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Reaction of aqueous catechol solutions with minerals

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APPROVED BY MEMBERS OF THE THESIS COMMITTEE:

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Morris B. Silverman

The effectiveness of catechol, an aromatic vic-diol, in dissolving silicate minerals was studied. A synthetic amorphous magnesium trisilicate, $Mg_2Si_3O_8 \cdot 5H_2O$, as well as the minerals olivine, sepiolite, diopside, augite, and enstatite were used to react with catechol in slightly acidic, basic, and neutral solutions. It was found, depending on the solvent used, that 33-52, 8-17, 14-30, 5-11, 3-6, and 0.5-1 % of the minerals dissolved, respectively.

The reaction with $Mg_2Si_3O_8 \cdot 5H_2O$ resulted in the formation of crystals of magnesium tris(catecholato)siliconate nonahydrate $Mg[Si(Cat)_3] \cdot 9H_2O$. Dehydration of the crystals at room temperature resulted in the loss of 6 moles of water to form a trihydrated complex, $Mg[Si(Cat)_3] \cdot 3H_2O$; further dehydration at 100°C gave an anhydrous complex, $Mg[Si(Cat)_3]$. By adding guanidine hydrochloride, CN_3H_6Cl, to the reaction mixture after filtering, crystals of guanidinium tris(catecholato)siliconate monohydrate, $(CN_3H_6)_2[Si(Cat)_3]\cdot H_2O$, were obtained. Infrared and nmr spectra, and analytical and x-ray powder diffraction data are presented. The possible structures of the magnesium salts of tris(catecholato)siliconate are also discussed.

The reaction of catechol with the minerals listed above gave a water soluble silicon-catechol complex, $Si(Cat)_3^=$, which was isolated as $(CN_3H_6)_2[Si(Cat)_3]\cdot H_2O$ by adding guanidine hydrochloride to the reaction mixture after filtering. The dissolution of these minerals by catechol to form $Si(Cat)_3^=$ leads to the conclusion that aromatic <u>vic</u>-diols in nature may play a role in chemical weathering, in transport of silicon into rivers or seas, in soil development, in interconversion of minerals, and in accumulation of silica in plants.

REACTION OF AQUEOUS CATECHOL SOLUTIONS WITH MINERALS

by
BOONTHONG POOCHAROEN

A thesis submitted in partial fulfillment of the
requirements for the degree of

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TO THE OFFICE OF GRADUATE STUDIES:

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I. INTRODUCTION

The natural breakdown or "weathering" of minerals occurs by both chemical and mechanical processes. Mechanical processes include wind erosion, grinding, fragmentation by thermal expansion and contraction, and mechanical forces exerted by growing plants. Chemical reactions have classically been believed to be due to simple dissolution by water, acidity due to dissolved carbon dioxide, and air oxidation. In recent years, however, it has been established that organic matter plays a role in certain geochemical reactions involved in soil formation and fertility (1, 3), weathering of rocks (4, 5), accumulation of metals in sediments (4), and the transport of certain metals as organic complexes in river water (6, 7, 8). Perhaps even more important is the role played by plants and microorganisms in dissolving or altering silicate minerals (9). Several examples are known of plants that accumulate silicon or aluminum (10, 11). Some recent investigations have shown that several plants exude organic compounds from their roots (1, 12, 13, 14) and these might play a role in dissolving soil minerals. Lichens bring about the dissolution of silicate minerals through the action of weak organic acids that constitute 1-5 % of the dry weight of the organism (5, 15). Parfenova and Yarilova (16) have given some quantitative data on the amount of various metals "mobilized" annually by grain plants. By "mobilized" they mean that the metals are taken from the soil as deep as the roots extend, transported to the top parts of the plant, and then returned to the humus layer at the very top of the soil profile when the plant dies.

In the laboratory studies it can be shown that organic acids, especially those capable of forming chelates with iron(III) and aluminium, are more effective in dissolving minerals than simple inorganic acids. For example, the solubility of chlorite, nepheline, and hornblende is greater in citric or tartaric acid solutions than in succinic and aspartic acid solutions (17). Furthermore, aspartic acid extracts more silicon and calcium from chlorite and kaolinite than does sulfuric acid at a slightly lower pH (18). In another study the order of decreasing resistance of minerals to dissolution in aqueous citric and tartaric acids at pH 5.5 was found to be: kaolinite > muscovite > clinochlore > hornblende > labradorite > biotite > nepheline. However, no dissolution at all was effected by succinic acid or aspartic acid at the same pH (19). In a study of iron(III) migration in soils it was found that α-hydroxy carboxylic acids mobilize iron but other non-chelating carboxylic acids do not (18).

