFS. 1. SiO_2

2. $K_2Cr_2O_7$

The room temperature sample has an average density of 2.3. Up to six hours of refluxing the density rises to 2.6. Thereafter the product becomes lighter again, the six day sample having a density of 2.3-2.4.

These results fit the observation that after one day of refluxing the slurry adsorbs more and more water to become opalescent in appearance.

The decrease in density then can be related to the increasing ability of the product to adsorb structural water. De Wit and Arens (1950) have shown the decrease in density in relation to the humidity of the environment for several days. With montmorillonite the density changed from 1.77 at 46% moisture content to 2.35 when dry.

Attempts were made to isolate the doughnuts intermediates shown in Plate 46. from $Mg(OH)_2$ and LiF. Samples were withdrawn from various regions of the column containing a sample of this material for examination in the electron microscope. The samples could be prepared simply by evaporation of the liquids from droplets containing the material on the support grids. The micrographs showed a greater concentration of the doughnuts but the purity of the separation was not thought high enough to justify larger scale experiments.

This technique was used to determine the completion of the slurry reaction very quickly, since aqueous droplets of slurry were miscible with the lighter liquid, ethanol. Samples were pipetted onto the column and when the density was in the region of 2.3-2.4, the reaction was complete.

Swelling behaviour of synthetic hectorite.

The synthetic hectorite prepared had in general an 001 spacing of about 13.6 Å. The effect of glycol adsorption and heating the product to 550°C were investigated.

Experimental.

The swelling behaviour of the synthetic hectorite from slurries containing a ratio $SiO_2/MgO/LiF$ of 2.0/1.0/0.25 treated in Pyrex and polypropylene were examined by X-Ray diffraction.

The products were saturated with ethylene glycol by a method described by Brunton (1955). The powdered sample was spread thinly over an inverted petri dish, and placed in a beaker containing ethylene glycol which was covered with a watch glass. The glycol was heated to 60°C and the sample exposed to glycol vapour for four hours.

Results.

Examples of X-Ray diffractometer traces from slurries containing a ratio $SiO_2/MgO/LiF$ of 2.0/1.0/0.25 are shown in Figure 13. Table 13A gives the comparison of the swelling behaviour of products made in glass (Pyrex) and polypropylene. Both products expand to about 18 Å. On heating the products at 550°C for 2½ hours the basal spacing contracts and is much reduced in intensity. If the compound was of a swelling chlorite then the basal spacing would have remained around 14 Å on heating to this temperature with an increase in its intensity.

These results illustrate that these products are consistent with the behaviour of swelling smectites.

Figure 13. X-Ray diffractometer traced of SiO_2/MgO/LiF = 2.0/1.0/0.25 synthetic products.

A. Product heated at 550°C for 2½ hours.

B. Product treated with ethylene glycol.

C. Untreated product.

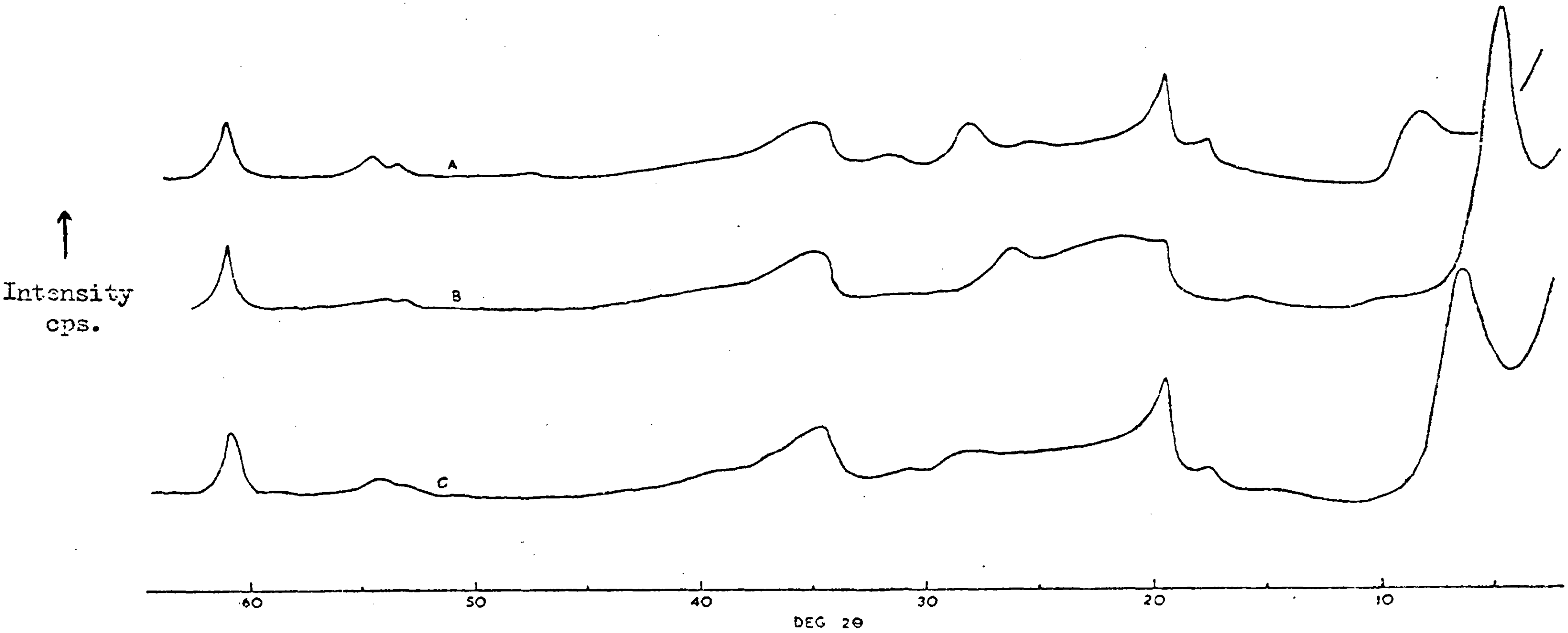

Intensity cps.
A
B
C
60
50
40
30
20
10
DEG 2θ

TABLE 13A.

Swelling behaviour of synthetic Hectorite

(001 spacings determined by X-ray diffraction (diffractometer))

Reaction Vessel	70°C Oven dried	Vapour saturation with ethylene glycol	550°C for 2½ hours
Pyrex	13.6	18.0	10.4
Polypropylene	13.6	18.4	10.6

(after Baird, Cairns-Smith, MacKenzie and Snell, 1971).

Stability of synthetic products in acid solution.

The stability of the synthetic product and intermediates formed by the refluxing of a slurry in glass with a ratio SiO_2/MgO/LiF of 2.0/1.0/0.25 towards acid treatment with HCl, was investigated.

Experimental.

Samples of $Mg(OH)_2$, a 2 hour reflux and a 6 day sample were dried at 110°C. Weighed portions, 0.02 g of each were dispersed in 10 mls of water. A sample of natural hectorite was prepared in the same way.

The solutions were then titrated with 0.1N HCl, allowed to equilibrate by shaking for one day and the pH recorded using glass electrodes. Solutions of the above samples containing 4 mls of acid were shaken for three weeks and the pHs were found to vary by about

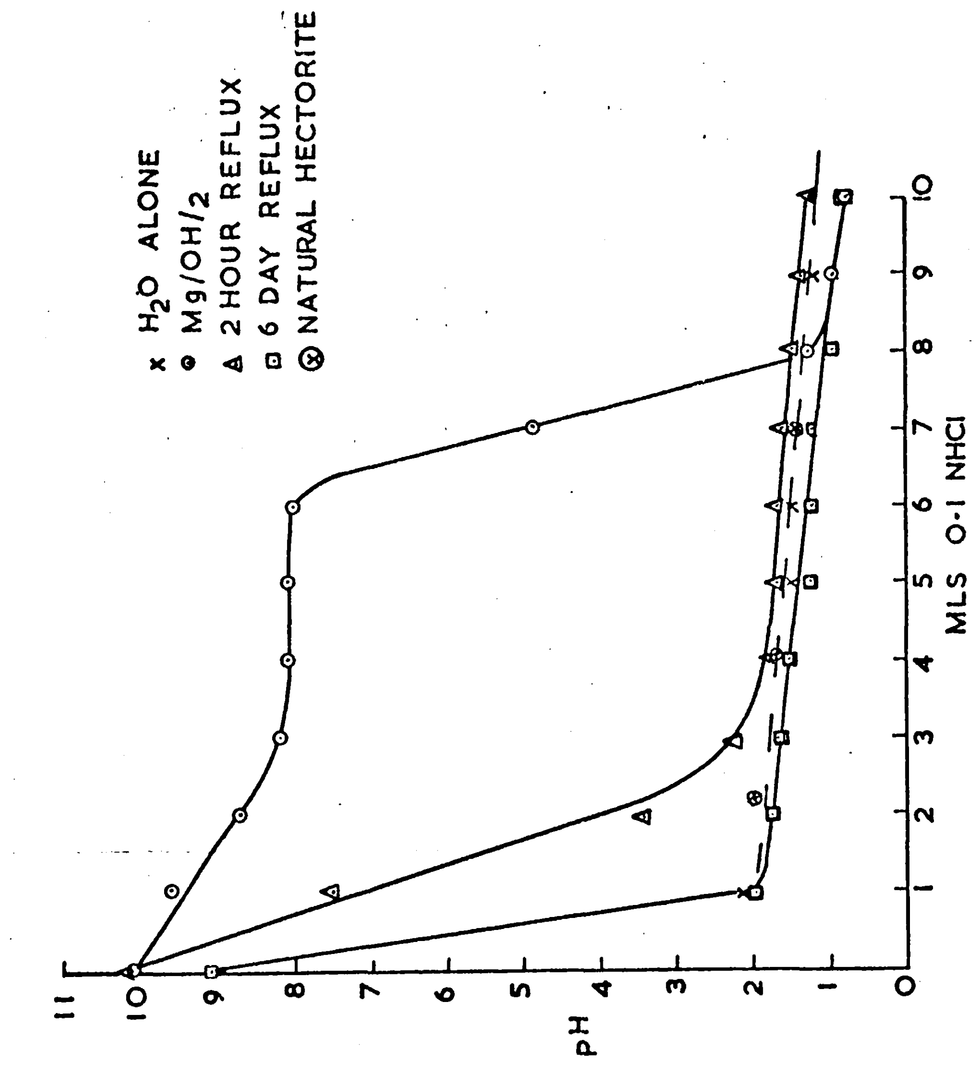

x H_2O ALONE
⊙ Mg/OH/2
Δ 2 HOUR REFLUX
⊡ 6 DAY REFLUX
⊗ NATURAL HECTORITE
pH
0
1
2
3
4
5
6
7
8
9
10
11
MLS 0-1 NHCl

FIGURE 18

0.1 of a pH unit showing that equilibrium had been attained after one day.

Results.

The results are shown graphically in Figure 18. The $Mg(OH)_2$ curve is typical of an acid titration against a simple base. The $Mg(OH)_2$ dissolved after the addition of 8 mls of acid. The two hour reflux product also showed a tendency to dissolve showing the product to be poorly formed. The six day reflux showed virtually the same curve as natural hectorite indicating that the product has the same resistance to acid attack as the natural product.

PART 4.

Slurries containing other ions.

Attempts were made to extend the technique to produce clays containing other ions namely Fe^{3+}, Ni^{2+}, Co^{2+}, Cu^{2+} and Al^{3+}. Trial experiments were made using Sn, Fe, Ni, Hg, Cs, Ag, Ca, Cr, Co, Cu, Ba, Al salts in up to 10% of the magnesium content. Most of these elements did not affect the synthesis of hectorite except those selected above.

Experimental.

Slurries were refluxed in glass and were prepared according to the ratios :-

$$SiO_2/MgO/R_xO_y/LiF = 2.0/0.25/0.75/0.25.$$

It was decided to add the ions in the form of solutions of nitrates rather than hydroxides or oxides to allow the ions a greater ability to achieve isomorphous replacement of Mg^{2+}. Chloride salts were not used since the chloride ion tends to adsorb onto hydroxides and would then inhibit the initial reaction. Samples were taken after one day, four days and seven days, washed and dried and then examined by X-Rays and electron microscopy.

Results.

With Fe^{3+}, Co^{2+} and Cu^{2+} no layer formation was found, the major phase being the oxides.

After seven days the Al^{3+} reflux gave material amorphous to X-Rays. With Ni^{2+} after seven days spacings of 2.67 Å and 1.54 Å were found, corresponding to some trioctahedral layer silicate formation. Tiller (1968) has shown that Cu^{2+} Zn^{2+} $(Co^{2+}Mn^{2+})$ Ni^{2+} are adsorbed at the octahedral edge sites on hectorite. It is possible that the ions used in these experiments are adsorbed at the edges of $Mg(OH)_2$ and thus inhibit the attack of silicic acid, the process postulated as being the initiator of the reaction. With Ni^{2+} being the least adsorbed, this allowed at least a poorly crystalline clay to be formed.

Slurry containing $Al(OH)_3$.

Since it has been proposed that hectorite forms by epitaxial growth on the brucite layer, the possibility arises that montmorillonite may be formed from a preformed gibbsite layer.

Experimental.

$Al(OH)_3$ was prepared by precipitation from an $AlCl_3$ solution with $NH_3(aq)$. The probable structure of this $Al(OH)_3$ is that of bayerite, one of the two forms of $Al(OH)_3$, the other being gibbsite.

The slurry was prepared according to the ratios :-

$$SiO_2/MgO/Al_2O_3/LiF = 2.0/0.25/0.38/0.25.$$

The slurry was refluxed in glass for seven days. Samples were taken after one, four and seven days, washed and dried prior to X-Ray and electron microscopy examination.

Results.

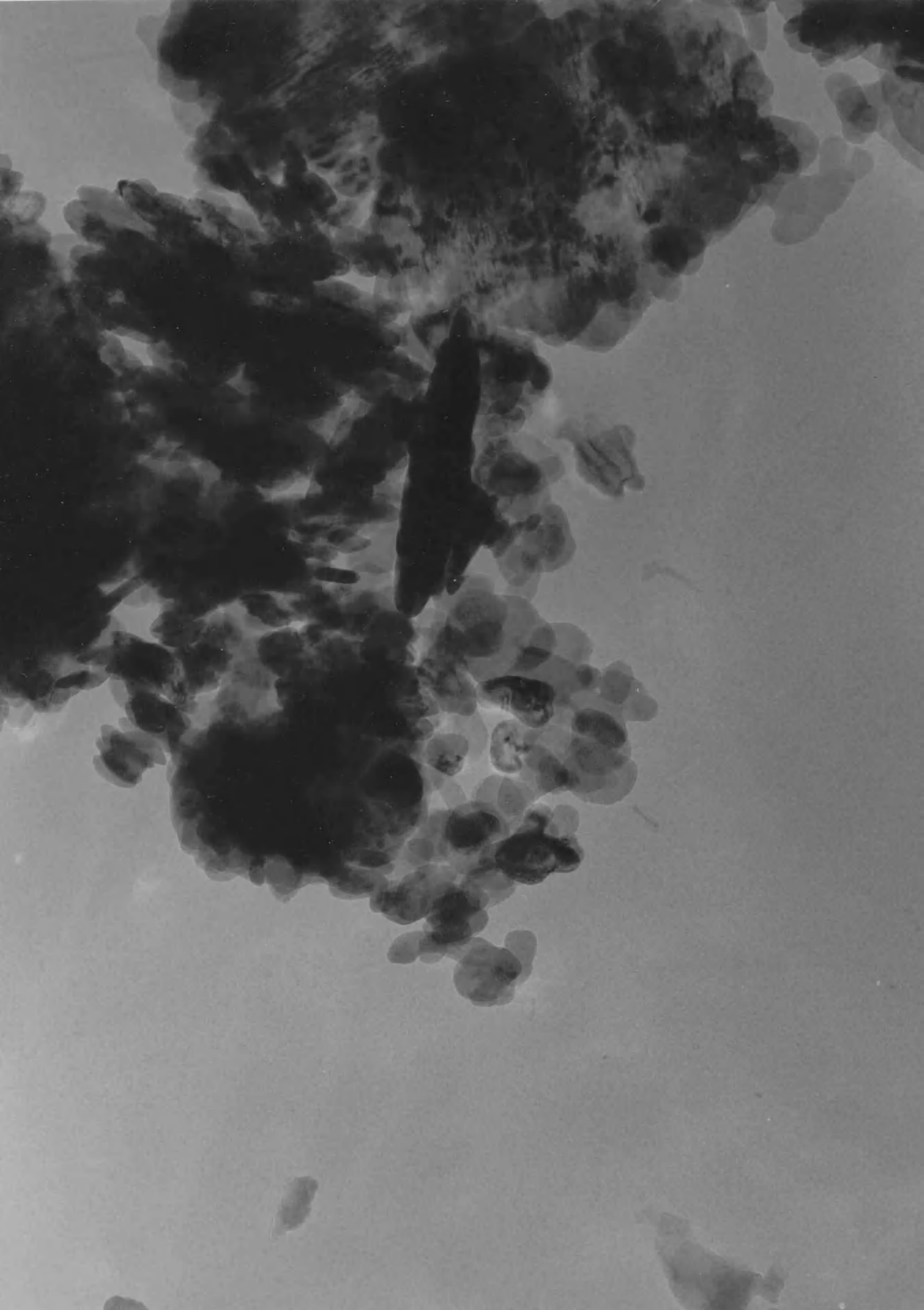
The spacings obtained from X-Rays are shown in Table 14.

TABLE 14.

$Al(OH)_3$ slurry dÅ	Saponite $(Mg,Al)_3(Al,Si)_4O_{10}(OH)_2$ dÅ
16.4	16.6
3.8	3.7
2.59	2.58
1.52	1.52

The correlation of the spacings was obtained with those of saponite. The presence of a preformed hydroxide in this case $Al(OH)_3$ provides the basic structure on which clay synthesis can occur.

Plate 1. $Mg(OH)_2$, showing plate-like morphology. (x 60K).



Selected Area Diffractions - Ratio Experiments (Glass)

(corresponding to plates 8 to 14)

The MgO/LiF ratio was kept constant throughout with a ratio of 1.0/0.25.*

Plate 2. $Mg(OH)_2$

Plate 5. $SiO_2/MgO = 0.4/1.0$

Plate 3. $SiO_2/MgO = 0.1/1.0$

Plate 6. $SiO_2/MgO = 0.7/1.0$

Plate 4. $SiO_2/MgO = 0.2/1.0$

Plate 7. $SiO_2/MgO = 2.0/1.0$

---

* The ratios stated for all the plates in this Chapter refer to the feed ratios of the slurries, which does not necessarily give the ratio of components in the final product. This is especially true of experiments using glass vessels, since additional silica may come from the glass.

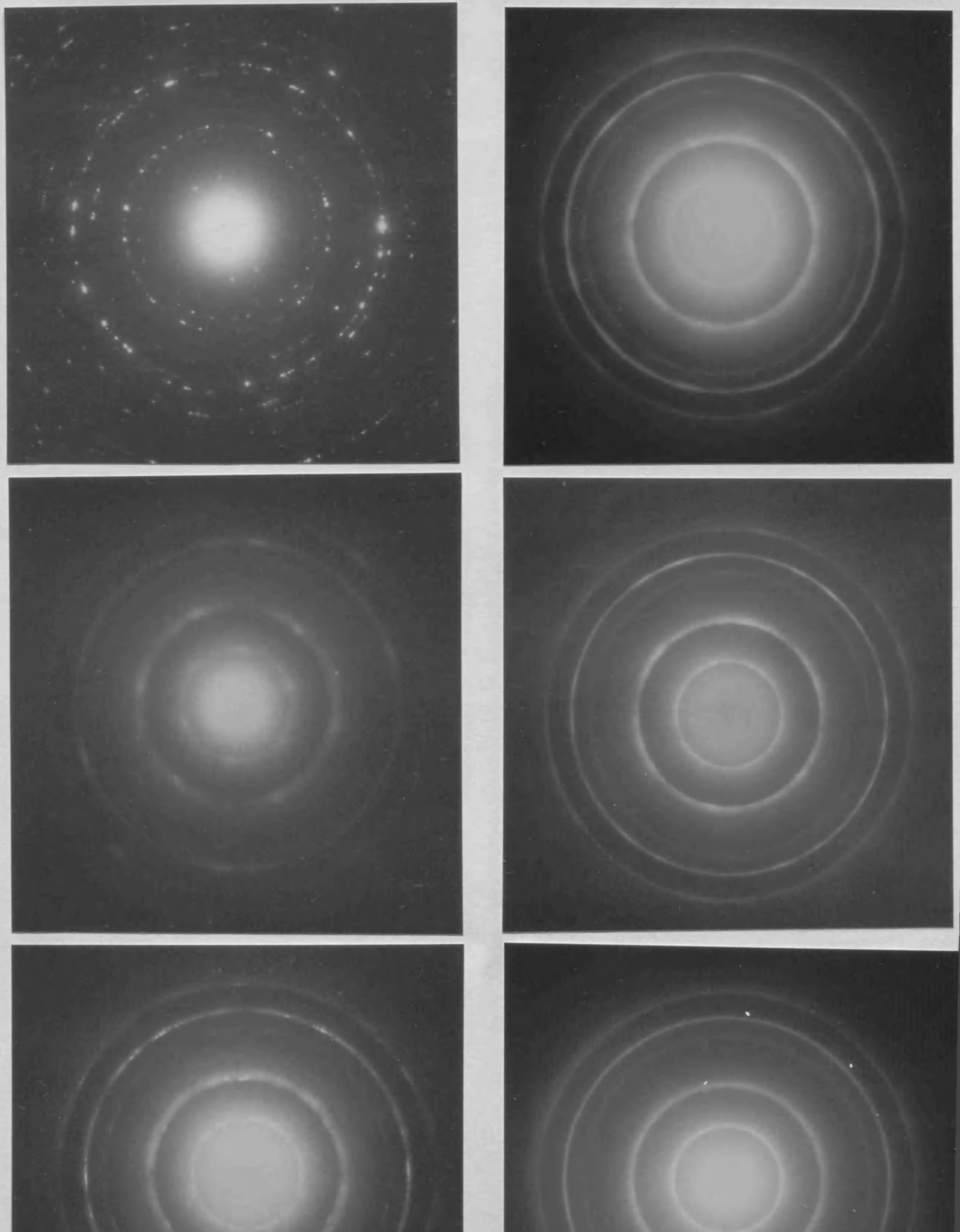


Plate 8. $SiO_2/MgO = 0.1/1.0$ (x 60K).