It is well established that humic and fulvic acids extracted from soils are capable of forming complexes with transition metals, aluminium, uranium, germanium, etc., (2, 3, 4, 20). Copper in sea water is partly present in a complexed form (21) and many other examples are known in which metals are intimately bound up with natural organic matter. Beyond this, however, very little information is available. For example, it is not certain that metal chelates are formed in every case. Very little is known about the kinds of organic compounds that react with minerals. What kinds of functional groups or complexing groups are required? Which minerals are attacked and which ones are not? Are the minerals completely dissolved or are they altered to other solid phases? Does the organic compound attack the mineral surface directly or is simple dissolution followed by complex formation?

The present study was undertaken in order to determine whether aqueous catechol solutions would react with silicate minerals and, if so, to learn something about the conditions required and the products of the reaction.

There is evidence in the literature that catechol and other aromatic vic-diols might be especially active in attacking minerals (2, 25). A silicon complex with catechol was first prepared in 1931 by refluxing an aqueous ammonium hydroxide and catechol solution with freshly precipitated silica ($SiO_2 \cdot xH_2O$) (22). The complex containing three moles of catechol per mole of silicon was formulated as Figure 2.

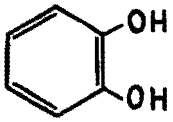

Figure 1. Catechol

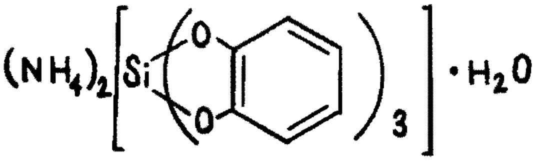

Figure 2. Silicon-catechol complex*

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*Variable amounts of water have been reported but it is now established that only one H_2O is present.

It has since been shown that the reaction will go just as easily at room temperature (23), that almost any aromatic vic-diol will form a complex (including tannic acid and gallic acid), and that even finely divided quartz will react, although slowly (24). Hess et al. (25) found that ammoniacal catechol solutions react with "Permutite" (a synthetic amorphous alumino silicate) but not with montmorillonite ($Al_2Si_4O_{10}(OH)_2 \cdot xH_2O$) or orthoclase ($KAlSi_3O_8$). These latter workers pointed out the possibility that aromatic vic-diols might play a role in soil chemistry. In another study it was found that 4-tert-butylcatechol is chemisorbed on the surface of kaolinite and montmorillonite (26), supposedly by chelation to aluminum ions, but the investigator did not consider the possibility of chelation with silicon. There is an initial rapid sorption of 4-tert-butylcatechol followed by additional slow sorption that continues even after 85 days at room temperature. This was interpreted as a slow attack on the kaolinite and montmorillonite by the butycatechol that opened up new sorption sites.

Germanium, which lies just below silicon in the periodic table, and forms a similar catechol complex, $(NH_4)_2[Ge(Cat)_3] \cdot 3/2\ H_2O$, is known to accumulate in coal and it has been suggested that this is due to the formation of an aromatic vic-diol complex (4, 27, 28).

Naturally, if aromatic vic-diols are to play a role in geochemical reactions it must be shown that they are present in the environment. Figure 3, 4, and 5 show three common constituents of tannins. Tannins are extracted by water from the wood and bark of many different plants and are generally present in ground water, streams, and lakes (29). Catechins (Fig. 6), and other compounds containing aromatic vic-diol