Plate 9. $SiO_2/MgO = 0.2/1.0$ (x 60K).

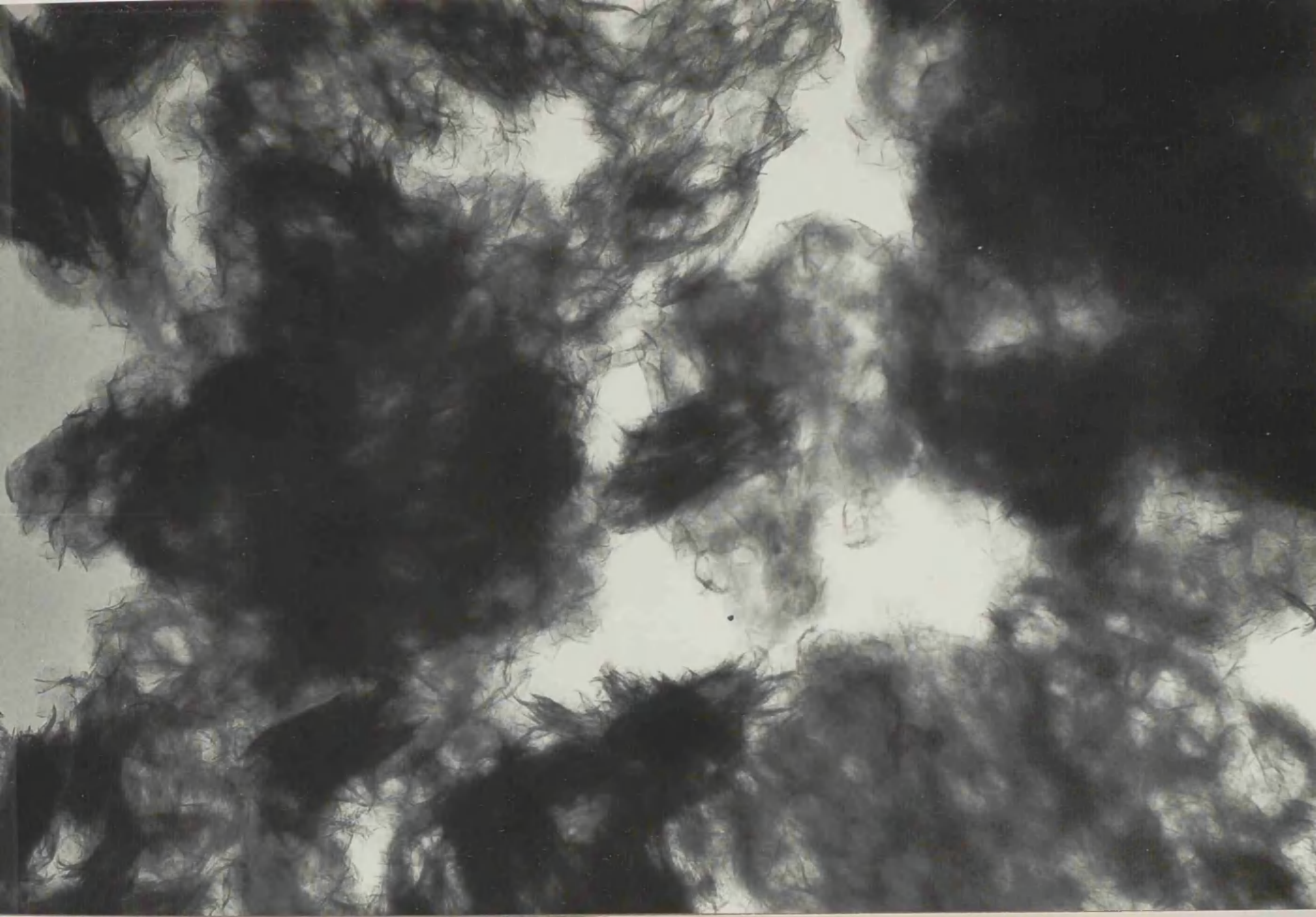


Plate 10. $SiO_2/MgO = 0.4/1.0$ (x 60K)

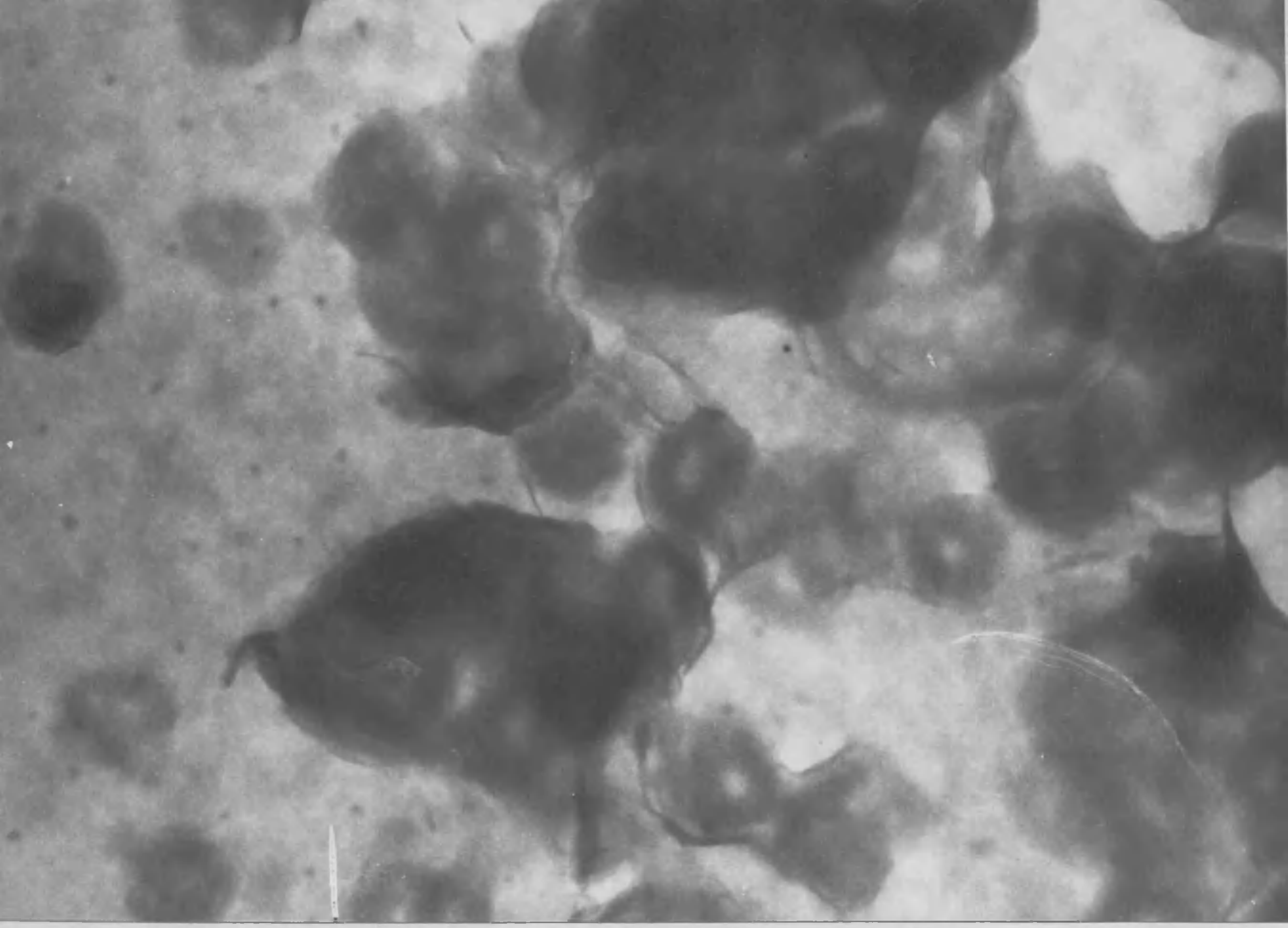


Plate 11. $SiO_2/MgO = 0.7/1.0$ (x 30K).

'Doughnut' morphology is arrowed.

Plate 12. $SiO_2/MgO = 0.7/1.0$ (x 60K)

Higher magnification of doughnut structures and curled edges.

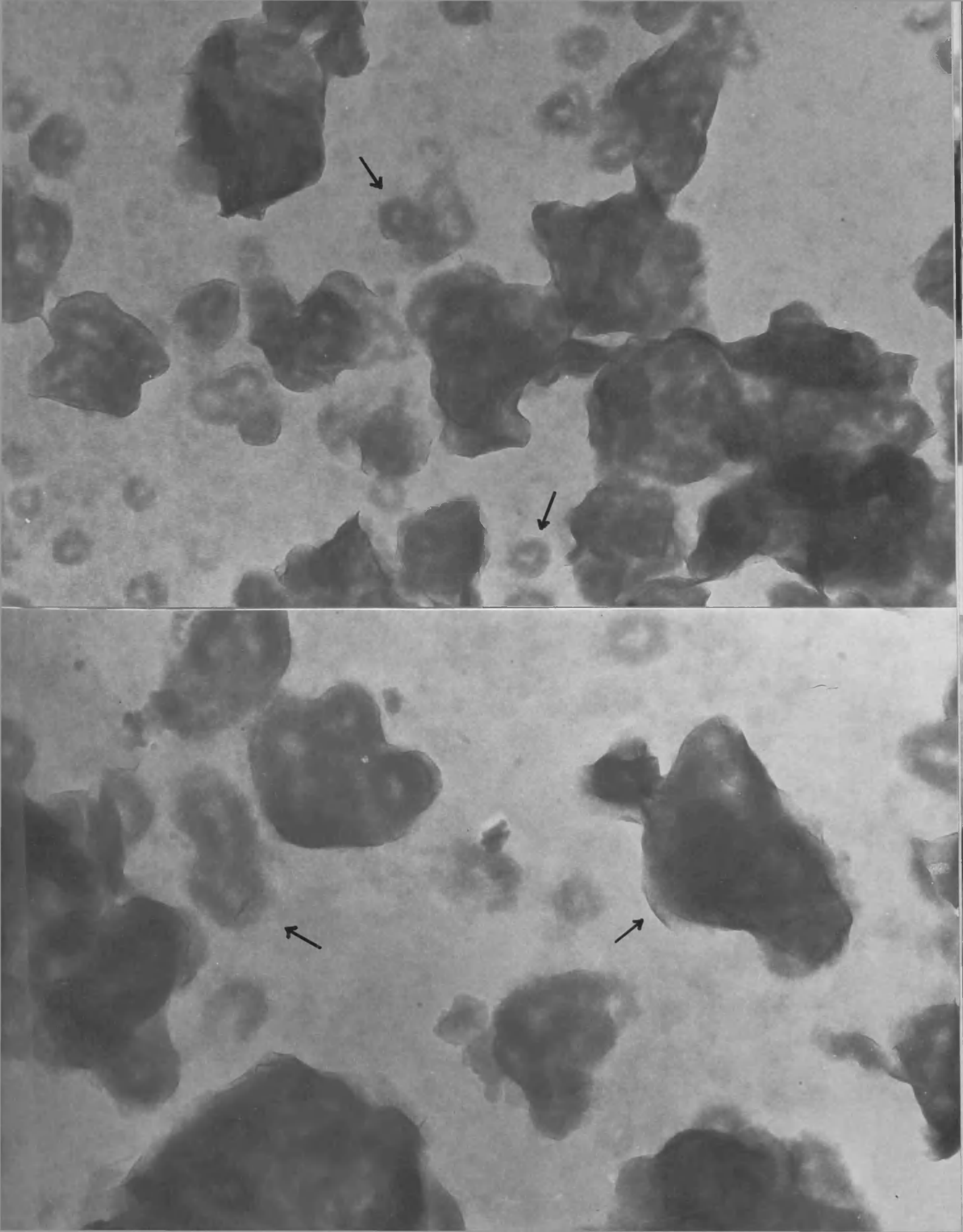


Plate 13. $SiO_2/MgO = 2.0/1.0$ (x 30K).

Shows folded sheet texture.

Plate 14. $SiO_2/MgO = 2.0/1.0$ (x 60K)

Higher magnification of folded edges.

Plate 15. Mg(OH)$_2$ alone refluxed in glass (Pyrex) (x 60K)

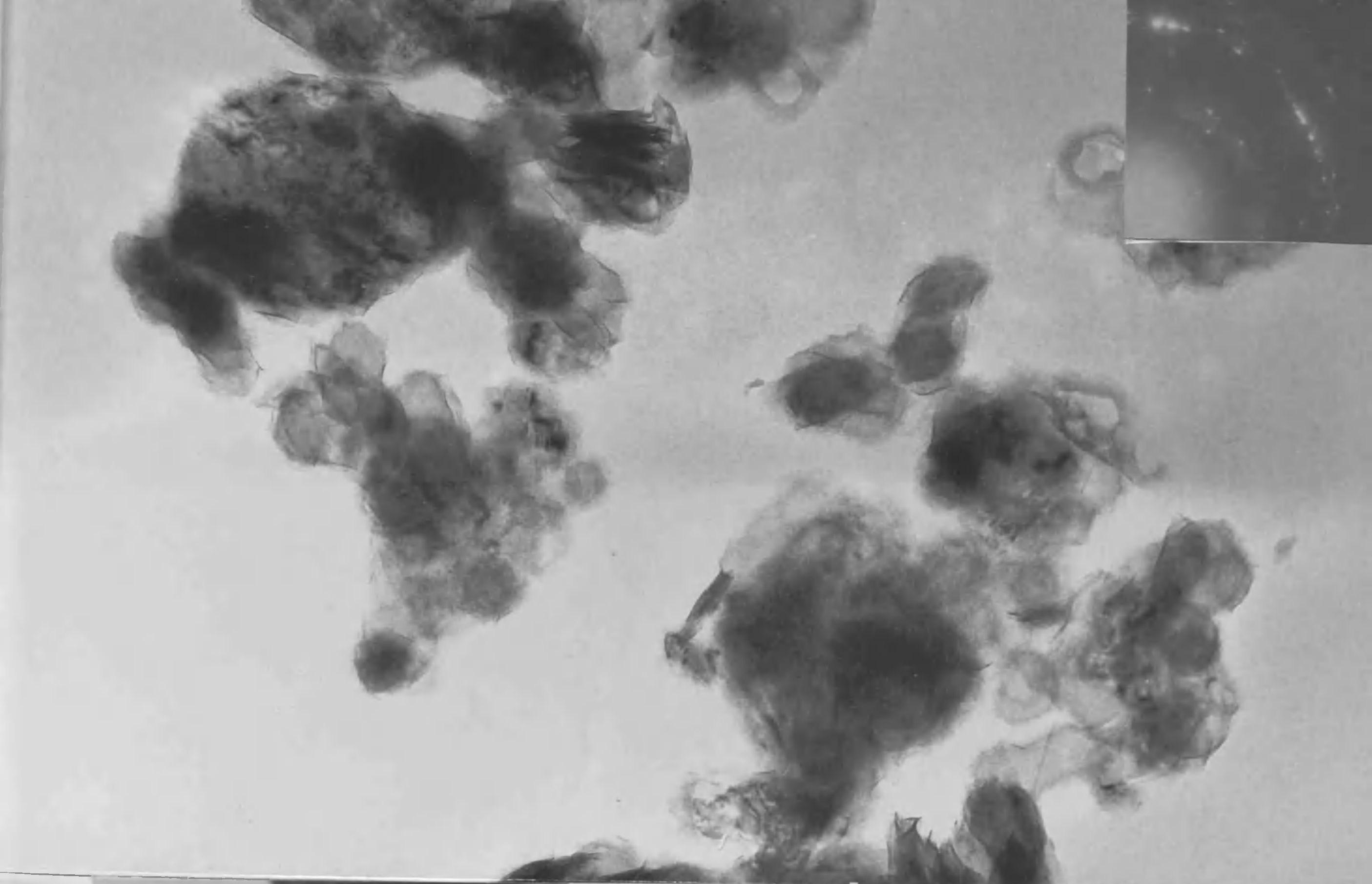
Plate 16. (inset) Diffraction pattern from above product

Shows presence of hectorite and Mg(OH)$_2$

Plate 17. Mg(OH)$_2$ and LiF refluxed in glass (Pyrex) (x 60K)

Plate 18. (inset) Diffraction pattern from above product

Only hectorite present.



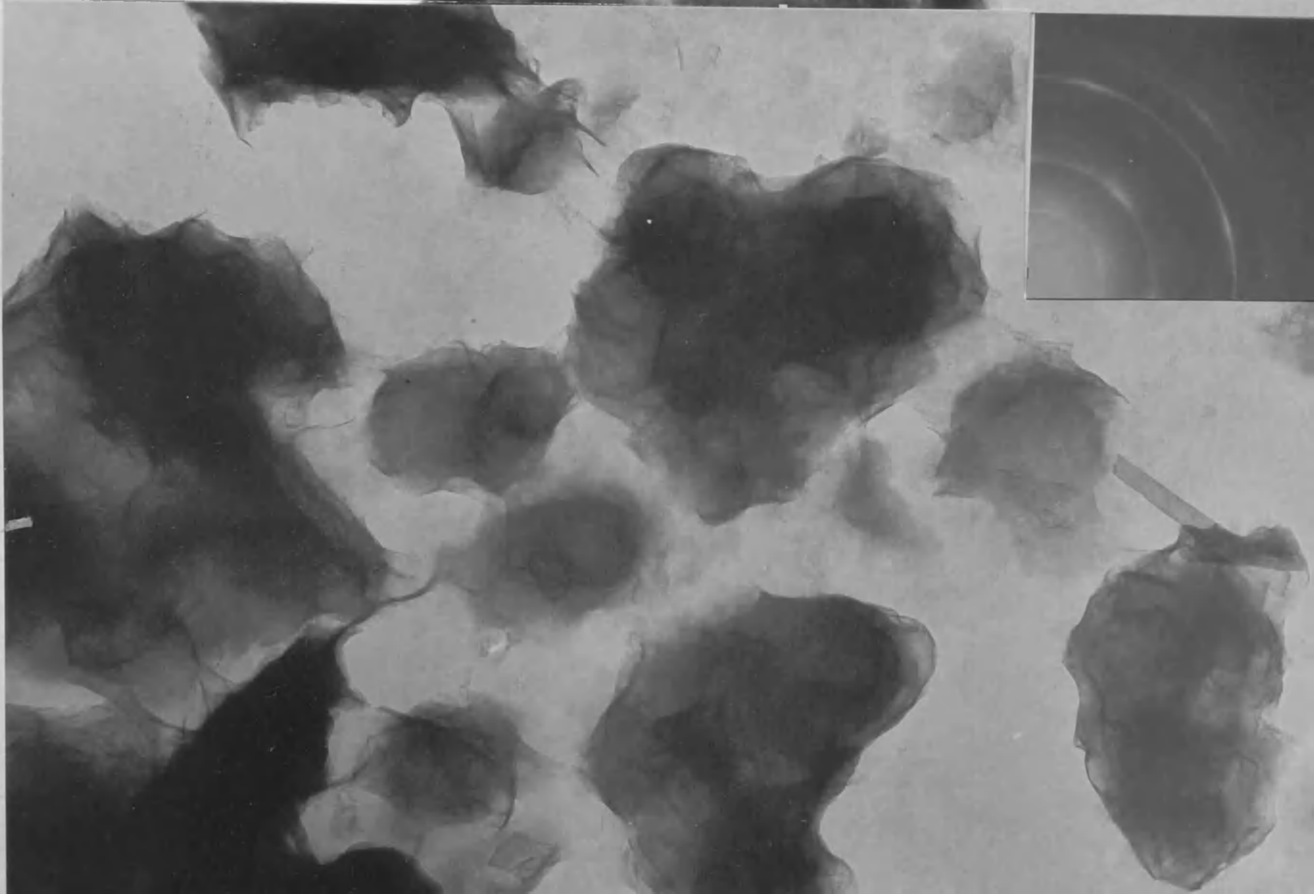


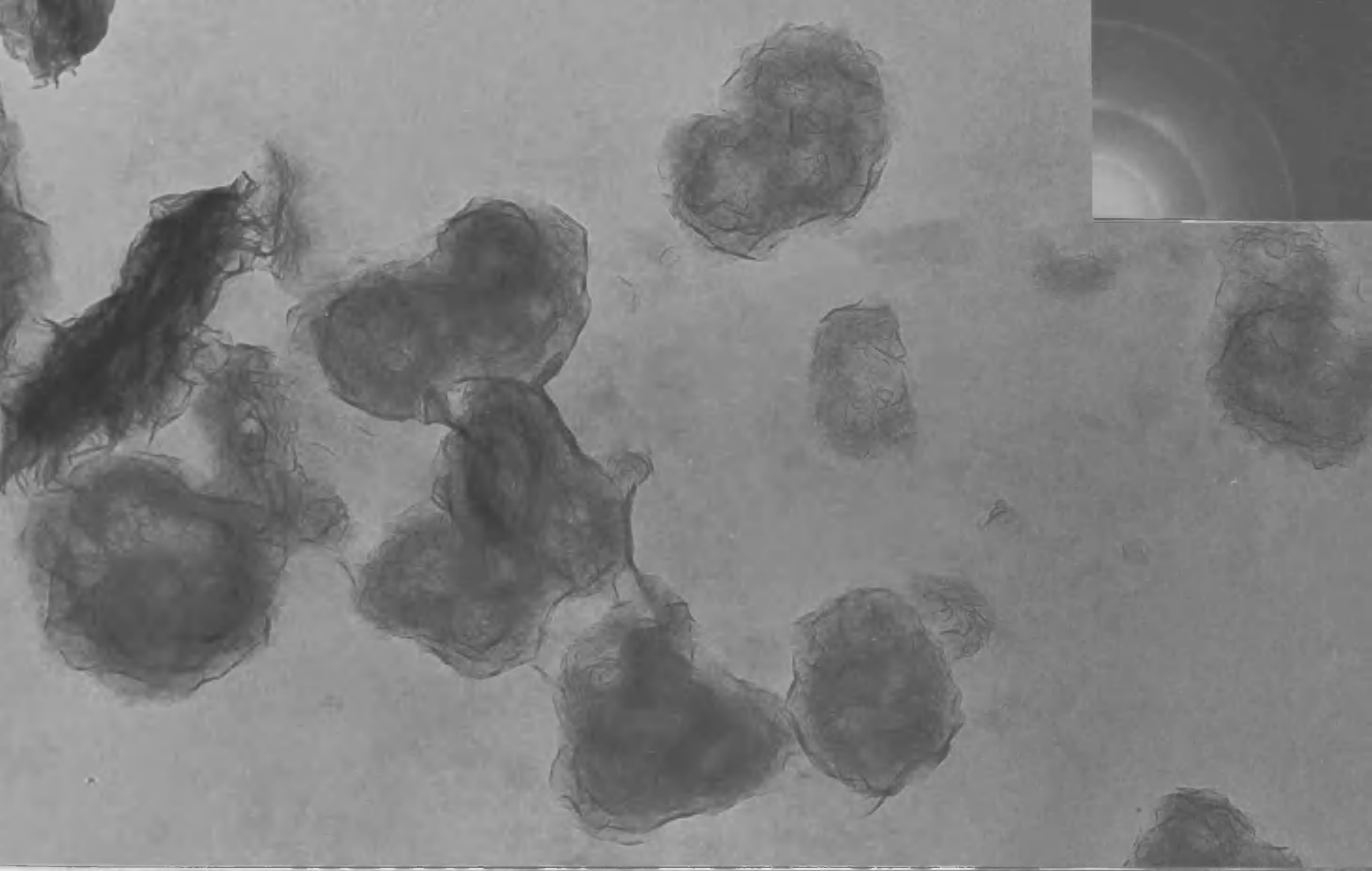
Plate 19. $SiO_2/MgO/LiF = 0.01/1.0/0.25$ (x 60K)

Product has highly curled edges.