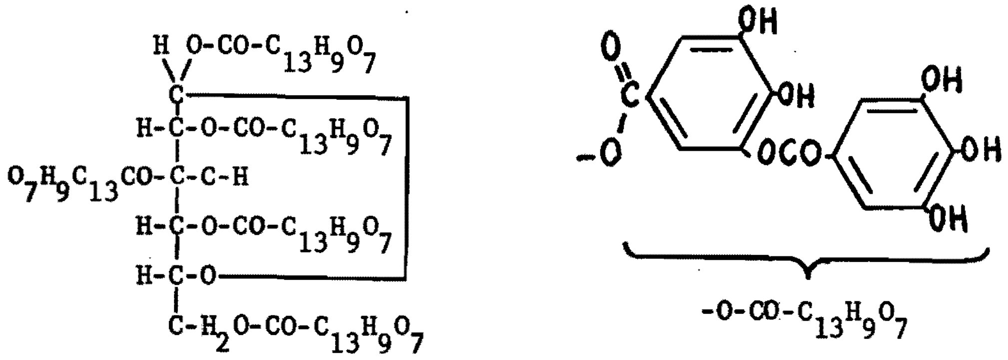


Figure 3. Penta-m-digalloyl glucose (29, vol. 3)

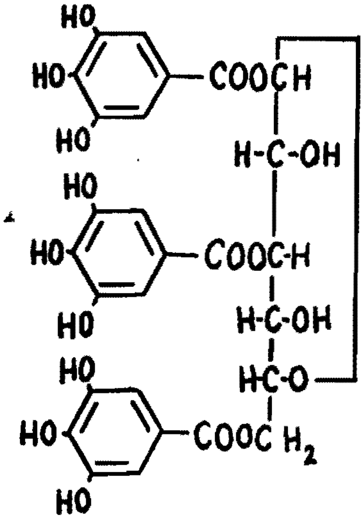


Figure 4. Corilagin

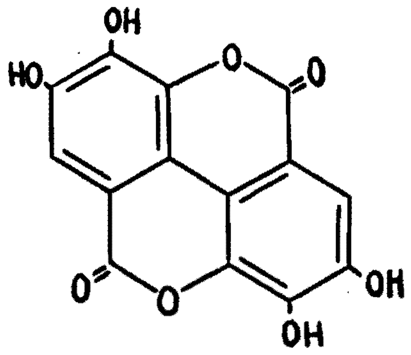


Figure 5. Ellagic Acid (29)

groups are leached by rain water from green leaves (especially beech leaves) and forest litter (30).

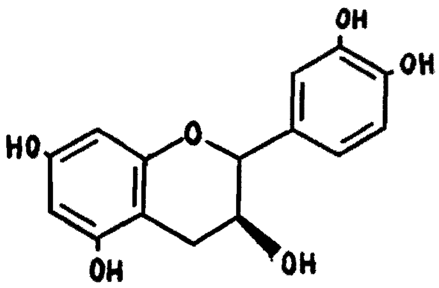
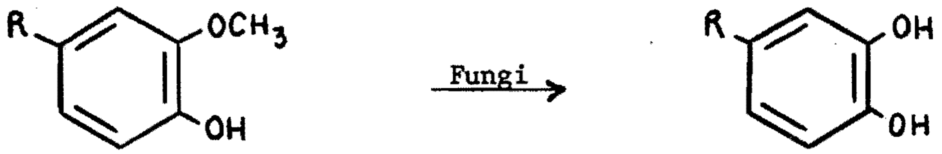


Figure 6. Catechin (six isomers)

The roots of cucumber, turnip, cabbage, tomatoes, and red peppers exude a variety of organic substances, among them several "phenolic acids" and "neutral phenols" that were not identified further (13). Several studies have expounded the importance of "polyphenols" in developing podzolic and lateritic soil profiles (31, 32, 33) but it has not been established that *vic*-diols are the active groups.

Structures proposed for himic and fulvic acids generally contain either one or more aromatic *vic*-diol groups or else the semi-quinone group (1, 4, 20). Hemwall (26) found that the semi-quinone and quinone of 4-tert-butylcatechol are just as effective in attacking kaolinite and montmorillonite as the unoxidized phenol. Steelink and Tollin (35) state that many, if not most, of the free radicals present in soil are the semi-quinones and quinones of aromatic *vic*-diols. Aromatic *vic*-diols might be formed from lignin by the action of fungi on dead, decaying plants (34):



part of a lignin

It was, in fact, shown in this work that several minerals do react at room temperature with aqueous catechol solutions, even under neutral or slightly acidic conditions. The results may be of particular significance in geochemistry where, despite the widespread acceptance of the importance of chelation, the formation of silicon complexes has only been considered in one previous case (25). Indeed, not many organic coordination complexes of silicon are known and most are unstable in the presence of water, so it is not surprising that this possibility has been overlooked.

In this study of the effectiveness of aromatic vic-diols, five silicate minerals--olivine, sepiolite, diopside, augite, and enstatite--and one synthetic amorphous magnesium trisilicate were chosen to react with catechol. The solvents used were 0.05 F acetic acid, 0.05 F potassium biphthalate, water, 1.0 F ammonium chloride, and 0.05 F ammonia. The products of the reaction with amorphous magnesium trisilicate were obtained as magnesium and guanidinium salts of tris(catecholato)siliconate for which the analytical and x-ray powder diffraction data, ir and nmr spectra were presented. For the reaction with the naturally occurring silicate minerals, the reaction products were investigated by precipitation as guanidinium tris(catecholato)siliconate monohydrate in which percent recoveries, as well as the percent mineral dissolved were also determined.

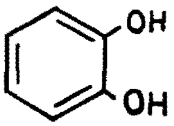
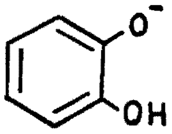
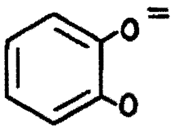
II. REACTION OF AQUEOUS CATECHOL SOLUTIONS WITH SYNTHETIC MAGNESIUM TRISILICATE

INTRODUCTION

A magnesium silicon complex was first prepared in this laboratory by D.W. Barnum by reacting aqueous catechol solution with synthetic magnesium trisilicate, $Mg_2Si_3O_8 \cdot 5H_2O$, but the structure, composition, and reaction conditions were not investigated. In the course of the present study it appeared that the same complex was the product of the reaction of aqueous catechol solutions with the minerals, olivine and sepiolite. It was, therefore, of interest to investigate this compound in more detail.

Another reason for further study is the problem of the structure of hydrated silicon-catechol complexes. Flynn and Boer (36) have shown by a single crystal x-ray structure determination that the pyridinium complex, $(C_5H_6N)_2[Si(Cat)_3]$,* contains octahedrally coordinated silicon, the catechol serving as a bidentate ligand (Figure 7). Barnum (23, 37) has suggested that those complexes containing "water of crystallization" may have one chelate bridge broken as shown in Figure 8.

* In this paper the abbreviations H_2Cat, $HCat^-$, and $Cat^=$ will be used for catechol and its ions:

H_2Cat =  ; $HCat^-$ =  ; $Cat^=$ = 

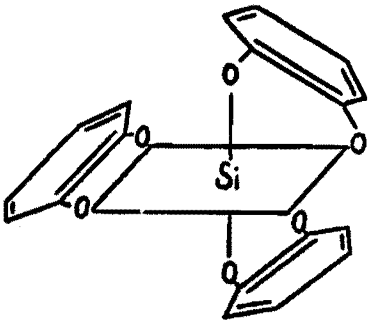


Figure 7. $[Si(Cat)_3]^=$

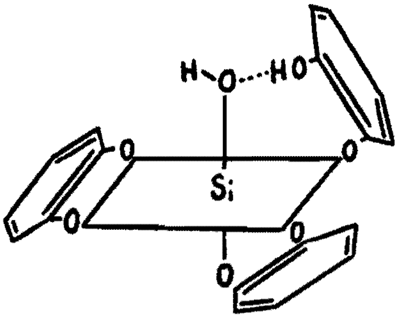


Figure 8. $[Si(OH)(HCat)(Cat)_2]^=$

It was hoped that an investigation of the magnesium salts, $Mg[Si(Cat)_3]\cdot xH_2O$, might provide additional insight into this problem.

In addition, the problem of recovering the product of the reaction of magnesium trisilicate with catechol as the guanidinium salt, $(CN_3H_6)_2[Si(Cat)_3]\cdot H_2O$, was investigated. Kelley (38) was not able from his data to determine the amount of "water of crystallization" in this compound. Additional data was obtained in the present study and together with Kelley's data good evidence for one mole of "water" per mole of silicon was obtained.

EXPERIMENTAL

Magnesium trisilicate, $Mg_2Si_3O_8\cdot 5H_2O$, was purchased from Alfa Inorganic. Its x-ray powder diffraction pattern showed it to be amorphous.