Plate 19a. Diffraction pattern of product.

Plate 20. High magnification of curled edge. (x 1,000 K)

The lattice spacing measured from this micrograph gave values of about 10 Å.



Selected Area Diffractions : Ratio Experiments (Polypropylene).

(corresponding to plates 31 to 40)

Plate 21. $SiO_2/MgO = 0.01/1.0$

Plate 24. $SiO_2/MgO = 0.6/1.0$

Plate 22. $SiO_2/MgO = 0.2/1.0$

Plate 25. $SiO_2/MgO = 0.8/1.0$

Plate 23. $SiO_2/MgO = 0.4/1.0$

Plate 26. $SiO_2/MgO = 1.0/1.0$

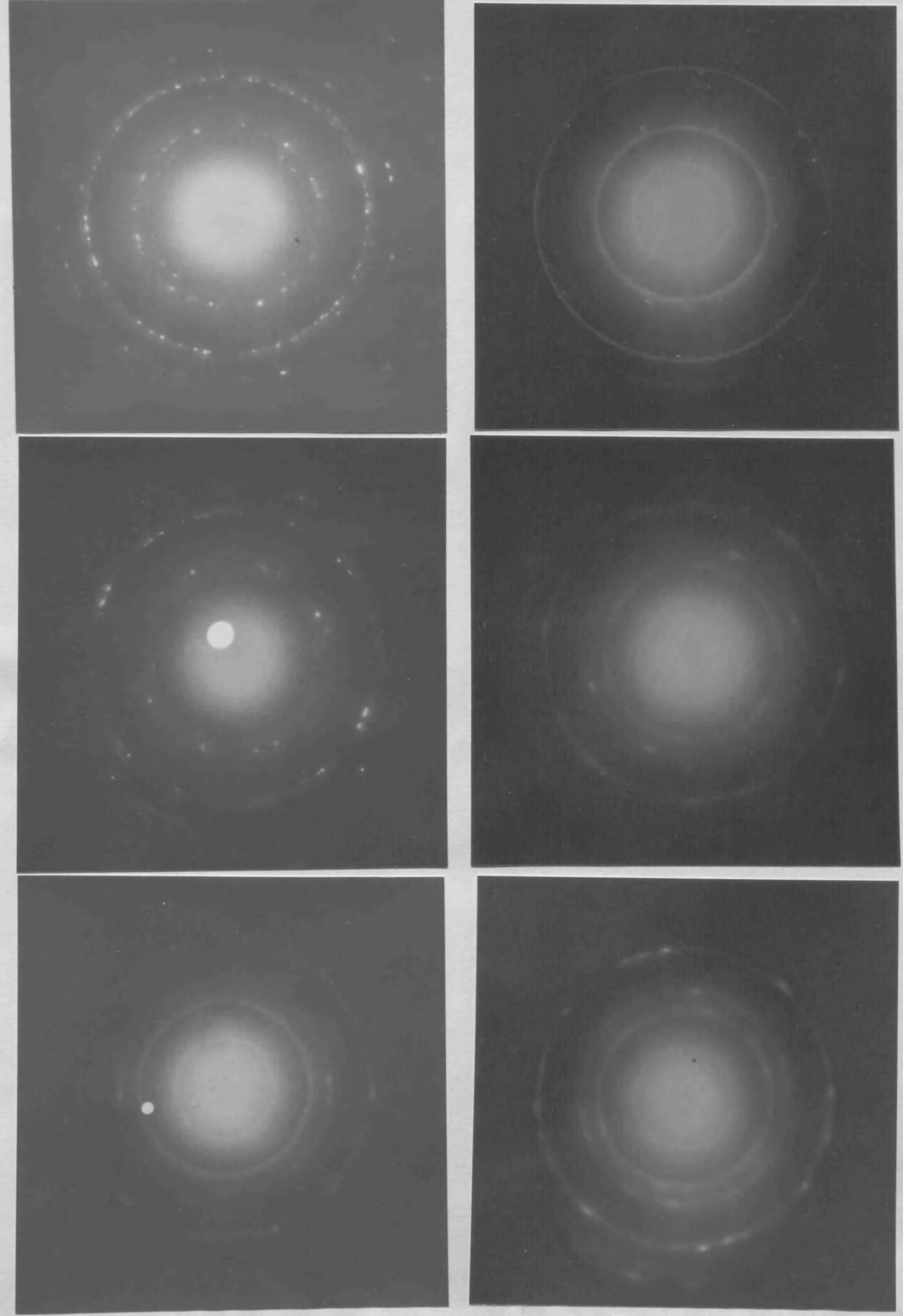


Plate 27. $SiO_2/MgO = 1.2/1.0$

Plate 29. $SiO_2/MgO = 1.6/1.0$

Plate 28. $SiO_2/MgO = 1.4/1.0$

Plate 30. $SiO_2/MgO = 2.0/1.0$

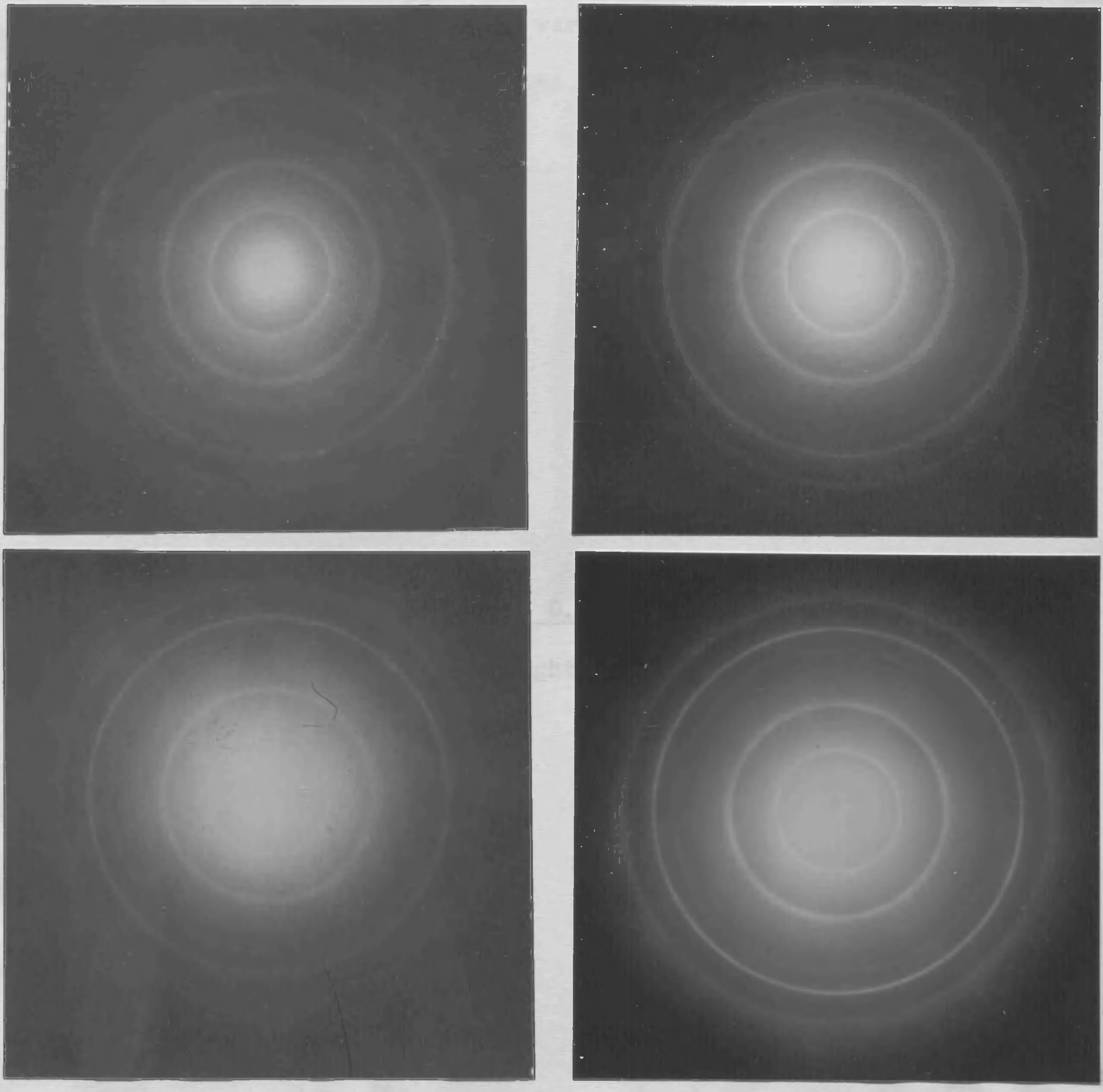


Plate 31. $SiO_2/MgO = 0.01/1.0$ (x 60K).

$Mg(OH)_2$ platelets very little affected by silica (cf. plate 19).

Plate 32. $SiO_2/MgO = 0.2/1.0$ (x 60K).

Platelets show slight curling at the edges.

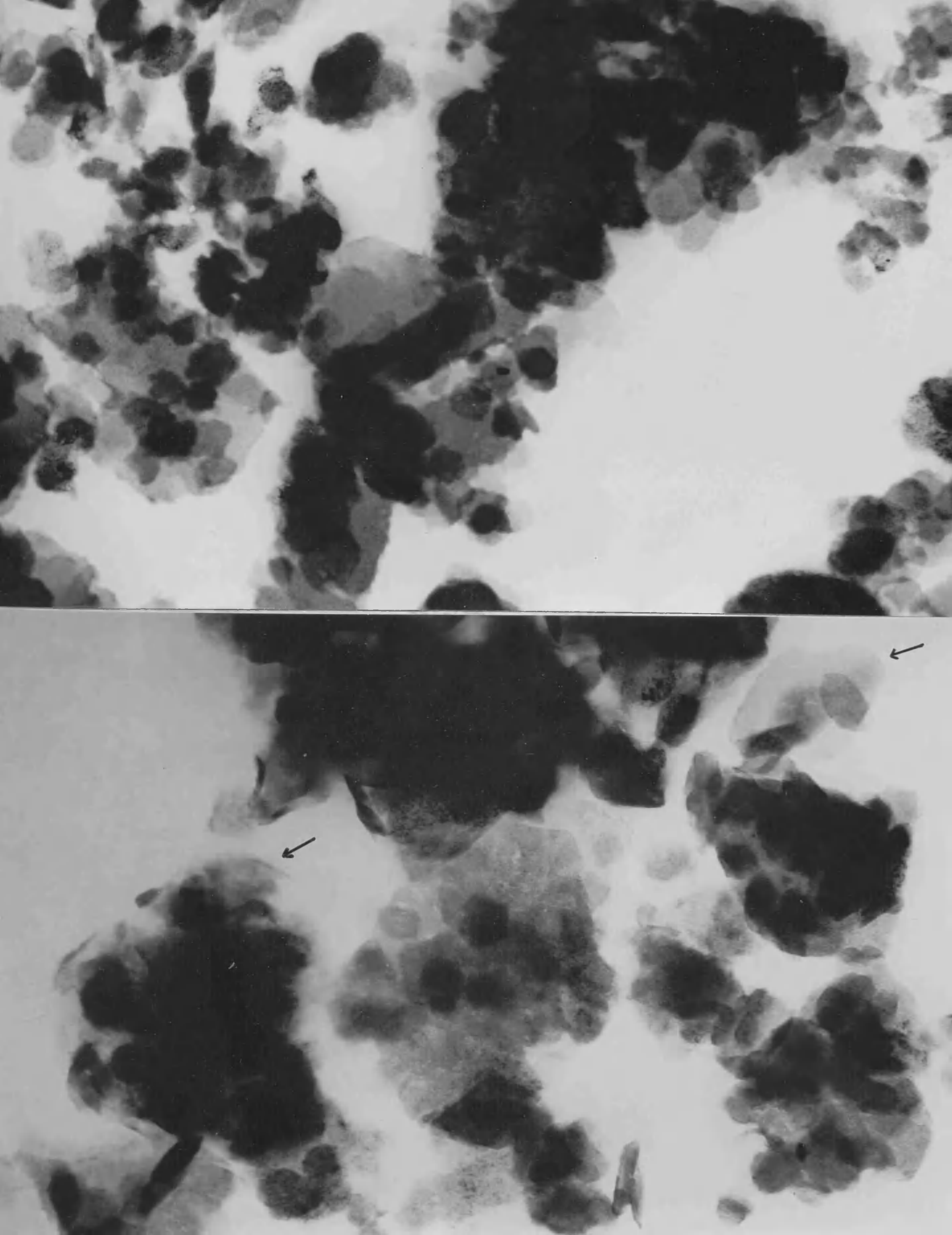


Plate 33. $SiO_2/MgO = 0.4/1.0$ (x 60K).

Edges of platelets show more extensive curling.

Plate 34. $SiO_2/MgO = 0.6/1.0$ (x 60K).

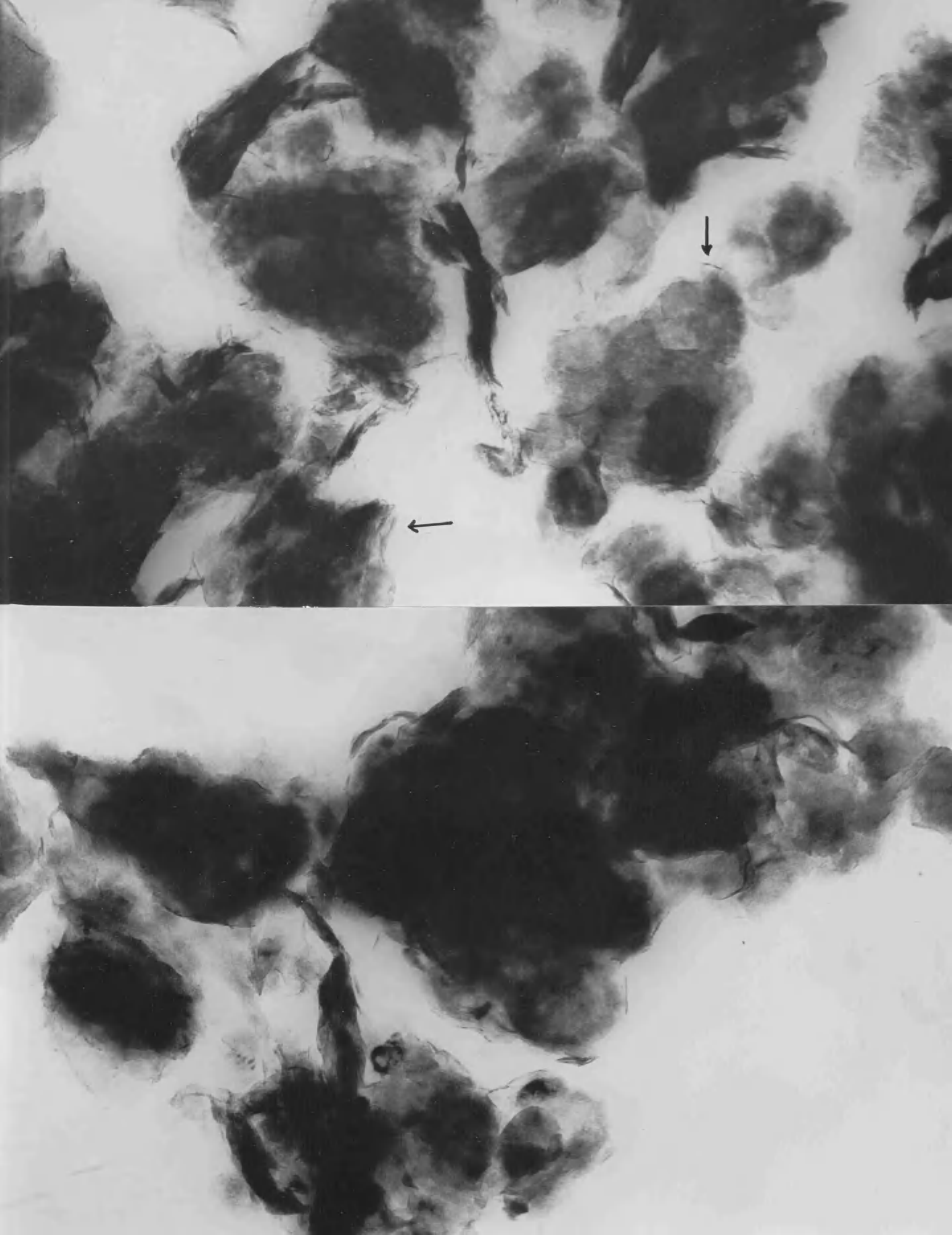


Plate 35. $SiO_2/MgO = 0.8/1.0$ (x 60K).

Shows curling edges and doughnut structures.

Plate 36. $SiO_2/MgO = 1.0/1.0$ (x 60K).

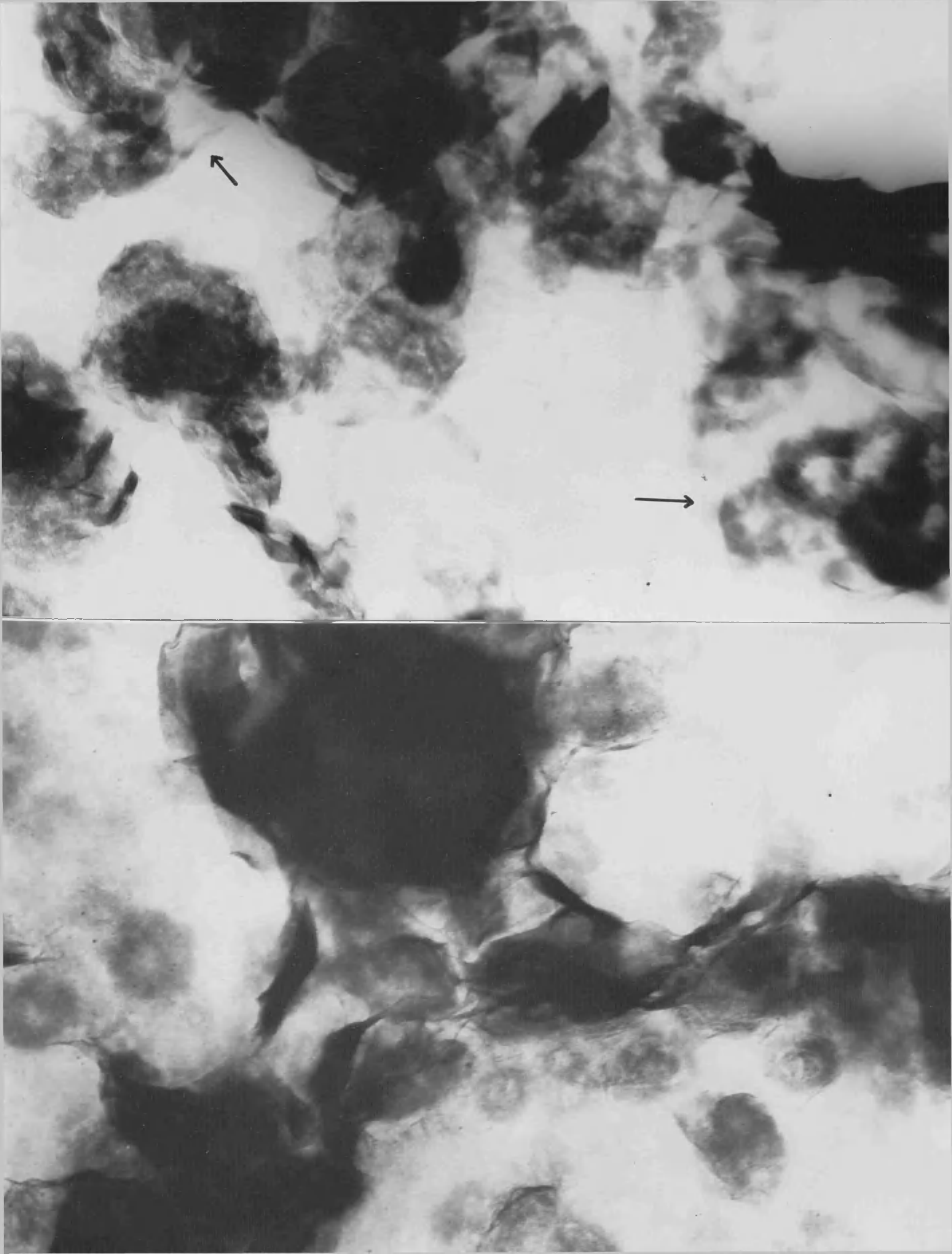


Plate 37. $SiO_2/MgO = 1.2/1.0$ (x 60K)

Product has beginnings of sheet like morphology of higher ratios.

Plate 38. $SiO_2/MgO = 1.4/1.0$ (x 60K).