Anal. Calcd for $Mg_2Si_3O_8\cdot 5H_2O$: Mg, 13.86; Si, 24.01. Found: Mg, 12.38, 12.47; Si, 23.31, 23.25.

Preparation of Magnesium Tris(catecholato)siliconate Nonahydrate, $Mg[Si(Cat)_3]\cdot 9H_2O$

Because catechol solutions, especially when basic, are easily oxidized by atmospheric oxygen, the following reactions were carried out under a nitrogen atmosphere. The techniques used have been reviewed by S. Herzog _et al_. (39). Once the crystalline products were dried, they could be exposed to air without noticeable decomposition. Hygroscopic compounds, however, were suitably protected from atmospheric moisture.

A 2.11 g portion of $Mg_2Si_3O_8 \cdot 5H_2O$ and 6.61 g of catechol (mole ratio $Si/H_2Cat = 3:10$) were placed in a 250-ml flask. The flask was evacuated, filled with nitrogen, and 40 ml of the desired solvent added. Solvents used were 0.05 F acetic acid, 0.05 F potassium biphthalate, water, 1.0 F ammonium chloride, and 0.05 F ammonia. The contents of the flask were swirled until all of the catechol was dissolved and then the mixture set aside at room temperature. The reaction time required depends somewhat on the solvent, but generally after one month tabular brownish crystals of $Mg[Si(Cat)_3] \cdot 9H_2O$ that had formed were several millimeters in diameter and could be separated from the unreacted magnesium trisilicate by picking them out with tweezers. These were washed with water and dried in a slow stream of nitrogen. The yield (see Table I) was on the order of 30-50 % based on $Mg_2Si_3O_8 \cdot 5H_2O$.

In another set of experiments, the reaction mixtures were refluxed for about 15 minutes before setting them aside at room temperature and generally somewhat better yields were obtained.

For preparative purposes the amounts of reactants were doubled and 0.05 F ammonia was used for the solvent. The yield was about 7 g of the nonahydrate.

When 15 F ammonia was used as the solvent there were at least two different kinds of crystals; feather-like and needle-like crystals were

TABLE I

RESULTS FROM REACTIONS BETWEEN MAGNESIUM TRISILICATE AND CATECHOL

Aqueous media	pH		Product, $Mg[Si(Cat)_3]\cdot 9H_2O$	
	initial	final	wt, g[b]	% yield[c]
.05 F acetic acid	5.4	6.4	2.76	43
.05 F potassium biphthalate	5.5	6.5	2.13	33
water	7.2	6.4	2.34	36
1.0 F ammonium chloride	6.5	5.8[a]	3.07	47
.05 F ammonia	7.8	6.4	3.36	52

a. this final pH was measured from the identical reaction which was refluxed 15 minutes for initiating the reaction.

b. weight of those crystals that could be separated with tweezers.

c. calculated, based upon $Mg_2Si_3O_8\cdot 5H_2O$ and Eq. 1.

formed. These were separated mechanically and upon drying under vacuum both crumbled to white powders which were identified by infrared as either $(NH_4)_2[Si(Cat)_3]\cdot H_2O$ or $(NH_4)_2[Si(Cat)_3]\cdot H_2O\cdot H_2Cat$, or possibly mixtures of both. These compounds have been described earlier by Barnum (23, 37).

Anal. Calcd for $Mg[Si(Cat)_3]\cdot 9H_2O$: C, 40.12; H, 5.47. Found: C, 39.74; H, 5.61.

Preparation of Magnesium Tris(catecholato)siliconate Trihydrate, $Mg[Si(Cat)_3]\cdot 3H_2O$

The crystals of the nonahydrate prepared by the above procedure were dried to constant weight in vacuum at room temperature (about 40 hours are required) or at 50-80°C (which requires about 20 hours), whereupon the crystals lost six moles of water and crumbled to a brownish powder of the trihydrate, $Mg[Si(Cat)_3]\cdot 3H_2O$.