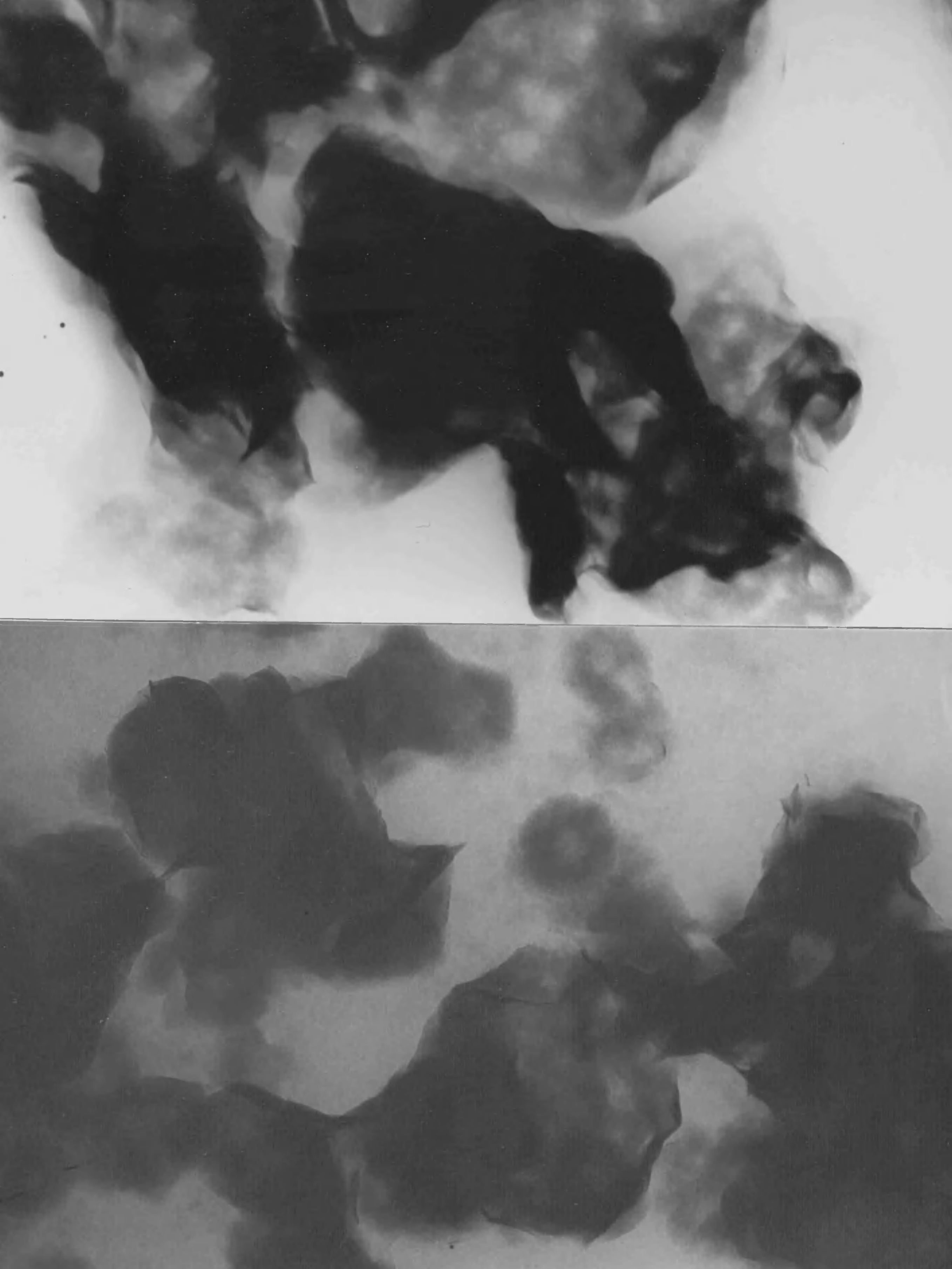
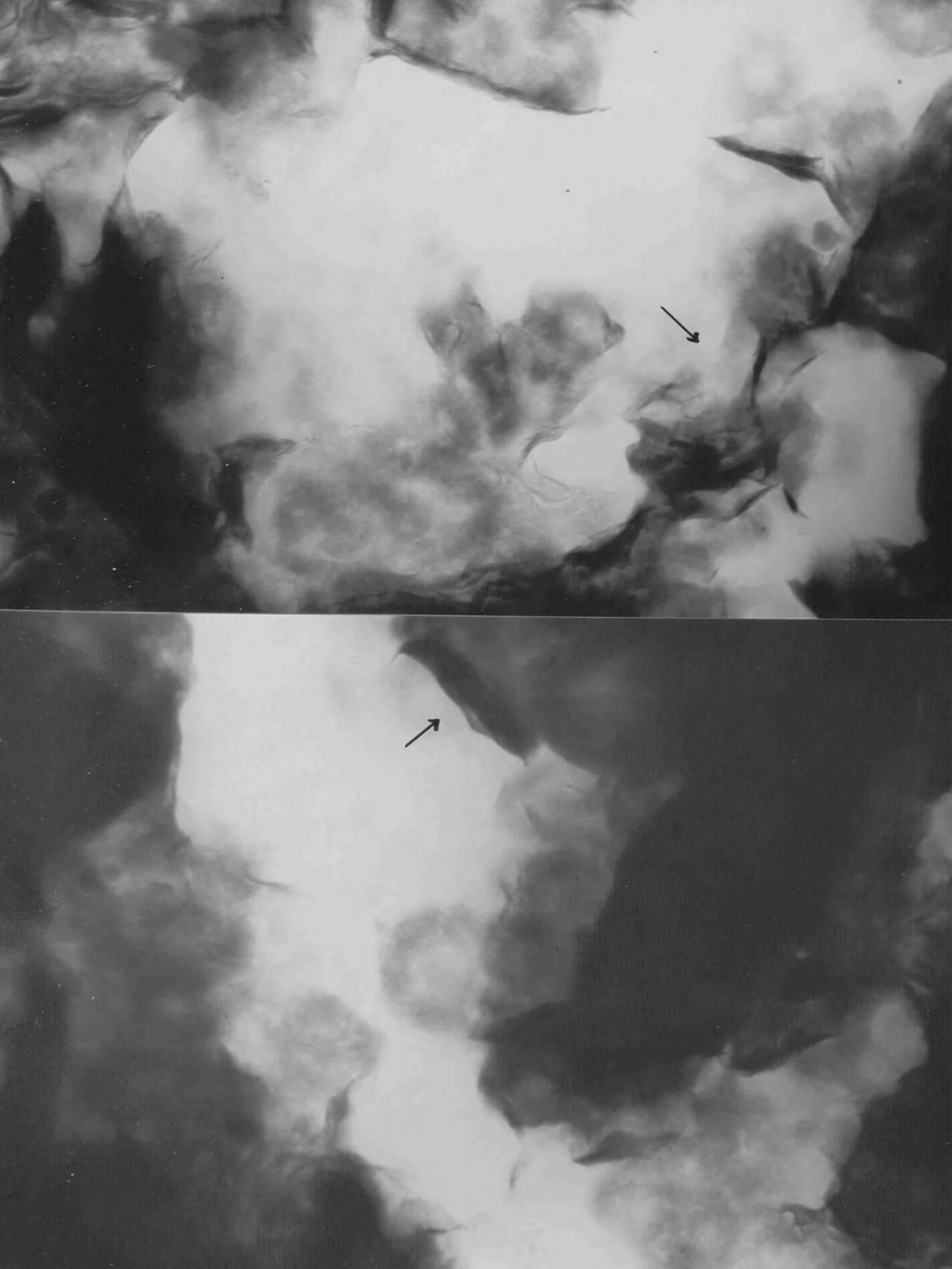


Plate 39. $SiO_2/MgO = 1.6/1.0$ (x 60K).

Highly folded sheets evident.

Plate 40. $SiO_2/MgO = 2.0/1.0$ (x 60K)

Extensively folded sheets and curled edges are shown.



Kinetic Experiments.

Feed mixture ratio : $SiO_2/MgO/LiF = 2.0/1.0/0.25$.

Plate 41. Slurry mixed at 0°C and mounted by freeze drying. (x 60K).

Shows $Mg(OH)_2$ platelets virtually unaffected by silica.

Plate 42. Above sample allowed to equilibrate to room temperature and then freeze dried. (x 60K)

Edges of $Mg(OH)_2$ platelets have undergone slight changes to become less sharp.

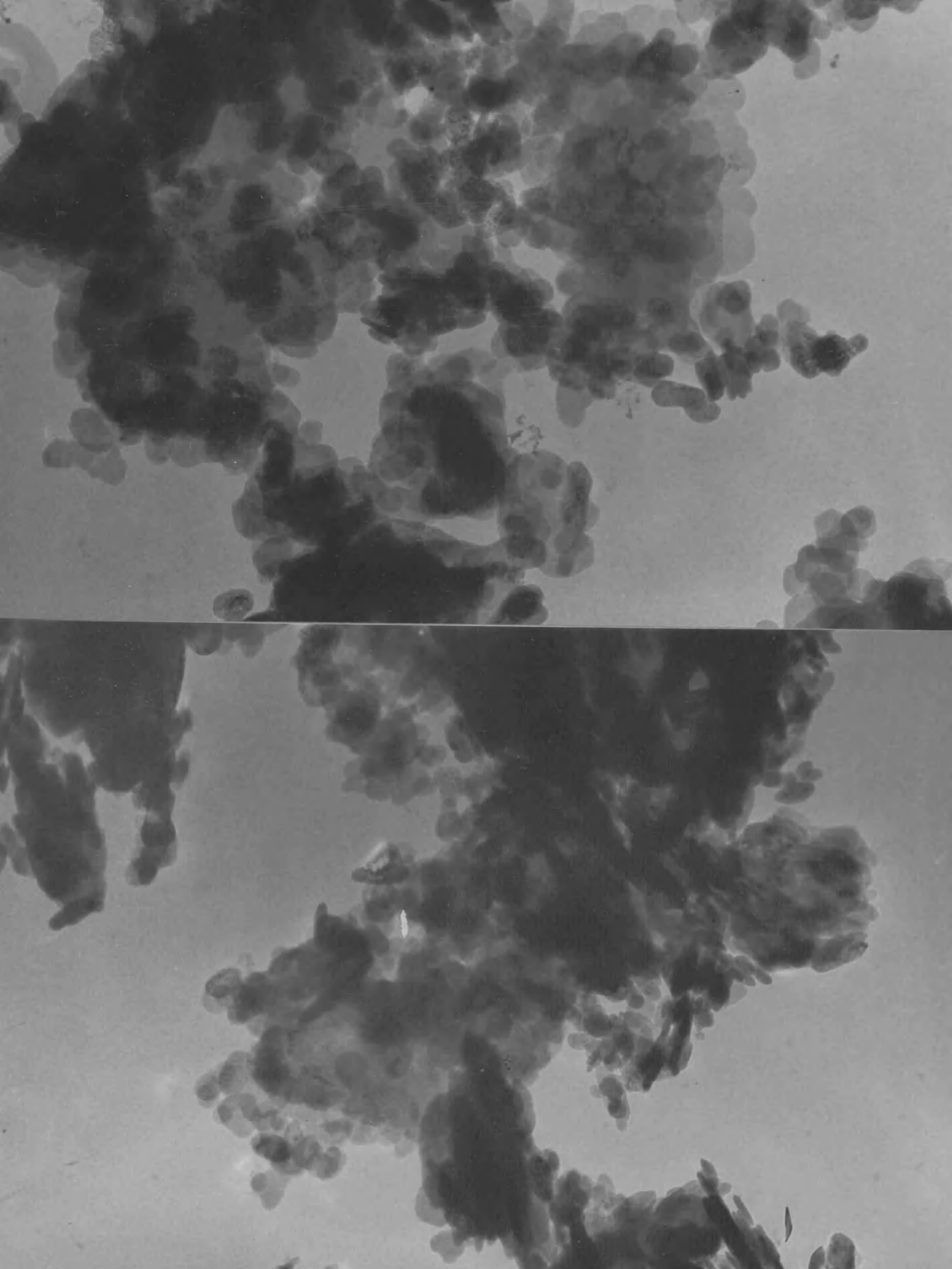
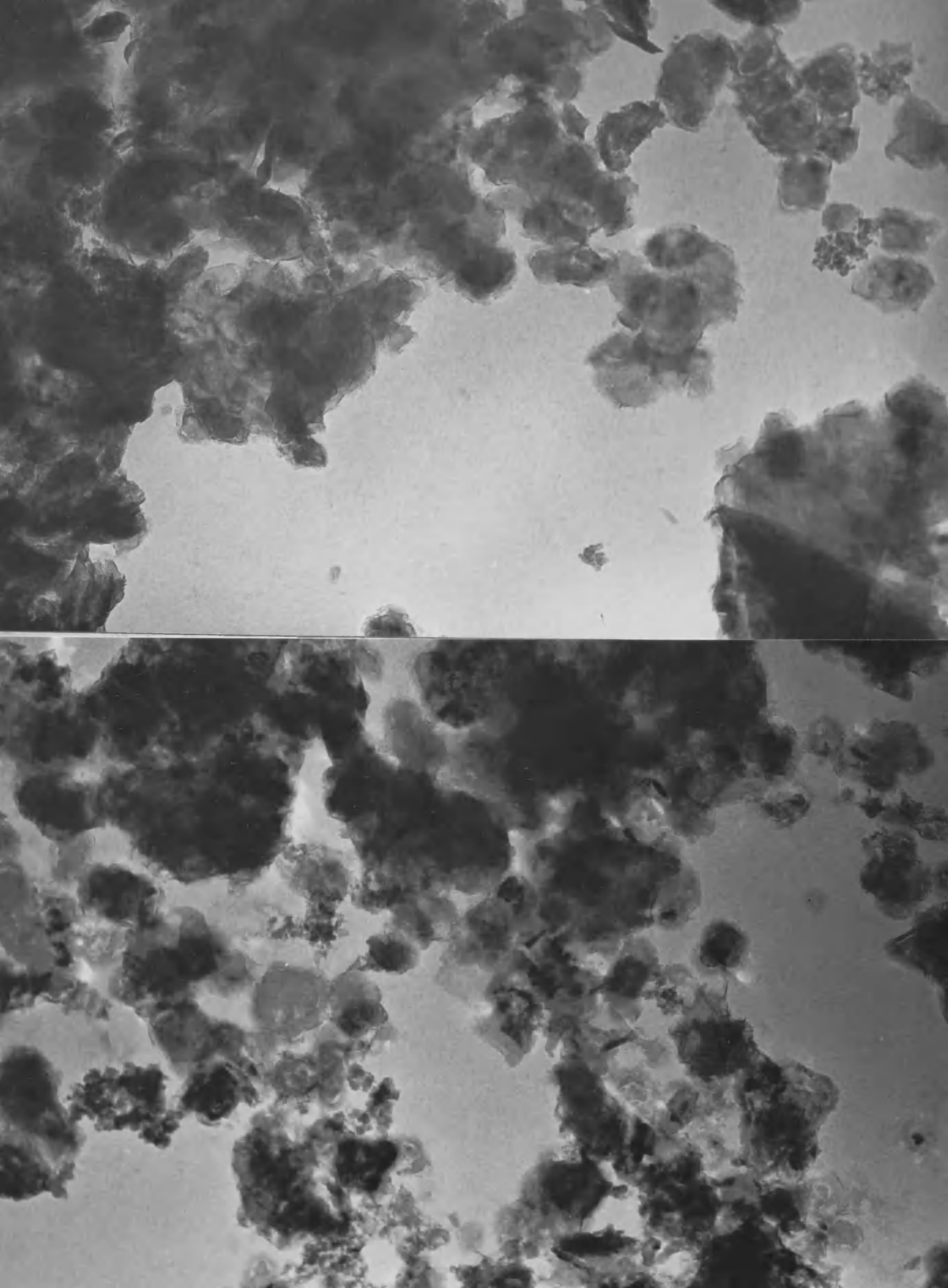


Plate 43. Sample taken at room temperature and mounted by evaporation at 30°C.

More extensive attack at the edges of platelets.

Plate 44. 1 hour of reflux time. (x 60K).

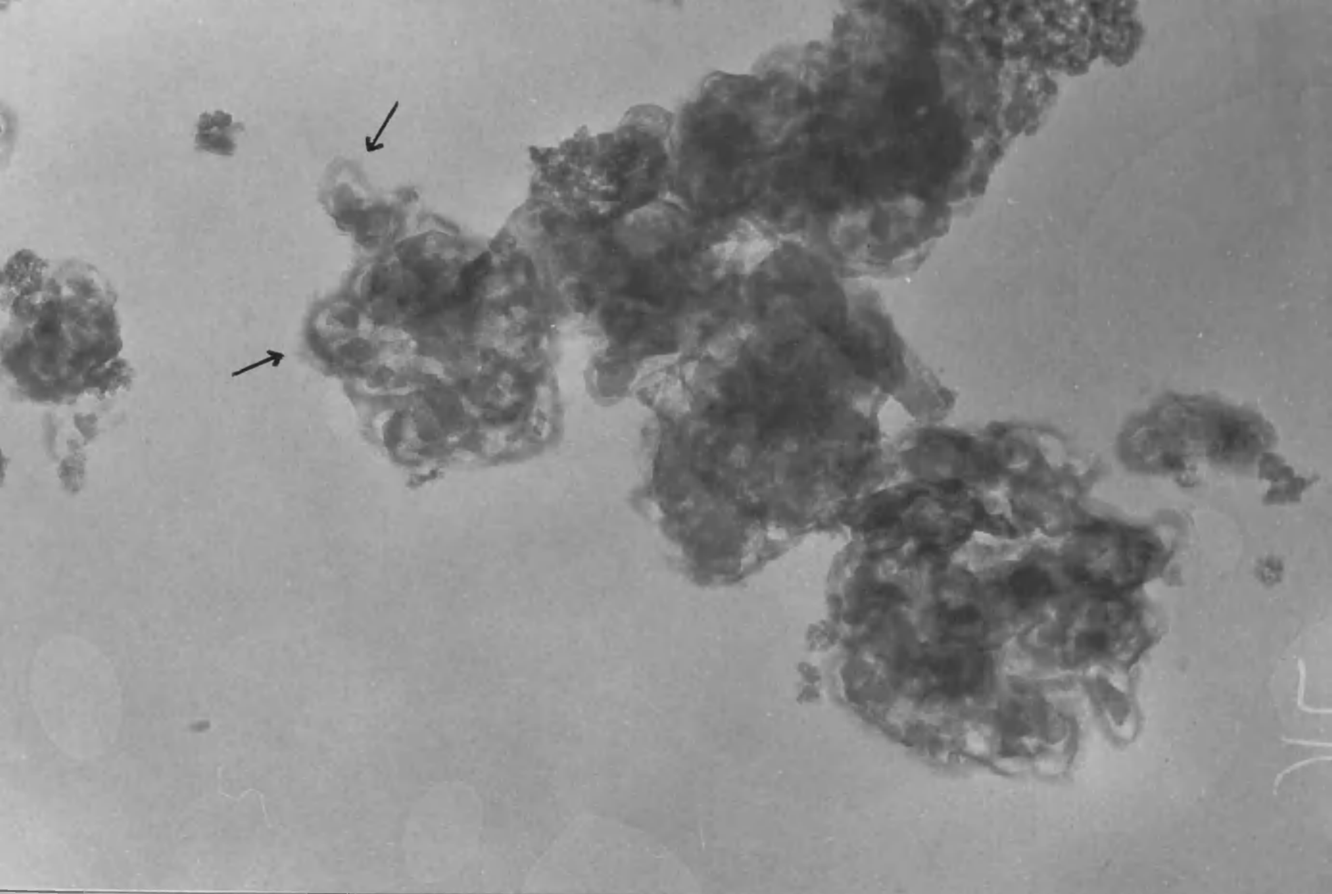


<u>Plate 45</u>. <u>1½ hours of reflux time</u>. (x 60K).

Appearance of doughnuts with displaced 'cones' of $Mg(OH)_2$.

<u>Plate 46</u>. <u>2 hours of reflux time</u>. (x 60K).

Doughnut structures evident.