Anal. Calcd for $Mg[Si(C_6H_4O_2)_3]\cdot 3H_2O$: C, 50.19; H, 4.21; Si, 6.52; Mg, 5.64. Found: C, 49.15; H, 4.27; Si, 5.96, 6.48, 6.29, 6.36; Mg, 5.68, 5.64, 5.59, 5.54. Silicon was determined by decomposition and dehydration with concentrated HCl, filtering off the insoluble hydrated silica, and ignition to SiO_2. Magnesium was determined in the filtrate by extracting the catechol (which interferes) into diethyl ether and titrating with standard EDTA using Eriochrome Black T indicator. Calcd weight loss on drying from $Mg[Si(Cat)_3]\cdot 9H_2O$ to $Mg[Si(Cat)_3]\cdot 3H_2O$: 20.1%. Found: 20.1; 20.4, 21.6% (these weight losses are also shown in Table II).

TABLE II

DEHYDRATION OF $Mg[Si(Cat)_3]\cdot 9H_2O$ AT REDUCED PRESSURE ($<$1 Torr) TO FORM $Mg[Si(Cat)_3]\cdot 3H_2O$ AND $Mg[Si(Cat)_3]$

$$Mg[Si(Cat)_3]\cdot 9H_2O \xrightarrow{-6H_2O} Mg[Si(Cat)_3]\cdot 3H_2O \xrightarrow{-3H_2O} Mg[Si(Cat)_3]$$

Sample No.	Temp., °C	Time, Hrs.	Weight[c] loss, %	Moles H_2O lost	Temp., °C	Time, Hrs.	Total Weight loss, %	Total[d] Moles H_2O, lost
1	22 (Room)	110[a]	20.1	6.0	-	-	-	-
2	22 (Room)	92	20.4	6.1	-	-	-	-
3	22 (Room)	96	20.4	6.1	100	166	30.2	9.0
4[b]	80	60	21.6	6.4	96-98	147	30.9	9.2

a. weight constant after drying 38 hours.

b. a small amount of sample was lost during the heating at 80°C.

c. theoretical weight loss is 20.1%.

d. total theoretical weight loss (from the nonahydrate to anhydrous) is 30.1%.

Preparation of Anhydrous Magnesium Tris(catecholato)siliconate, $Mg[Si(Cat)_3]$

The anhydrous salt was obtained by drying either the crystal of nonahydrate or trihydrate to constant weight in an Abderhalden pistol drier at about 100°C. The time required to reach constant weight was 160-220 hours.

Calcd weight loss on going from the nonahydrate to the anhydrous compound: 30.1%. Found: 30.2; 30.9% (also see Table II).

Preparation of Guanidinium Tris(catecholato)siliconate Monohydrate, $(CN_3H_6)_2[Si(Cat)_3]\cdot H_2O$

Into a 250-ml flask were placed 13.2 g of catechol and 4.2 g of amorphous magnesium trisilicate. The flask was evacuated, filled with nitrogen, and then 80 ml of 0.05 F ammonia was added. After stirring overnight with a magnetic stirrer, the unreacted magnesium trisilicate was filtered off and 40 ml of 1.0 F guanidine hydrochloride was added to the filtrate. A pale yellow precipitate of the guanidinium salt, $(CN_3H_6)_2[Si(Cat)_3]\cdot H_2O$, began to form within a few minutes. After at least three hours the precipitate was filtered off, washed with small portions of water, and dried in vacuum to constant weight at room temperature. The yield was about 2.5 g.

Anal. Calcd for $(CN_3H_6)_2[Si(C_6H_4O_2)_3]\cdot H_2O$: Si, 5.73; C, 48.97; H, 5.34; N, 17.13. Found: Si, 5.80; C, 49.04; H, 5.27; N, 17.21.

RESULTS

Magnesium Salts of Tris(catecholato)siliconate

Nearly neutral aqueous solutions of catechol react at room temperature with amorphous magnesium trisilicate forming crystals of the magnesium salt of a silicon-catechol coordination complex:

$$Mg_2Si_3O_8 \cdot 5H_2O + 9H_2Cat + 5H_2O \longrightarrow 2Mg[Si(Cat)_3] \cdot 9H_2O + 2H^+ + Si(Cat)_3^= \qquad \text{Eq. 1}$$

An excess of catechol was used (10 moles of catechol per 3 moles of silicon) and the nonahydrate (see Table I) was the only complex formed using 0.05 F acetic, 0.05 F potassium biphthalate, water, 1.0 F ammonium chloride, and 0.05 F ammonia as the solvents. The yield was 30-50 % based on the weight of magnesium trisilicate and the stoichiometry in Eq. 1. The initial pH of the reaction mixture varied from 5.4 to 7.8, depending on the solvent, but in every case (except one) the final pH was 6.4-6.5 after a reaction time of one month. In the one exception (see Table I) the reaction mixture had been treated slightly different. It appears that the combination of catechol and magnesium trisilicate acts as a buffer. Silicate minerals apparently play a similar role in controlling the pH of natural waters (40).