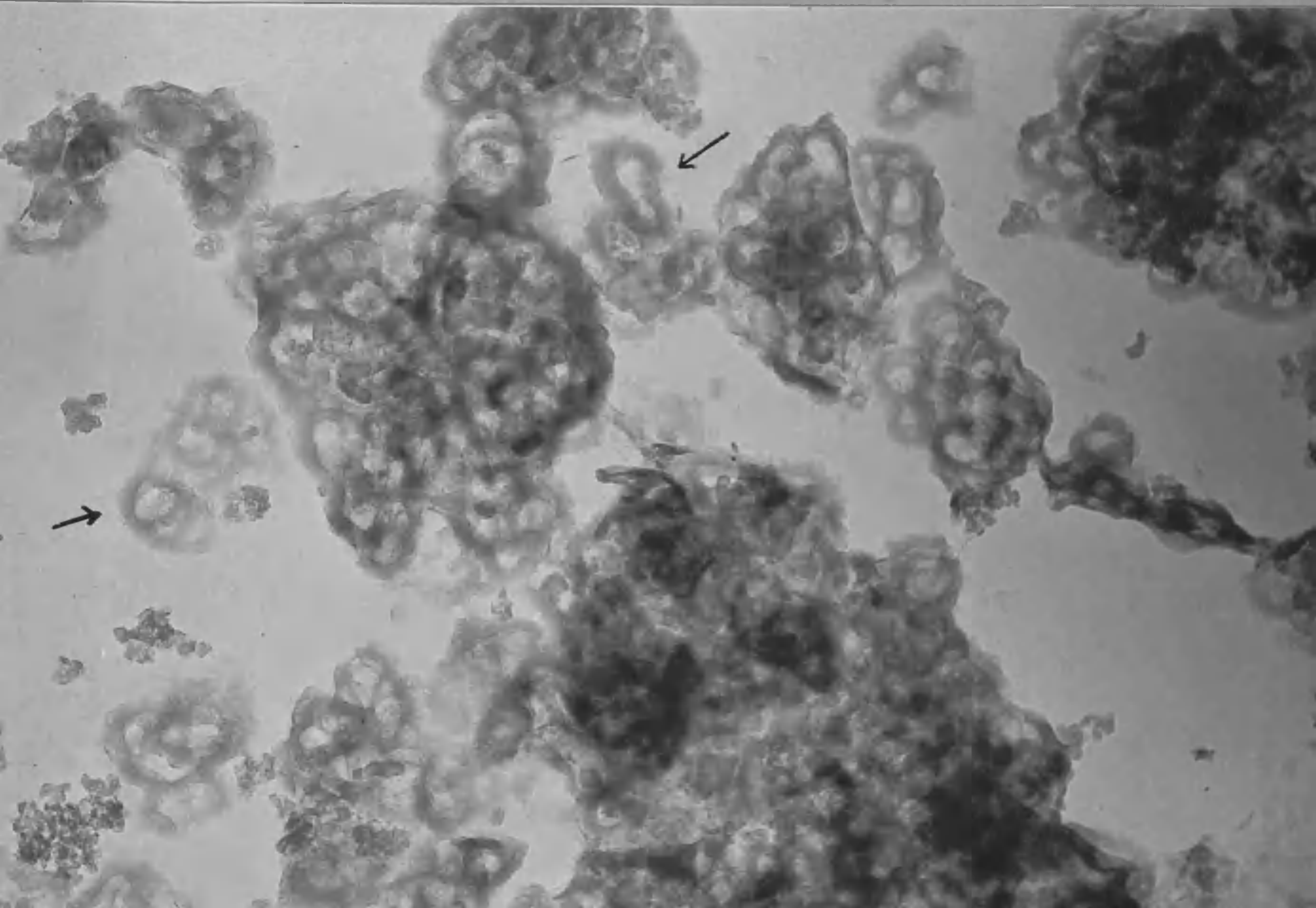
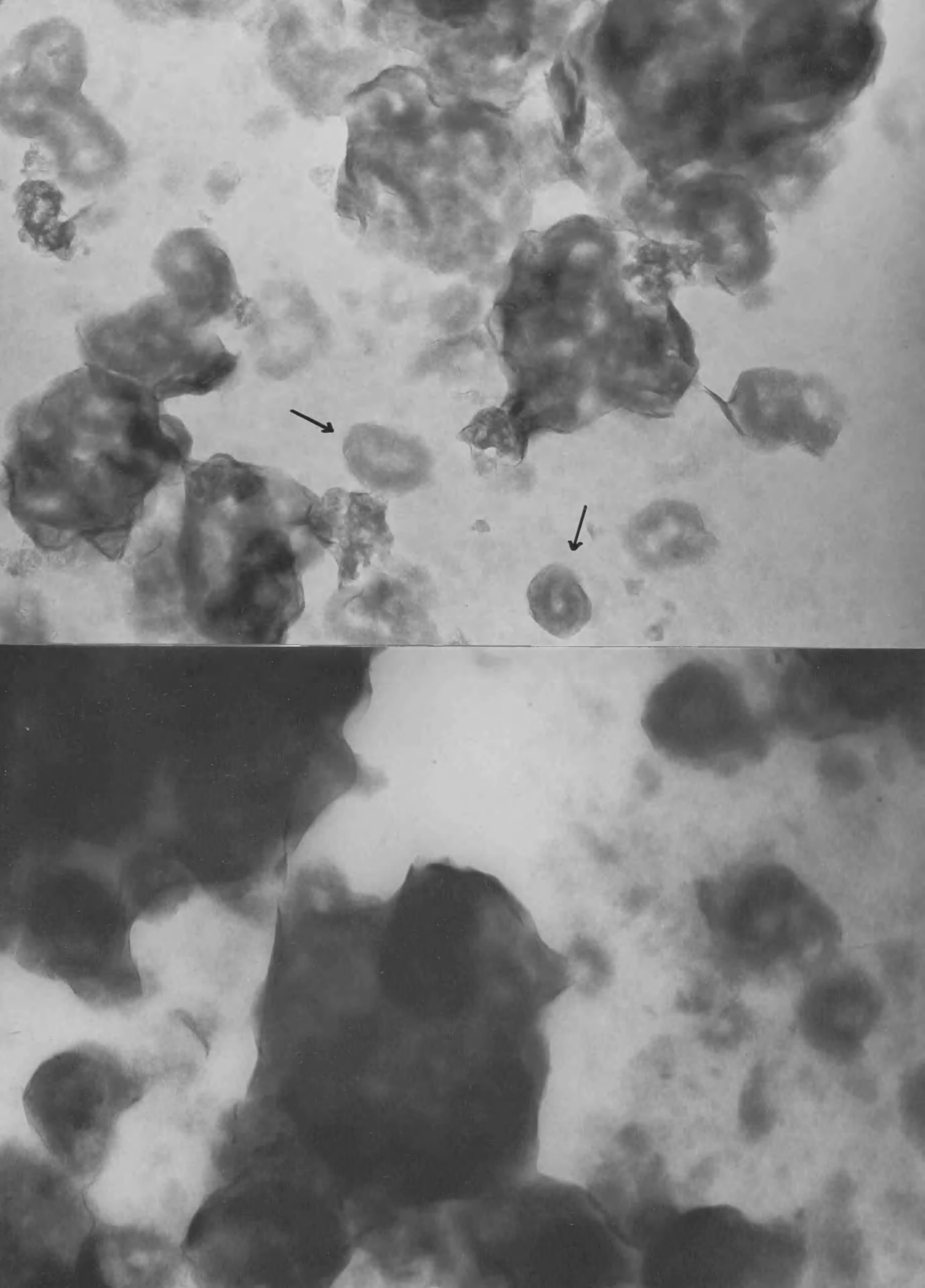


Plate 47. 7 hours of reflux time. (x 60K).

Doughnuts appear to have filled in slightly: sheet-like morphology developing.

Plate 48. 1 day of reflux time. (x 60K).

Shows overall sheet-like structure.



Selected Area Diffractions of Kinetic Experiments.

(corresponding to plates 41 to 48).

Plate 49. Diffraction from sample mixed at $0^{\circ}C$. (freeze dried).

Plate 50. Diffraction from sample equilibrated to room temperature (freeze dried).

Plate 51. Room temperature sample.

Plate 52. 1 hour reflux.

Plate [illegible]. 15 hours ageing.

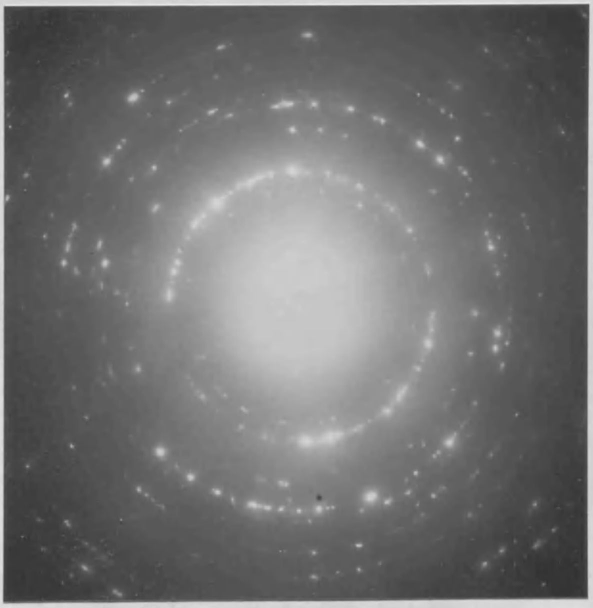
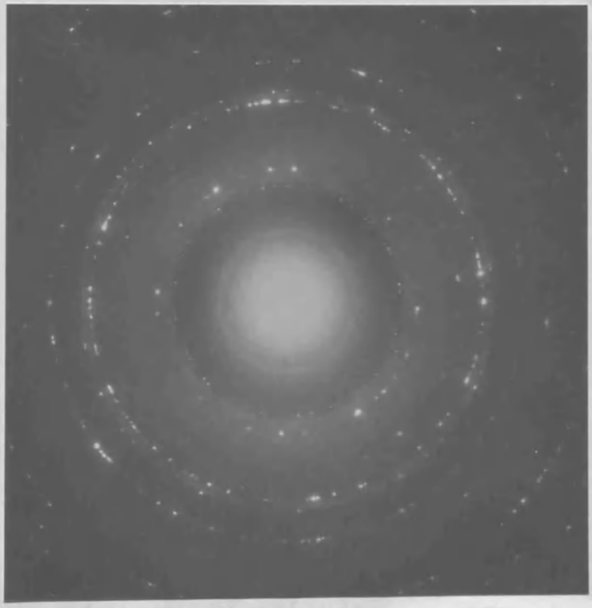
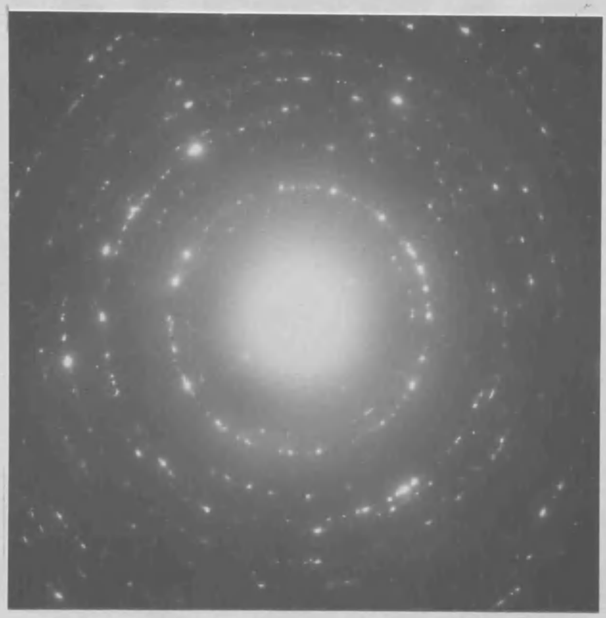


Plate [illegible]. 3 hours ageing.





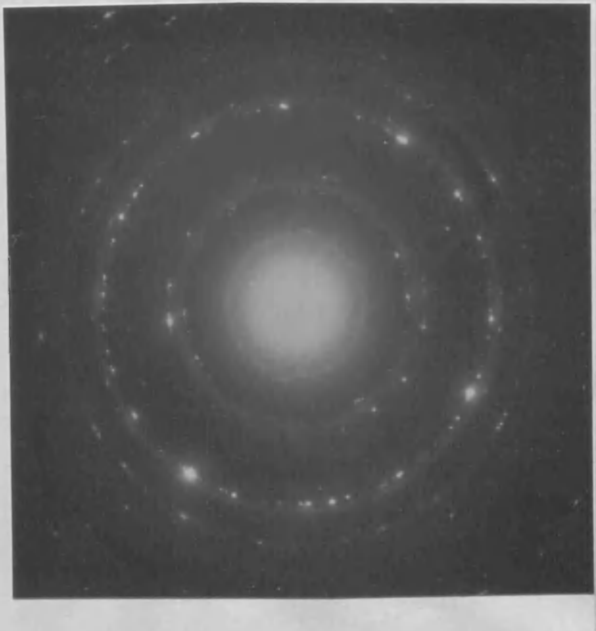
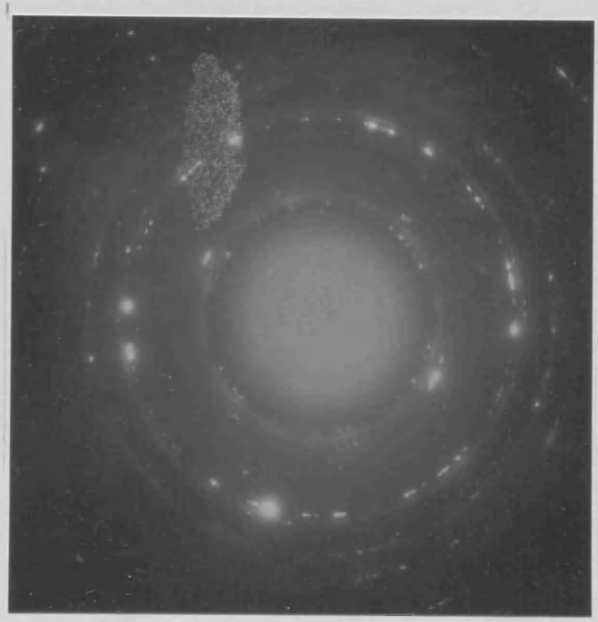


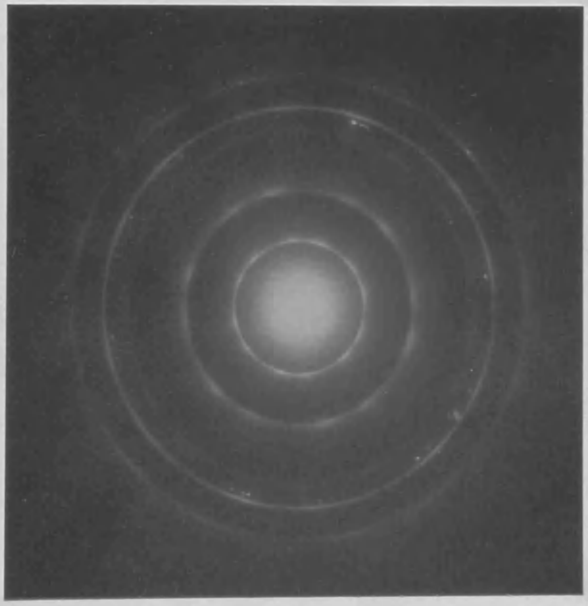
Plate 53. $1\frac{1}{2}$ hours reflux.

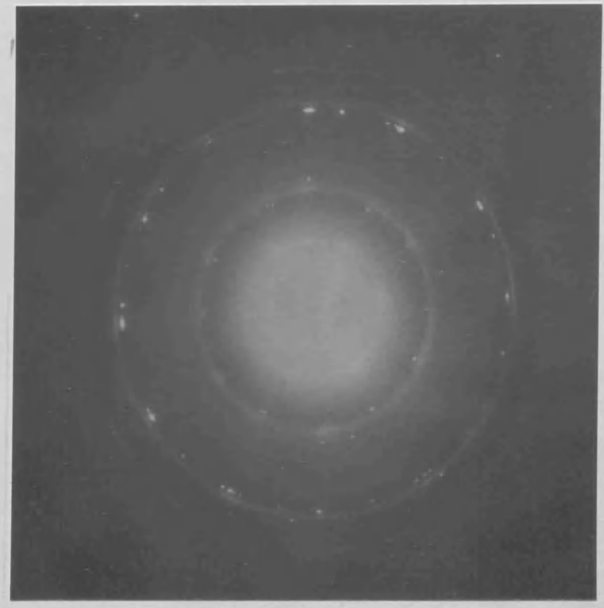
Plate 55. 7 hours reflux.

Plate 54. 2 hours reflux.

Plate 56. 1 day reflux.







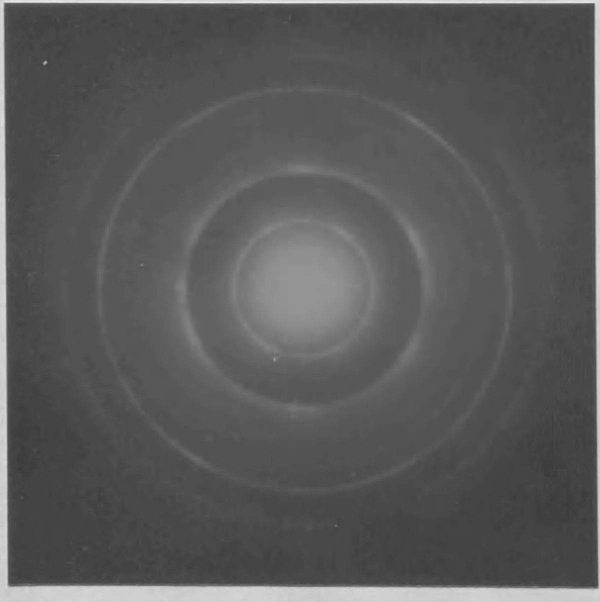
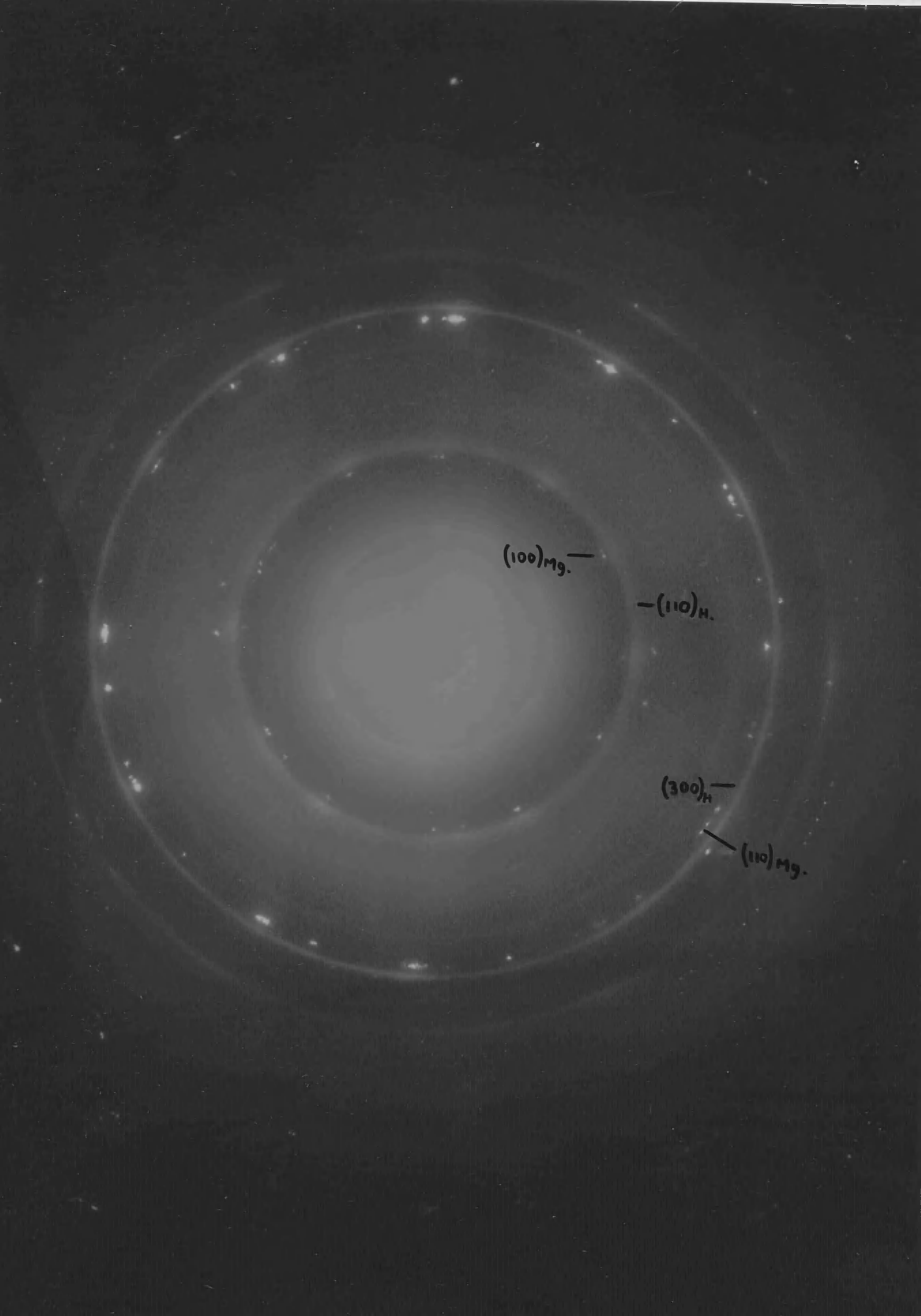


Plate 57. Indices of planes of hectorite and $Mg(OH)_2$ with epitaxial fit.

(enlargement of Plate 54).


(100)Mg.
(110)H.
(300)H
(110)Mg.

CHAPTER IV

General Discussion

It is now proposed to review more broadly the mechanisms of clay formation that have been proposed by other authors and then restate and extend the main mechanistic ideas proposed in earlier chapters.

In general there are many factors which influence the type of clay product formed but as stated by De Kimpe, Gastuche and Brindley (1961), the most influential parameters are pH, salt concentration, and the stoichiometry of the feed mixtures.

Clay synthesis from dilute solutions.

Caillere, Henin and Esquerin (1953) prepared clays by electrolytic attack of various metals soaked in a solution of alkaline silicate. The only metals that were successful with this technique were magnesium, nickel and cobalt. They suggested that only metals which readily give brucite type hydroxides can form clay like minerals. Henin (1955) prepared montmorillonite, mica and antigorite from dilute boiling solutions and again postulated that a hydroxide layer must be present initially upon which silica can deposit.

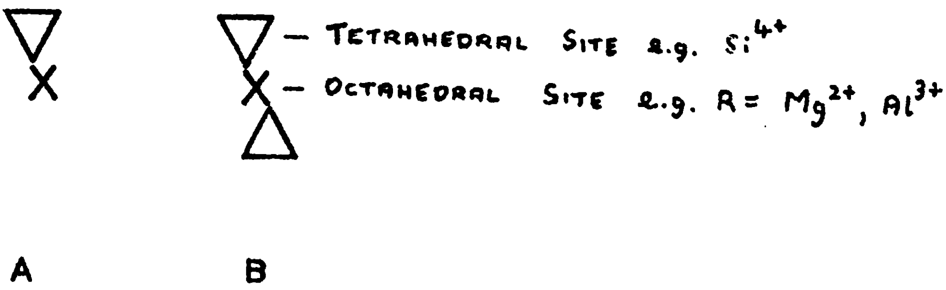
Previously, however, Henin and Robichet (1954) had prepared magnesium montmorillonites at pH 8.0, well below the pH required for the precipitation of brucite.

In a later paper by Henin and Caillere (1963) they modified their hydroxide hypothesis. The synthesis of 1:1 clay minerals is difficult to rationalise with a hydroxide sheet as the basis building unit since there is no reason why the silica tetrahedra should absorb preferentially on one side. They proposed that silicic acid could combine with divalent cations (R) to give the following species :-

$$(OH)_3\text{-Si-O-R-OH} \qquad A$$

$$(OH)_3\text{-Si-O-R-O-Si-}(OH)_3 \qquad B$$

schematically :-



They also propose that species of the type $R(OH)_2$, called C, exist in solution. Different types of clay minerals are formed by the condensation of these elementary units, for example :-

2A + C	antigorite
2B + C	talc, stevensite
3B + C	sepiolite
4B + C	palygorskite.