A reaction also occurs in 15 F ammonia, but the product is either $(NH_4)_2[Si(Cat)_3] \cdot H_2O$ or $(NH_4)_2 \cdot [Si(Cat)_3] \cdot H_2O \cdot H_2Cat$ instead of the magnesium salt.

Crystals of $Mg[Si(Cat)_3] \cdot 9H_2O$ are often several millimeters in diameter and when dry can be exposed to the open atmosphere for weeks or even months without noticeable air oxidation or loss of water of crystallization. The crystals are insoluble in benzene, carbon tetrachloride, and p-dioxane, but decompose (probably dehydration) in N,N-dimethylformamide, pyridine, dimethylsulfoxide, and acetone (no attempt was made to identify the decomposed products). Analytical data support the formula $Mg[Si(Cat)_3] \cdot 9H_2O$. The infrared spectrum is shown in Figure A-1 and A-2 and the x-ray powder diffraction data are tabulated in Table A-1 of Appendix A.

If the nonahydrate is taken to constant weight by drying in vacuum, either at room temperature or at 50-80°C, six moles of water are lost per mole of silicon and the product is a fine hygroscopic powder of $Mg[Si(Cat)_3]\cdot 3H_2O$. The decomposition of this compound was established by analytical data, the weight loss upon going from the nonahydrate to the trihydrate, and the relative intensities of the phenyl proton and the water absorption in the nmr spectrum. Data on the weight loss during dehydrtion are tabulated in Table II.

The trihydrated magnesium salt, $Mg[Si(Cat)_3]\cdot 3H_2O$ is somewhat hygroscopic and decomposes to a yellow-greenish grey product after exposure to the air for about one month.

Infrared spectra of $Mg[Si(Cat)_3]\cdot 3H_2O$ are shown in Figure A-3, A-4, and A-5, and x-ray powder diffraction data are tabulated in Table A-2 of Appendix A.

The nmr spectrum of $Mg[Si(Cat)_3]\cdot 3H_2O$ in N,N-dimethylformamide (2.7% solution) is shown in Figure A-6 of Appendix A. The peak at τ = 3.55 ppm (relative to TMS) arises from phenyl protons, and the peak at τ= 6.38 ppm is due to water. The spectrum of the pure solvent showed no absorption that could be attributed to traces of water, although it might be hidden under the large methyl proton peak of the solvent itself. Addition of microliter quantities of water to a solution of $Mg[Si(Cat)_3]\cdot 3H_2O$ in N,N-dimethylformamide caused the 6.38 peak to move downfield toward τ= 5.25 ppm, which is the position of the proton peak of pure water. Integrations of thephenyl and water peaks yielded ratios of 12:6.02, 12:5.95, 12:6.00, and 12:6.02, in good agreement with that expected for a trihydrate which would exhibit a ratio of 12:6.

Under more severe drying conditions, i.e., more than 166 hours at about 100°C under vacuum, anhydrous $Mg[Si(Cat)_3]$ was obtained. The weight loss, shown in Table II, is in good agreement with this formulation. It is a greyish-white powder, more hydroscopic than the trihydrate, and also more rapidly oxidized by atmospheric oxygen to a yellow-greenish grey product within about two weeks. The x-ray powder diffraction pattern, which is tabulated in Table A-3 of Appendix A, shows unusually broad lines indicating that the compound has poor crystallinity. The infrared spectrum is shown in Figure A-7, and A-8, Appendix A, and summarized in Table III. It should be noted that absorption bands due to O-H stretching and H-O-H bending modes are clearly visible in the spectra of the nonahydrate and trihydrate but are absent in this spectrum.