The type of product formed will depend on the proportion of C that is present.

This scheme would explain 1:1 clay formation with silica on one side since the most stable configuration will be achieved with the linking of the silica tetrahedra and the coalescing of the magnesiums into an octahedral layer.

Wey, Siffert and Wolff (1968) also take the view that basic salts, of the type A, are essential to the synthesis of layer silicates.

No direct evidence is given by any of the above authors for the existence of these basic salts. However, as described in Chapter I, Stock and Davies (1944) established the existence of the $Mg(OH)^+$ ion. Species of type A and B could then be formed as follows :-

$$\begin{array}{lll} Si(OH)_4 & H^+ + Si(OH)_3O^- + Mg(OH)^+ & Si(OH)_3OMg(OH) \\ & Si(OH)_3OMg^+ + Si(OH)_3O^- & Si(OH)_3OMgOSi(OH)_3. \end{array}$$

The influence of pH in this initial process will then be critical. The pH of the mother solutions would determine the relative concentrations of the ions in the above reactions. Henin and Robichet (1954) carried out experiments with silicate and magnesium solutions at pH 8.0. The SiO_2/MgO ratio of the solution varied from 0.06 to 1.40, but the SiO_2/MgO product ratio only varied from 0.51 to 1.9. At low pHs the products could not be identified. They concluded that pH 8.0 constituted the lower limit for the formation of magnesium montmorillonite. Caillere, Henin and Esquevin (1955) reported that the pH of the solution plays an important role in the synthesis of iron bearing minerals. For $pH > 8$ montmorillonite was produced, at $pH < 6$, Fe_2O_3 or goethite formed, and at $6 < pH < 8$ mixtures of silicates and oxides were found.

With syntheses involving aluminium, basic salts have again been invoked in synthetic mechanisms (Henin and Caillere, 1963). The synthesis of kaolinite is thought to be initiated by the basic salt formed from the $Al(H_2O)_4(OH)_2^+$ ion :-

$$Si(OH)_4 \rightarrow H^+ + Si(OH)_3O^- + Al(H_2O)_4(OH)_2^+ \rightarrow (OH)_3\text{-}Si\text{-}O\text{-}\ Al(OH)_2(H_2O)_3$$

By condensation and elimination of water kaolinite could be formed. However the existence of the $Al(H_2O)_4(OH)_2^+$ ion has not yet been proved. The ion $Al(H_2O)_5OH^{2+}$ however does exist, and combined with two silicic acid molecules gives a basic salt from which 2:1 silicates could be synthesised. These salts would form so long as Al^{3+} is 6-coordinated : this is ensured in dilute solutions where the pH is less than 6.

As mentioned in the Introduction other methods of maintaining Al^{3+} in 6-coordination by complexing the ion with organic molecules, have led to the synthesis of kaolinite like products. Wey and Siffert (1961) complexed Al^{3+} with oxalic acid and produced protokaolin; Linares and Huertas (1971) synthesised kaolin by first complexing Al^{3+} with fulvic acid. The later workers suggest that a hydroxide layer is formed slowly by a competitive reaction among the organic ligands and hydroxyl ions leading to a pregibbsite structure. The silica layer is then adsorbed as mono-silicic acid onto the surface. In this respect the idea of an octohedral layer forming first is similar to Henin's original hypothesis.

To form clays in which aluminium replaces silicon, the Al^{3+} ion should have 4-coordination. The aluminate anion $Al(OH)_4^-$ can be formed in dilute solutions at about pH 6. At lower pHs gel formation tends to occur. This ion can then replace silicon and thus become incorporated into a tetrahedral layer.

The mechanism of formation depends also on the method of preparation. Simultaneous mixing of a metal salt solution and a silicate solution will, by adjusting the pH, form coprecipitates composed most probably of basic salts. Coprecipitates can also be formed by adding one of the solutions to the other and then adjusting the pH. By ageing these coprecipitates for a sufficient time the possibility arises that these precipitates will react to yield clays.

If a silicate solution is added to a metal salt solution the pH of which is adjusted to precipitate the hydroxide, then the mechanism will involve adsorption of the silicic acid monomers on the surface of the hydroxide.

In the experiments described in Chapters I and II the metal salt solution was added to the silicate solution set at about pH 11.0.

Here it is likely that the more facile reaction, the precipitation of the hydroxide, will occur first rather than the formation of basic salts, thus allowing the adsorption mechanism, as outlined in Chapter I, to proceed. A mechanism for the formation of a 1:1 clay via silica adsorption on a hydroxide layer will be discussed in the following sections.

Clay synthesis from solid reactants.

The main factors which influence clay synthesis from gels at room temperature and pressure are similar to those in dilute solutions studies, that is, pH and salt concentration : the ratio of aluminium or magnesium to silica content is more important in this case (De Kimpe, Gastuche and Brindley, 1961). This is probably due to the fact that gels will be fairly soluble, so that clay synthesis will tend to occur in solution from the components supplied by the gels.

The above authors found that with aluminium, the gel phase was the most stable and identification of clay crystals was only possible using electron diffraction. Magnesium gels gave higher yields of clays. They observed the change from 6-fold to 4-fold coordination of Al^{3+} with increasing pH, micas being produced at higher pH presumably because the $Al(OH)_4^-$ proxies for $Si(OH)_4$ in the tetrahedral layer. In the lower pH range, with Al^{3+} in 6-fold coordination, kaolinite was formed.

Studies of clay synthesis from gels make it difficult to reach definite conclusions as to possible mechanisms of growth since the structure of the gels themselves are not understood sufficiently.

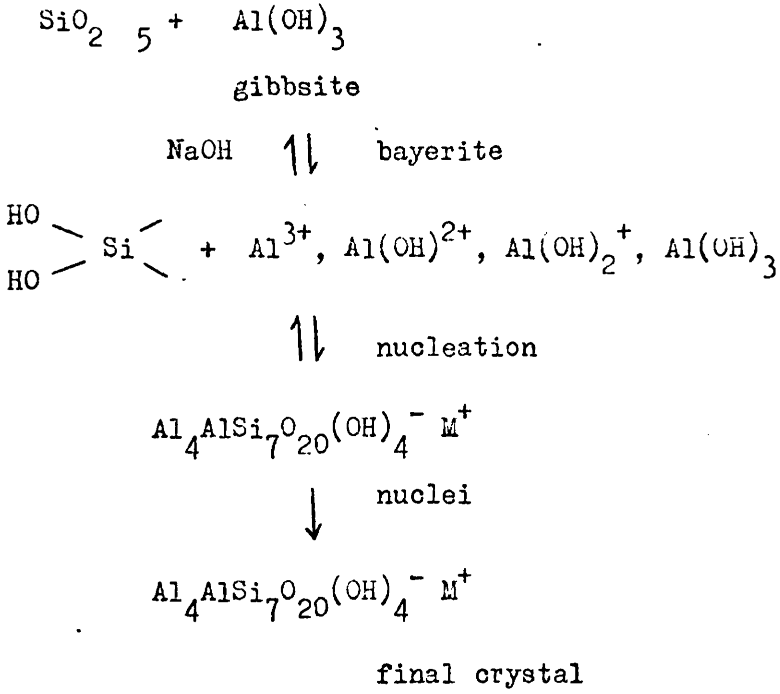
A study of the transformation of albite to kaolinite by Tchoubar (1965) has proved more informative. The transformation was performed in water at 200°C and was followed by electron microscopy and X-Ray diffraction. At pH 5.0 the solution contained 150 ppm SiO_2 which caused the dissolution of cleavage lamellas which results in the formation of kaolinite through an intermediate stage of poorly crystalline boehmite. The fibres of boehmite seemed to serve as centres capable of fixing $Si(OH)_4$. Interestingly, no gel formation was observed on the surface of albite. The author suggests that there is the possibility of local organisation of $Si(OH)_4$ molecules in tetrahedral beds on boehmite.

Tchoubar and Oberlin (1966) found that albite in the presence of 700 ppm colloidal silica transforms to a smectite. In later work Tchoubar, Oberlin and Cadoret (1968) confirmed that albite alters to kaolinite through an intermediate of boehmite when the solution is poor in silica and Na^+ ions, but forms a turbostratic beidellite when the Na^+/H^+ ratio increases or when the silica concentration is raised by addition of highly amorphous silica.

More recently Oberlin and Couty (1970) have studied the alteration of montmorillonite at 200°C under acid conditions. They showed that with high acid concentrations amorphous gels formed while at low concentrations, the mineral was stabilised under supersaturated silica conditions by adsorbtion of silica around the clay particles. Under conditions that favoured the formation of boehmite, no subsequent clay minerals were formed if the boehmite was well crystallised. However by inserting an aluminium hydroxy polymer, using the method of Poncelet and Brindley (1967), with a crystal structure of pseudo-boehmite into the interlayer spacing the formation of kaolinite was induced. They regard it as essential that aluminium should be temporarily 'stored' in a poorly crystallised mineral (oxide or hydroxide) which then allows silica monomer, contained in the solution to saturate active sites to give a 2:1 or 1:1 layer silicate according to its concentration.

Kittrick (1970) has shown that montmorillonites when left in acid solution for three to four years yield solutions supersaturated with respect to kaolinite components from which kaolinite eventually precipitates. However the presence of a poorly crystallised 'Aluminium store' seems to greatly accelerate the clay formation process.

Granquist and Pollack (1967) feel that the process involves crystallisation from solution and is made up of general steps: solution of the solid reactants, nucleation of the lattice, and growth of these nuclei to the final crystalline product. They suggest a mechanism along the lines of Caillere. Henin and Esquevin (1953), that is. that the formation of clay minerals at room temperature and ordinary pressure requires the existence of a brucite-type hydroxide layer. It is then suggested that for aluminosilicate, $Al(OH)_3$ molecules form followed by the condensation with $Si(OH)_4$ to produce the desired structure, as follows :-



SiO_2 5 + $Al(OH)_3$

gibbsite

NaOH $\rightleftharpoons$ bayerite

$\begin{matrix}HO\\HO\end{matrix}\!>Si<$ + Al^{3+}, $Al(OH)^{2+}$, $Al(OH)_2^{\ +}$, $Al(OH)_3$

$\rightleftharpoons$ nucleation

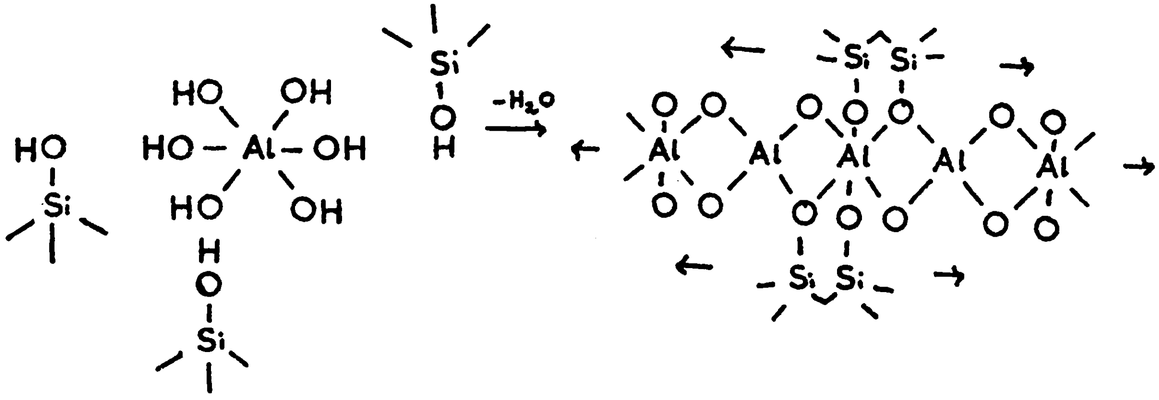
$Al_4AlSi_7O_{20}(OH)_4^{\ -}\ M^{+}$

$\downarrow$ nuclei

$Al_4AlSi_7O_{20}(OH)_4^{\ -}\ M^{+}$

final crystal

Or, schematically :-



This condensation process creates Si-O-Al bonds. The gibbsite layer would continue to grow with accompanying condensation of gibbsite - OH with $Si(OH)_4$ to yield a crystallite of increasing size in the ab plane. As an explanation of random interstratification (indicated by X-Ray data) they suggest that single layers stack together probably as a result of an energy minimisation process. De Kimpe and Gastuche (1964) on the other hand report that the transformation of gibbsite to boehmite is necessary to induce synthesis.

The differences in the forces that exist between the layers of magnesium and aluminium hydroxides give an indication of the expected reactivity of these hydroxides towards silica.

In brucite the layers are held together by weak secondary forces between the opposed sheets. Boehmite has a similar structure to brucite (Reicherty and Yost, 1946): the crystals are easily cleaved in the direction of the interlayer spacing. Gibbsite, however, has stronger forces acting between the layers. Silicic acid molecules will therefore find it easier to penetrate into the interlayers of brucite and boehmite than into gibbsite.

According to the experiments performed in this work, the adsorption of silicic acid is visualised as either being triple hydrogen bonding or chemisorption by the filling of +ve holes in the brucite-type hydroxide lattice. Further justification for the latter idea comes from the statement of Henin and Robichet (1953) that OH ions have a high mobility compared with other anions enabling vacancies to be created faster than they are filled by $Si(OH)_3O^-$ ions. Once adsorbed, or 'stored', the 'argillification', or clay formation processes, can occur. The polymerisation of silica to form tetrahedral layers will be accelerated by the presence of salts, which probably accounts for its importance in clay syntheses (Gibblett, 1963).

Summary of mechnisms proposed in earlier chapters.

In the presence of a brucite-type hydroxide layer, or with experimental conditions which will lead to the formation of a hydroxide layer, silica undergoes rapid uptake from solution. This suggested that it is adsorbed onto the surface of the hydroxide either by hydrogen bonding, triple hydrogen bonding being the strongest, or by a form of chemisorption of $Si(OH)_3O^-$ ions.

In the SiO_2-MgO system the SiO_2/MgO product ratio of 0.5 indicates that each interlayer surface is covered with a monolayer of adsorbed silica.

In the $Al_2O_3.SiO_2$ system clays form in the presence of boehmite.

With systems involving $Mg(OH)_2$, its presence can still be detected despite the rapid coverage by silica where there is an excess of $Mg(OH)_2$ or silica is added in a solid form in which case time is required to allow the silica to dissolve.

With an excess of silica, under cold dilute conditions all the surfaces are covered to give amorphous material. If these solutions are heated or refluxed this amorphous material tends to argillify to give star-like or finger like material.

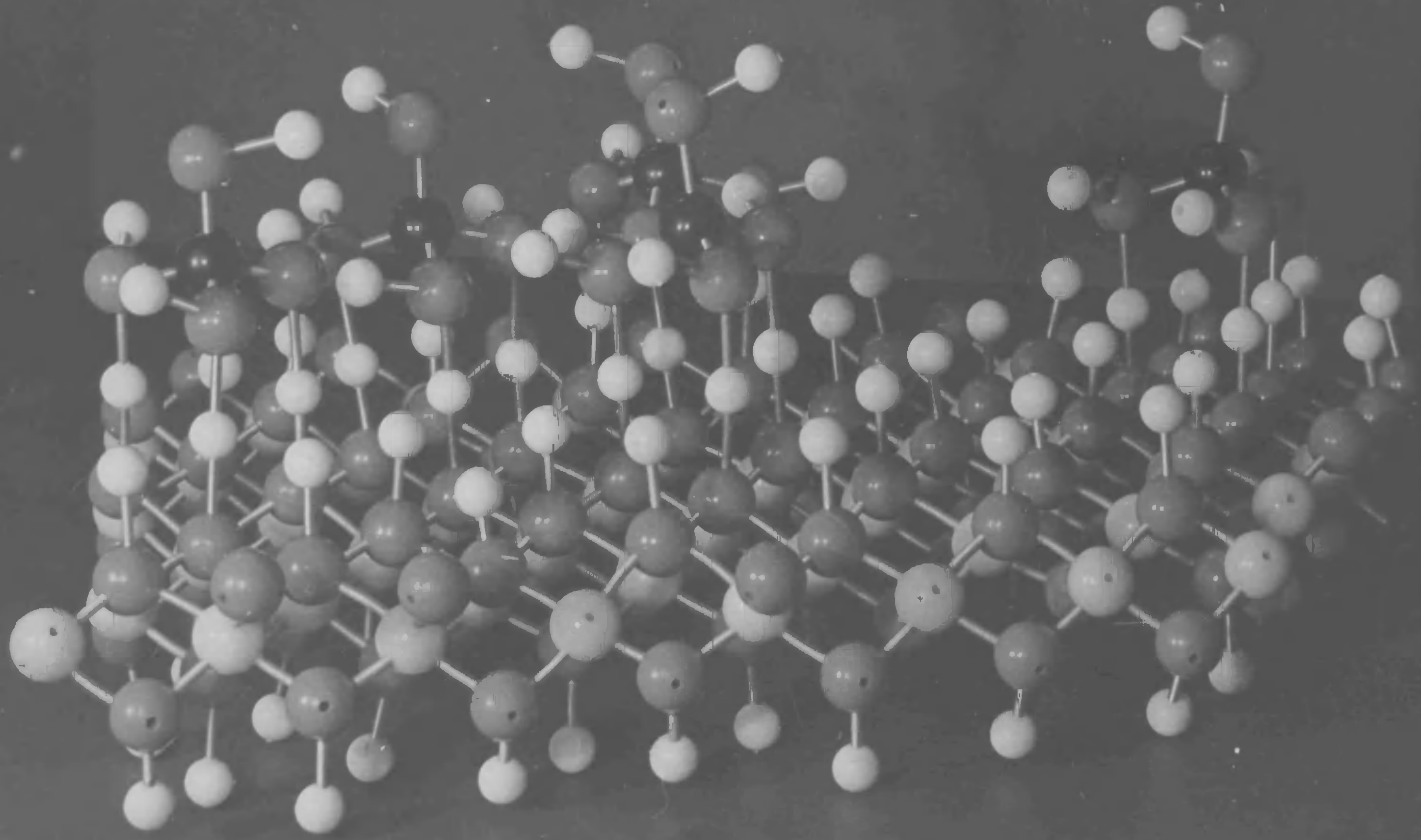
From studies carried out here, syntheses of clays using the slurry technique appear to again involve mechanisms based on the existence of a brucite-type hydroxide layer.

As described in Chapter III, in the SiO_2-MgO slurry system the initial reaction was thought to be the adsorption of silicic acid monomers either by triple hydrogen bonding, as shown in Figure 1, or by chemisorption of $Si(OH)_3O^-$ ions into + ve holes in the brucite surface . The hydrogen bonded arrangement could give rise to Si-O-Mg bonds by an S_N2 like reaction. Complete coverage by either method gives a maximum SiO_2/MgO ratio of 0.67. These structures could be the doughnut forms observed. The complete penetration of silicic acid molecules is not achieved as seen from inspection of these doughnuts: this may account for the observed SiO_2/MgO ratio of about 0.5 which is lower than the theoretical value.

The hydroxide surface with chemisorbed silicas will now be referred to as 'silicated magnesium hydroxide' or simply 'silicated hydroxide'.

One could imagine at least two ways in which the silicated hydroxide could argillify. These are shown in Figure 2.

Figure 1. Triple hydrogen bonded silicic acid molecules on the surface of brucite.



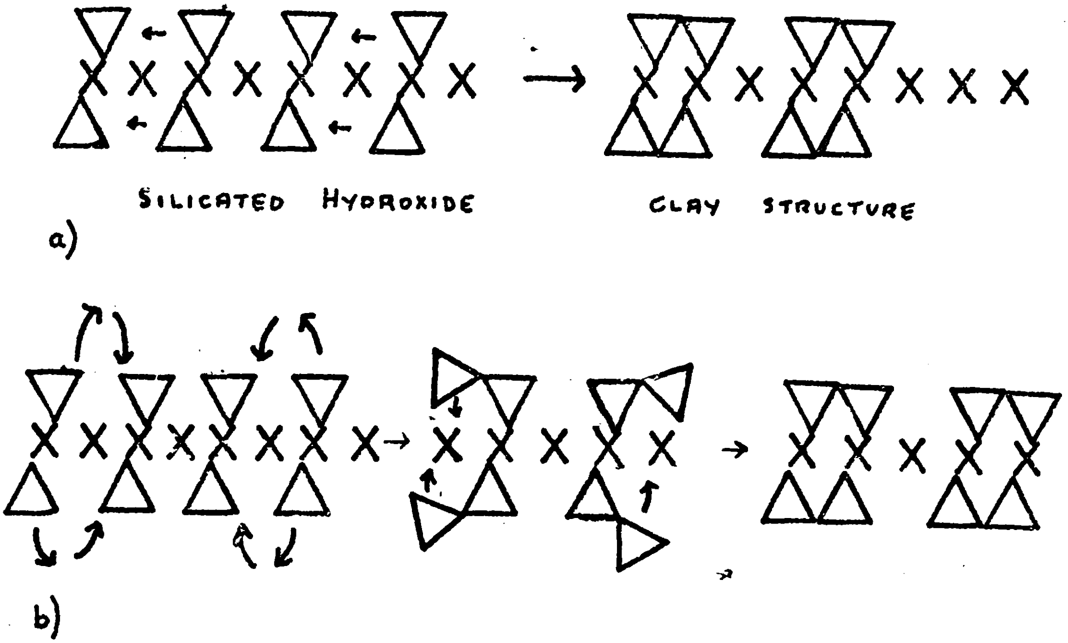
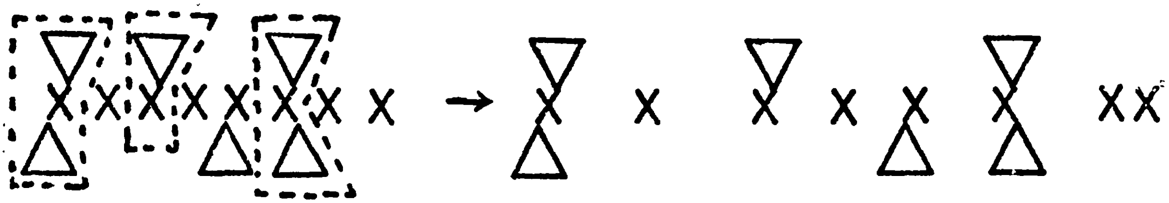


Figure 2. Argillification of silicated magnesium hydroxide.

In process a, silica tetrahedra are able to move to adjacent sites by the migration of OH groups. Thus tetrahedra may polymerise by simultaneous formation of Si-O-Si and Si-O-Mg bonds. In process b, some silica tetrahedra desorb and then polymerise to a neighbouring molecule. Migration of an OH group would then create a vacancy allowing the polymerised molecule to 'fold down' onto the hydroxide surface. Due to steric hindrance the silica tetrahedra cannot adsorb onto adjacent sites, so the Si-O-Si bond has to form first before the folding down process. A difficulty in assessing these possibilities is that it is not known how mobile the tetrahedra would be once they are chemisorbed onto the hydroxide surface. In any case the need for the simultaneous formation of both the Si-O-Si and Si-O-Mg bonds is a difficulty with a. In b, too there is a steric problem, since silica molecules may congest the surface at the polymerisation stage thus preventing the folding down process occurring. Once formed however, these structures could act as nuclei for further growth: additional ions, such as Li^+, could be encorporated at this stage.

Alternative proposed mechanism for final argillification.

Another possibility would involve the formation of 2:1 and 1:1 basic salt units from the silicated hydroxide. as shown in Figure 3.



where a 1:1 double salt unit is

and a 2:1 triple salt unit is

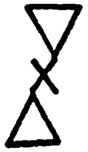
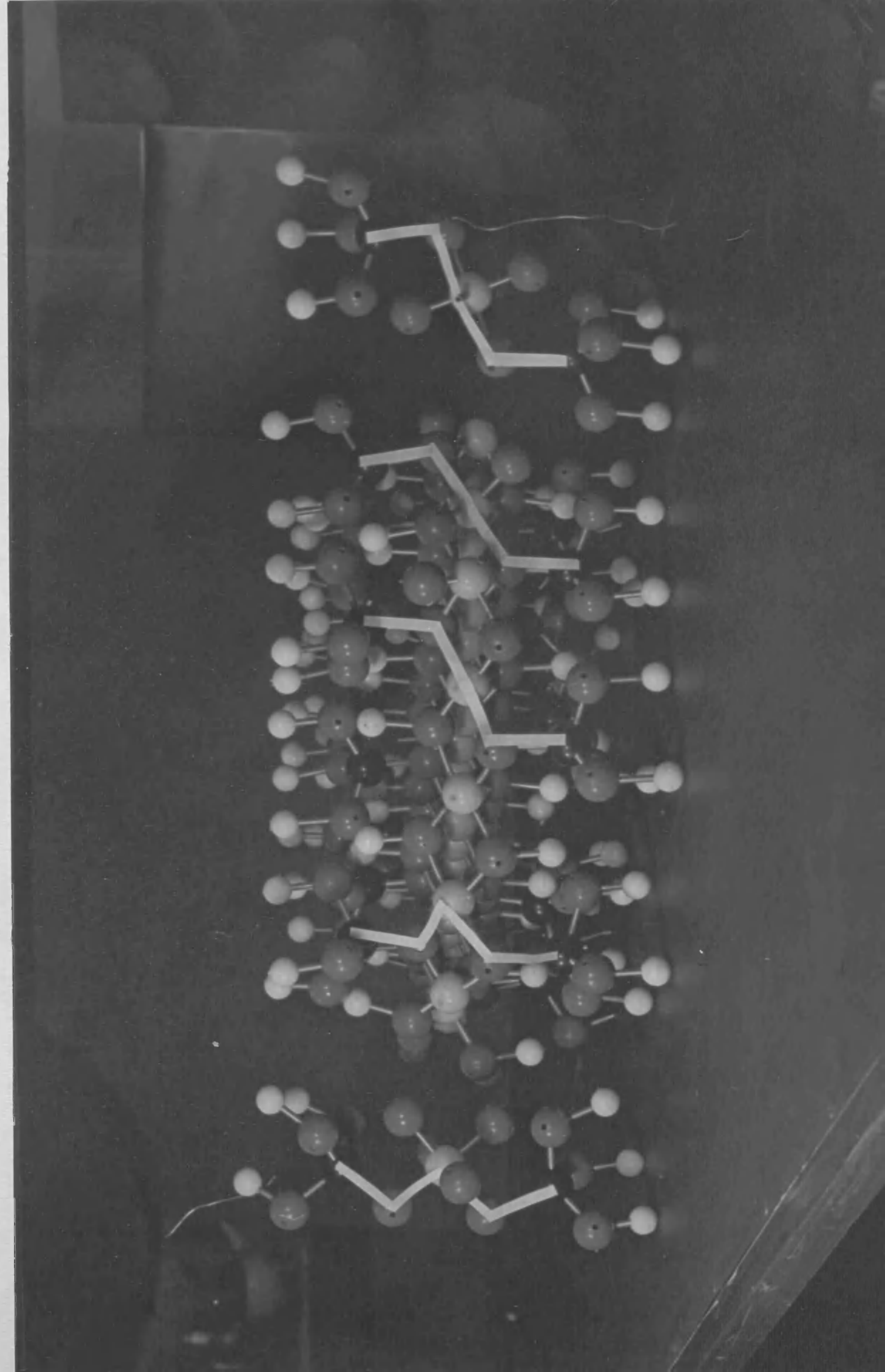


Figure 3. Proposed formation of clay forming units from silicated hydroxid

Figure 4. Relationship between 2:1 units and silicated magnesium hydroxide.

('cis', left, 'trans', right - for definition of these terms see later).



The stoichiometry of the slurry would be expected to exercise some control on the final product since the extent to which the brucite was silicated would affect the proportion of double and triple units available in solution. In the experiments described previously the SiO_2/MgO feed ratio was high, normally 2.0/1.0.

Figure 4 shows the relationship between a 2:1 unit and the silicated hydroxide.

Clay synthesis would be achieved by the dissolution of the silicated hydroxide into salt units which would then link up to form a clay, as shown in Figure 5.

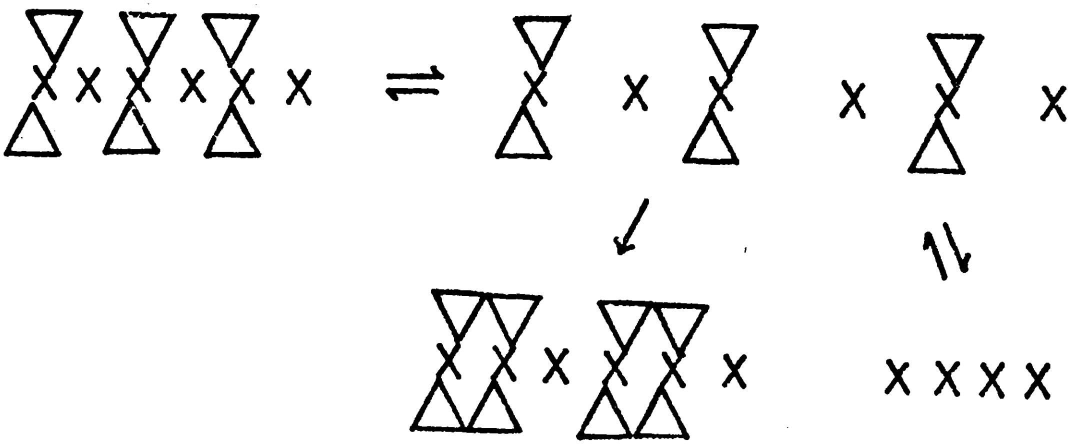
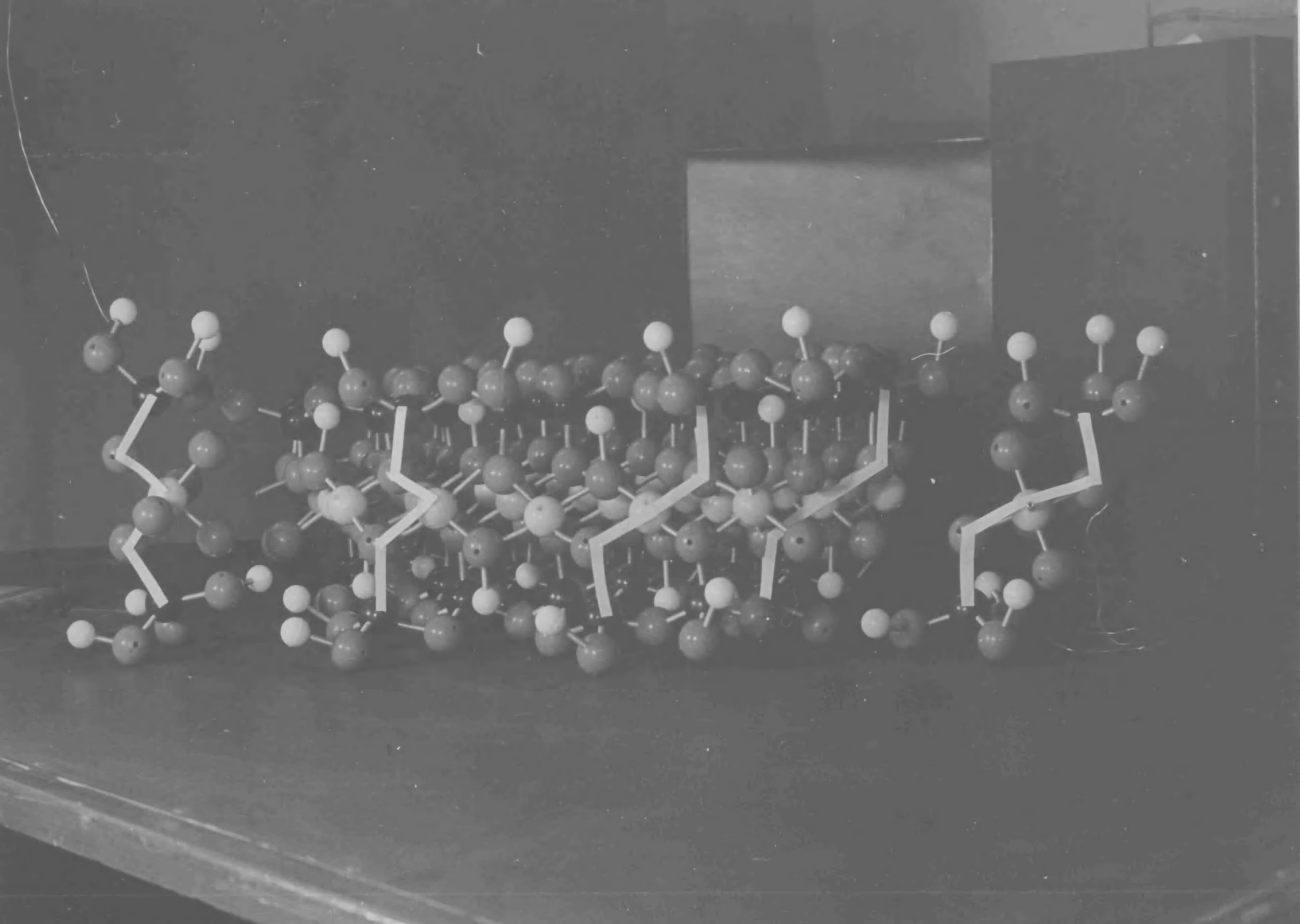


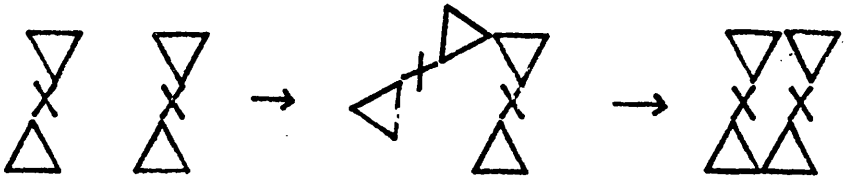
Figure 5. Clay synthesis from dissolution of silicate hydroxide.

Inspection of Figure 6 shows the relationship between a 2:1 unit and a 2:1 clay.

Figure 6. Relationship between 2:1 units and 2:1 layer silicate.



For steric reasons the silica tetrahedra would link first when a pair of such units combined :-



The additional magnesiums required would be supplied from solution. The mechanism is shown schematically in Figure 7.

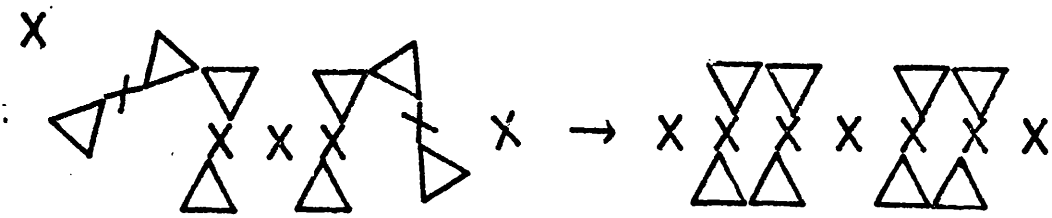
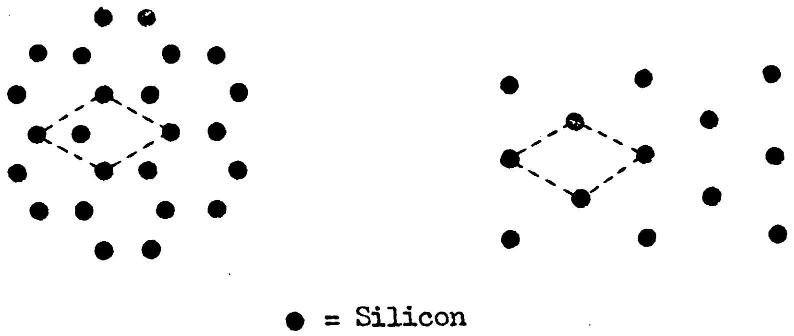


Figure 7. Linking of 2:1 units and magnesium to form 2:1 clay.

Here, additional ions, such as Li^+, could replace Mg^{2+} from the start of the growth stage, rather than later as in the previous mechanism.

The idea of a silicated hydroxide intermediate is consistent with the observation that the c-spacings of samples refluxed for up to one day were of the order of 14-15 Å, while later spacings were of about 13.6 Å. These longer spacings could be due to the orientation of the hydroxyl groups, shown in figure 2.

The electron diffraction series shown in Plates 49-55, Chapter 3, is consistent with a contribution from silicated hydroxides as well as from hectorite. Inspection of the two tetrahedral layer structures, shows that they have the same unit cell (Figure 8).



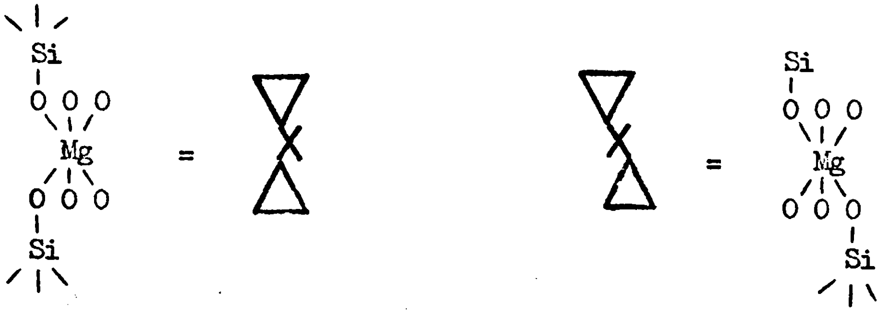
a) hectorite

b) silicate hydroxide.

Figure 8. Unit cells of hectorite and silicated hydroxide.

The diffractions observed could then arise from both the silicated hydroxide and particles of hectorite within the selected diffraction area. Structure b has less silicons and so will contribute less diffraction spacings than hectorite.

Studies on models of clays and on the unit structures suggest that the 'trans' configuration, rather than the 'cis'. of the 2:1 salt leads to more facile synthesis of clay (Figure 9).



Cis **Trans**

Figure 9. Configurations of 2:1 salt units.

One would expect the trans structure to be more stable since it is less crowded.

In summary then the mechanism is envisaged as follows. The initial adsorption of silicic acid onto brucite by hydrogen bonding to give slightly curled edges on brucite (Plate 43, Chapter III). The hydrogen bonded silica then forms Si-O-Mg bonds to give silicated hydroxide (Si-O-Mg bonds could be formed initially by chemisorption) which has the form of the doughnuts shown in Plate 46. The silicated hydroxide then dissolves to give 2:1 salt units which with additional magnesium and lithium ions link together to give hectorite which has the form of sheets (Plate 48). Thus the original brucite layers are not present in the final clay. The role of these original layers is thought of as acting as a kind of jig to fix the silica in such a way as to favour the formation of potential clay forming units, that is double or triple units rather than unorganised gel forming polymers.

By this mechanism the synthesis of more complex clay minerals can be envisaged, for instance, sepiolite and antigorite, by the alternative linking together of 2:1 and 1:1 salts respectively, as shown in Figures 10 and 11.

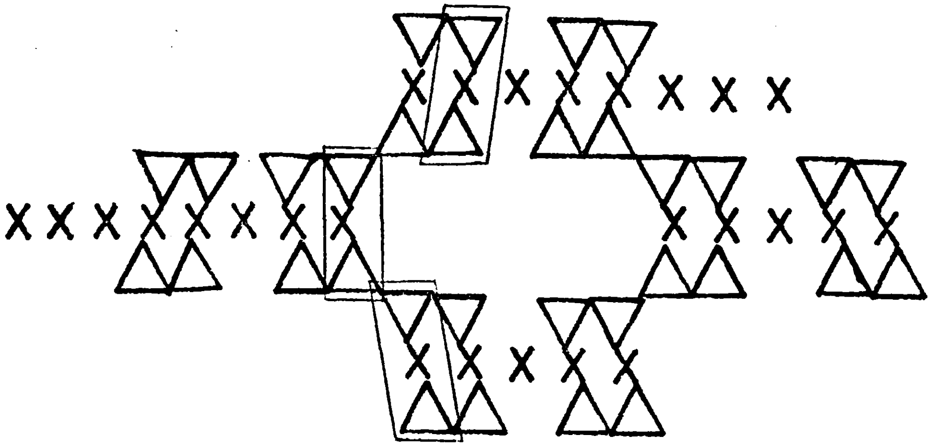


Figure 10. Formation of sepiolite by alternation of 2:1 basic salt units.

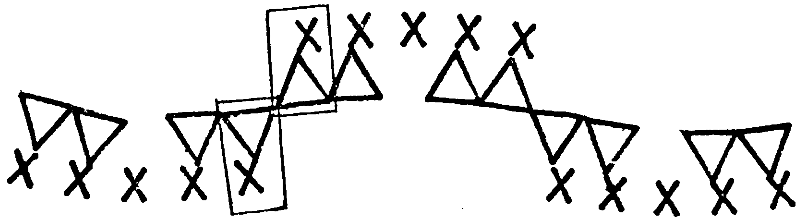


Figure 11. Formation of antigorite by alternation of 1:1 basic salt units.

APPENDIX A.

Experimental Methods.

Contents :-

1. Silica Analysis.

The determination of silica was based on the work of Alexander (1953). The silica was complexed with molybdic acid and then reduced to 'molybdenum blue' according to the method of Shapiro and Brannock (1963).

All the glassware required was cleaned by filling with a 1:1 mixture of HNO_3 and H_2SO_4 and allowed to stand overnight. After thoroughly washing with distilled water, the vessels were stored containing distilled water.

The reagents were as follows :-

Ammonium Molybdate solution

Ammonium molybdate (7.5 g) was dissolved in 75 mls H_2O, to which was added 25 mls of 20% H_2SO_4. The solution was stored for 24 hours before use and prepared fresh weekly.

Tartaric Acid solution

An 8% $^{w}/v$ solution was prepared.

Reducing solution

a) Sodium sulphite (0.7 g) was dissolved in 10 mls H_2O, to which was added 1-amino 2-naphthol-4 sulphonic acid.

b) Potassium metabisulphite (10 g) was dissolved in 90 mls H_2O.

Solutions a and b were mixed. This mixture had to be discarded after three days.

The procedure was as follows. Duplicate portions of the sample solutions, in 2 ml aliquots, were pipetted into 100 ml graduated flasks, 80 mls of distilled water were added and well mixed.

Molybdate solution, 2 mls, was added and allowed to stand for ten minutes.

The tartaric acid solution, 5 mls, was added and the mixture stood for four minutes.

Finally, the reducing solution, 1 ml, was added.

The solutions were then made up to volume, mixed well, and allowed to stand for thirty minutes.

The absorption readings were taken at about 815 m using a Bausch and Lomb, 'Spectronic 20', spectraphotometer. The concentrations of silicas were taken from calibration curves constructed simultaneously with the samples using sodium metasilicate as a standard.

2. Atomic Absorption

Magnesium concentrations were determined by a standard atomic absorption technique using a Unicam 'SP. 90' spectrophotometer, with an acetylene/air flame mixture.

Standard magnesium solutions were prepared by dissolving 'specpure' magnesium in 'Analar' hydrochloric acid.

Solutions containing phosphates were sometimes used : when combined in magnesium, inert, non volatile compounds reduce the magnesium levels and so 5% lanthanum solutions were added to absorb the phosphate component.

3. Differential Thermal Analysis

This analysis was performed with a differential micro thermal analyser, Model M-3, supplied by the Bureau de Liaison.

The probe is equipped with hollow thermocouples, with sample and reference being placed inside the thermocouples. This gives a very high efficiency of energy transfer from sample to detector with micro volume samples, (about 50 mg), with negligible internal temperature gradients.

The instrument is capable of detecting signals as low as a few tenths of a microvolt.

Unfortunately there were periodic difficulties with base line drift and flat topped peaks which curtailed more extensive use of this technique in this work.

4. Electron Microscopy

The experimental techniques and principles of electron microscopy have been described by Hirsh, Howie, Nicholson, Pashley and Whelan (1965).

A Siemons Elmiskop 1 was used in the present work. Magnifications from 200 to 160,000 times are obtainable with operating voltages of 40, 60, 80 and 100 KV. The specimen can be illuminated by either single or double condenser lens systems with subsequent three stage magnification by objective, intermediate and projector lenses (Figure 1).

Resolution

The Elmiskop 1 is capable of resolving 8 Å limited by spherical aberration of the objective lens. An objective aperture of 50 μ in diameter gives optimum resolution.

Astigmatism of the whole system is a factor which causes deterioration of the resolution as it leads to a deformation of the focussing field from rotational symmetry.

A number of other factors, for example, chromatic aberration influence the resolution but most of these have been eliminated by modern instrument design and specimen preparation techniques.

The single condenser illuminating system (Figure 1) gives an illuminated specimen area of about 50 μ. By using the double condenser system a demagnified image of the electron source is obtained

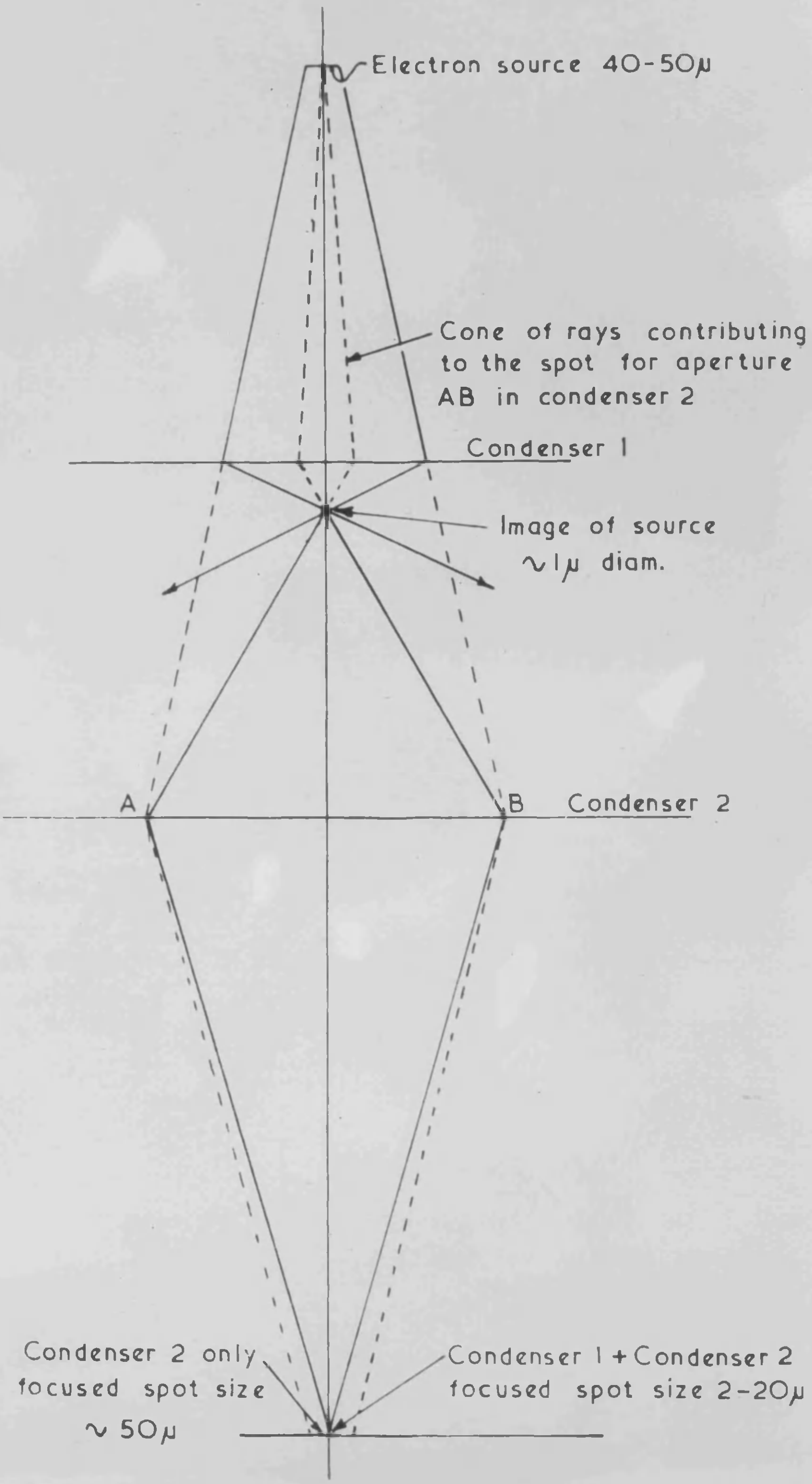

Electron source 40-50μ
Cone of rays contributing to the spot for aperture AB in condenser 2
Condenser 1
Image of source ∼1μ diam.
A
B
Condenser 2
Condenser 2 only focused spot size ∼ 50μ
Condenser 1 + Condenser 2 focused spot size 2-20μ

Fig. 1

and this is projected by the second condenser lens to give an illuminated area of about 2 μ . This means that heating effect on the specimen will be more pronounced when using the two condensers. Double condenser imaging produces a more coherent beam of electrons and reduces the scattering angle of the electrons leaving the specimen so that for high resolution work, when increased brightness is required at high magnifications, the double system is favoured.

Specimen Contrast

The contrast in an electron microscope image arises from the differential scattering of electrons in the object. A dense region of the object will scatter more electrons out of the beam than a less dense region and will appear darker in the final image viewing screen.

The contrast can be improved by reducing the size of the objective aperture or by operating the microscope at a lower accelerating voltage which causes more interaction between the beam and the object consequently increasing the electron scatter.

An accelerating voltage of 80 KV was normally used in this work.

Specimen Preparation

Specimens were normally prepared by evaporating a drop of an aqueous suspension of the sample, onto a carbon coated grid.

An aerosol spray was sometimes used : this creates a fine spray of minute droplets containing the sample, requiring much less

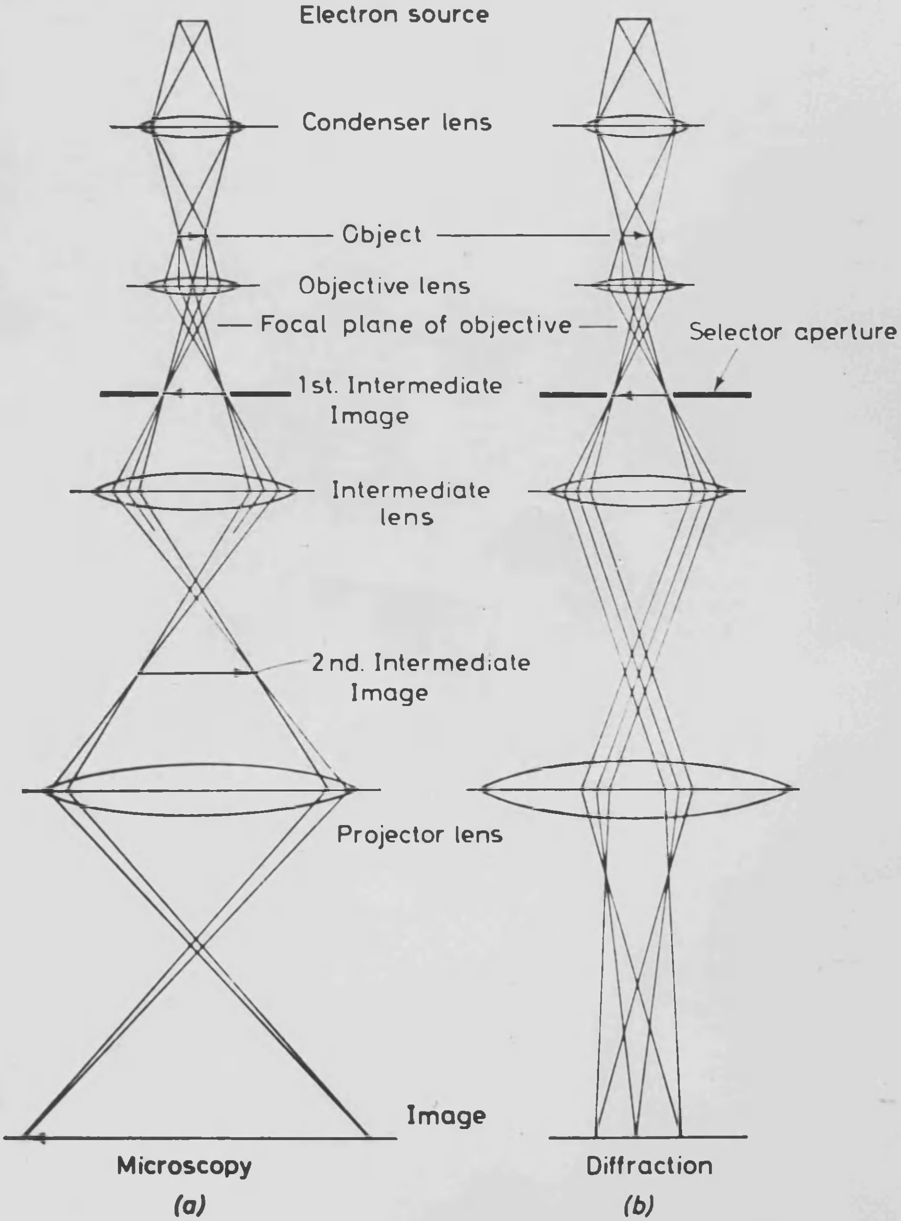


FIG. 2. Ray Diagrams for (a) Transmission Microscopy and (b) Selected Area Diffraction. (From Hirsch, Howie, Nicholson, Pashley and Whelan, 1965).

evaporation time and thus helps to eliminate any drying down effects.

Electron Diffraction

The technique used here was that of selected area diffraction which allows an observed pattern to be correlated to a small defined area of the specimen. The diffracted beams are focussed on to the back focal plane of the objective lens (Figure 1) together with the undeviated beam. The beams are subsequently magnified to form the final image. The lattice spacings (d) of the specimen can be determined by the relationship, $d = \frac{K}{R}$, where K is an instrument constant, and R is the radius of reflection of the observed pattern. It is necessary to determine K for each pattern and this is achieved by making measurements of a substance of known d-spacing. Thallous chloride was employed as a standard here. The accuracy is of the order of 1% and this is usually sufficient to allow identification of an unknown substance.

5. X-Ray Diffraction

A Philips X-Ray diffractometer fitted with a goniometer, proportional counter and ratemeter was used to record X-Ray diffractions from powdered samples.

The settings normally used were as follows :-

X-Ray source	35 KV, 20mA
Goniometer speed	1°/minute
Ratemeter	1×10^3
Time constant	2 seconds
Chart speed	600 mm/hour.

The powders were ground to the finest consistency possible in about five minutes in an agate mortar and pestal. The powders were then pressed into a 1 x 2 mm sample holder and then mounted in the goniometer.

APPENDIX B.

Crystals and the Origins of Life.

Crystals have been regarded as primitive models of organisms due to their ability to seed their growth from supersaturated solutions of their components. In this respect they only fulfill one of many requirements of an organism, their ability to reproduce.

Marquand (1968) has reviewed the possible role of minerals in biopoesis. Attempts were made up the 1930s to devise mediums for the cultivation of viruses outside the living cells of the host. Twort constructed incubators illuminated by light reflected from mineral surfaces and used special clay extracts to prepare his media, but the viruses failed to replicate. Goldschmidt (1952) stressed the catalytic activities that might result from the adsorption of components of the prebiotic soup on the edges and corners of mineral crystals. Hydrated silica, alumina, cyanides, phosphates and carbonates adsorb molecules and hold them in a spatial arrangement comparable to that in which they are held, or thought to be held by proteins.

As indicated in the Introduction Bernal (1951) proposed a similar adsorption and catalytic role for clays. The formation of asymmetric molecules which are characteristic of compounds occurring in living organisms might have first occurred, according to Bernal, through preferential adsorption of a pair of asymmetric molecules on the surface of quartz, which is the only mineral possessing an asymmetric structure.

Cinatl (1968) has studied the properties of calcium structures in an environment of concentrated salt solutions culture media and biological fluids. It appears that inorganic and inorganic-organic crystalline formations with agglomerate spherical morphology similar to budding yeasts, appear from these mixtures. He has shown that they resemble organisms in their ability to reproduce, age, adapt, degenerate and disintegrate.

Cairns-Smith (1966) suggested that some crystals may be able both to store and replicate genetic information. He regards the adsorption of other molecules by crystals as a function that could be important in the evolution of primitive organisms.

As he has pointed out clay minerals, in principle, have the capacity to store information, for instance, by the isomorphous replacement of aluminium for silicon in the tetrahedral layer or iron for magnesium and aluminium in the octahedral layer. That this information can be duplicated is shown by Gatineau's (1964) structure determination of muscovite. Here a pattern of aluminium for silicon substitutions in one layer leads to a complimentary substitution pattern in the next layer, thus giving a two layer periodicity.

Nacrite also has a two layer periodicity as shown by Blount, Threadgold and Bradley (1969).

Clays can also seed their own growth : Barrer (1952) describes a general method of demonstrating this. De Kimpe and Gastuche (1964) have seeded the growth of muscovite at low temperatures. Anikin and Kochetkova (1969) have grown micas from seeds at room temperatures, and hectorite has been shown to be seedable in this work.

The fact that clays appear to have flexible structures enables them to exhibit varied morphologies which could have had a role as organelles in primitive organisms i.e., they could have had a phenotypic as well as genetic function.

The tubular structures postulated to explain the micrographs shown in Plate 23 , Chapter I, could be envisaged as being useful to a primitive organism by, say, its enhanced ability to adsorb other molecules, or to act as an organism in its own right : it may survive better in a flow environment than, say, a plate-like clay.

Diamond and Bloor (1970) have shown that endellite can exist in globular clusters of quasi-tubular particles radiating from common centres. It may be that their ability to form organised colonies gives these structures a better chance of survival.

Clay organisms could have a similar life cycle to phytoplankton cells. This organism is slightly denser than sea water and survives near the surface of the sea. It adsorbs nutrients from the water immediately around it, becomes denser and sinks. This appears to initiate replication by causing the cell to divide and the cells then to float to nearer the surface to continue the life cycle. One could imagine clay particles being 'selected' for their efficiency of seeding their growth by using up all the available 'nutrients' more quickly than its competitors. Its changed morphology, that is, by being larger may cause it to move to regions of say stronger ionic content, causing it to cleave and thus propagate by further growth of the cleaved particles.

The extent to which such processes were important to early life is at present highly speculative but many organisms today depend for their existence on being able to control crystal growth processes, for example, in bone and shell formation.

APPENDIX C.

Attempts to develop a micro detection technique for minerals.

Systems were devised in an attempt to identify minerals produced by synthetic methods.

The idea arose from crystallisation effects displayed by agar gels mixed to contain supersaturated solutions of organic components. .

Figure 1 shows a gel containing p-nitrophenol. Careful inspection of the dendritic crystal growth shows that practically all the growth originates from one point (circled).

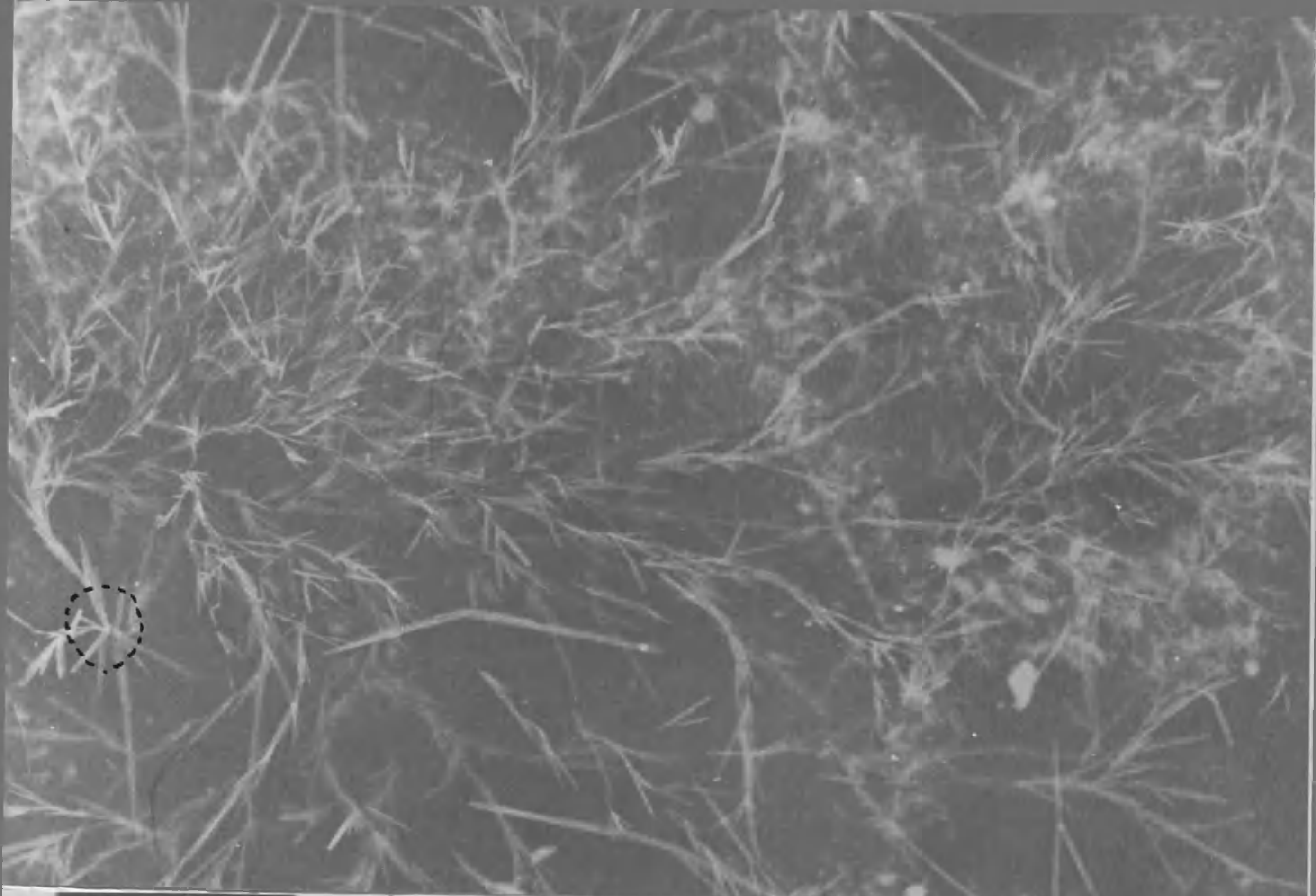
It was thought that very small amounts of clay might be detected by their ability to seed such a crystallisation in a carefully filtered 'clean' gel. Furthermore, the type of clay might be identified by a unique secondary crystal growth pattern or by differential seeding effectiveness for different organic molecules.

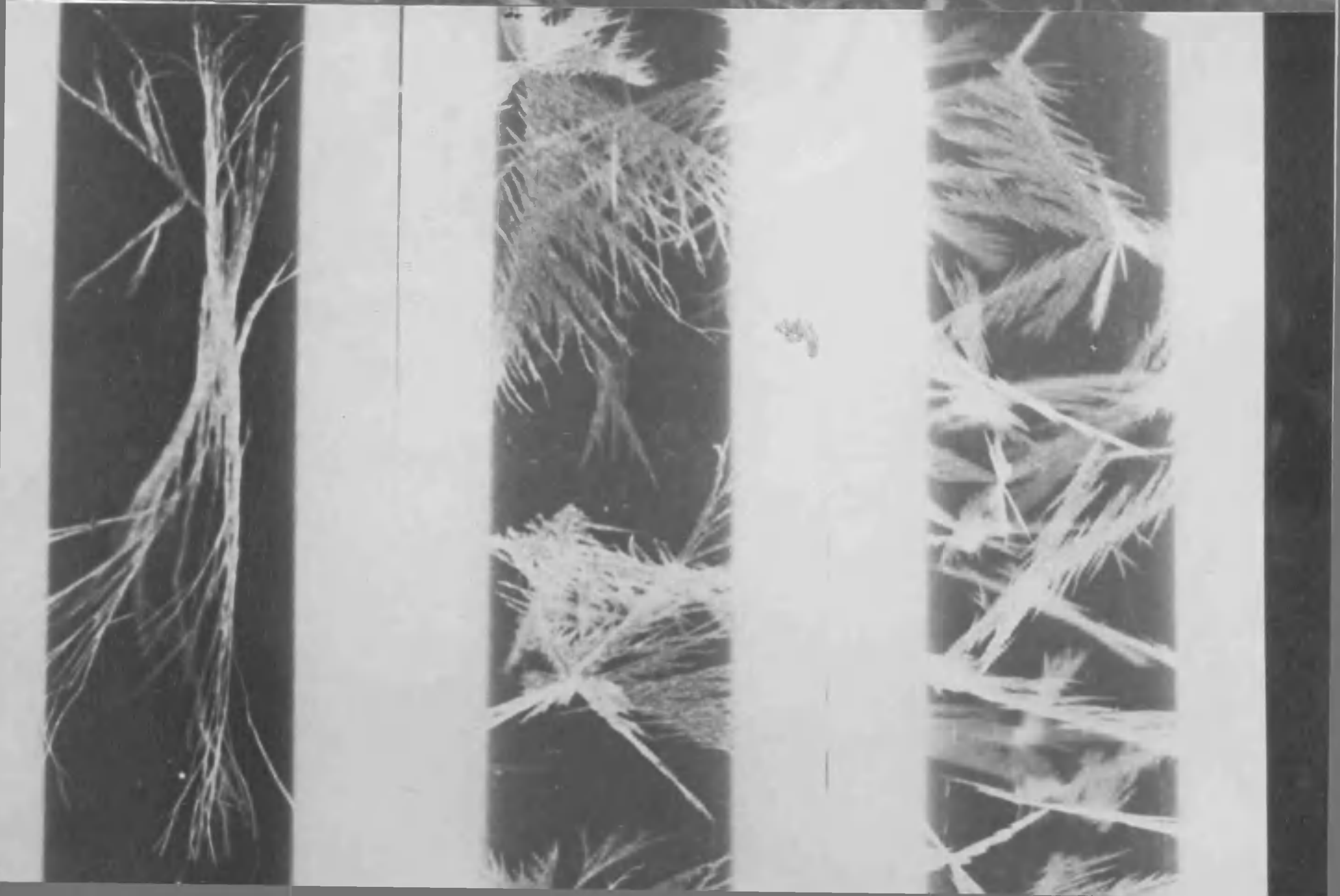
The crystallisation of benzoic acid at various concentrations is shown in Figure 2.

However, because most of the compounds studied were to a certain extent self nucleating, and gels that were not, tended to crystallise non-specifically with various minerals, attempts to develop the systems further were not pursued.

Fig. 1 Gel containing supersaturated solution of p-nitrophenol.

Fig. 2 Gels containing increasingly supersaturated solutions of benzoic acid.





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