Guanidinium Salt of Tris(catecholato)siliconate*

The pale yellow color of this guanidinium salt does not change during drying in vacuum to constant weight. It is somewhat hygroscopic, but less than the trihydrated magnesium salt, insoluble in ethyl ether, acetone, pyridine, p-dioxane, but soluble in N,N-dimethylformamide, dimethylsulfoxide, and slightly soluble in formamide and water. In ethylenediamine, it dissolves giving a pink solution. The solid de-

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* Kelley (38), who prepared this identical guanidinium salt from the reaction of catechol with silicic acid and with wollastonite, has also reported analytical data, ir, and nmr studies.

TABLE III

SUMMARY OF INFRARED SPECTRA OF MAGNESIUM SALTS OF TRIS(CATECHOLATO)SILICONATE

Assignment	$Mg[Si(Cat)_3 \cdot 9H_2O$ cm^{-1}	$Mg[Si(Cat)_3] \cdot 3H_2O$, cm^{-1}	$Mg[Si(Cat)_3]$, cm^{-1}
O-H stretching (Si-OH)	$\left.\begin{matrix}3555\\3531\end{matrix}\right\}$ (db)	3551 (s)	none
H-O-H[a] stretching	3000-3400 (br)	3311 (sd) 3106 (sd)	none
H-O-H bending	1646 (s)	1623 (s)	none
C-H in-plane - bending	$\left.\begin{matrix}1103\\1096\end{matrix}\right\}$ (db) $\left.\begin{matrix}1021\\1014\end{matrix}\right\}$ (db)	1100 (s) 1016 (s)	$\left.\begin{matrix}1100\\1090\end{matrix}\right\}$ (db) 1019 (s)
$Pw(OH_2)$,[b] $Pr(OH_2)$, $Pt(OH_2)$	650-750 (br)	671 (s) 658 (s) 632 (s)	none

Abbreviations: sd = shoulder; db = doublet; br = broad; s = sharp

[a] Nakamoto (43, p 166) suggested that the asymmetric and symmetric OH stretchings of lattic water absorb at 3550-3200 cm^{-1}.

[b] Pw, Pr, Pt are wagging, rocking, and twisting modes respectively of water coordinated to metal.

composes readily in acid to give silica. It discolors and loses ~6 % of its weight over a period of 155 hours in a vacuum at 100°C and ~4 % over a period of 218 hours at 80°C.

The infrared absorption spectrum of the guanidinium salt is shown in Figure A-9 of Appendix A. The bands at 3391, 3129 and 1659 cm^{-1} are believed to be due to symmetric N-H stretching, asymmetric N-H stretching and N-H bending modes, respectively. The same bands are also found in guanidine hydrochloride at 3358, 3131, and 1640 cm^{-1}. The band at 3570 cm^{-1} possibly arises from OH stretching. The C-H in-plane-bending bands as proposed by Kelley (38) are tabulated in Table IV.

The nmr spectrum of the guanidinium salt in N,N-dimethylformamide (~32% solution) is shown in Figure A-10, Appendix A. There are two peaks at τ = 3.06 ppm and at τ = 3.65 ppm which are due to phenyl protons and the rapid exchange of N-H and O-H protons, respectively.

The x-ray powder diffraction data are also presented in Table A-4, Appendix A.

DISCUSSION

Magnesium Salts of Tris(catecholato)siliconate

The fact that the reaction of catechol with magnesium trisilicate occurs in slightly acid solution serves to emphasize the strength of the silicon-catechol complex. According to Eq. 1 the overall reaction produces H^+. However, it is probably not an equilibrium and, therefore, not necessarily inhibited by acid. However, the silicon complex is decomposed by acid to hydrated silica according to Eq. 2 and Eq. 3:

$$Si(Cat)_3^{=} + 4H_2O + 2H^+ \rightleftharpoons Si(OH)_4 + 3H_2Cat \qquad \text{Eq. 2}$$

$$Si(OH)_4 + (x - 2)\ H_2O \rightleftharpoons SiO_2 \cdot xH_2O \qquad \text{Eq. 3}$$

The equilibrium constant* for Eq. 2 has been measured independently from which it can be calculated that under the conditions which give a product of crystalline $Mg[Si(Cat)_3]\cdot 9H_2O$, i.e., approximately 1.0 M catechol and pH = 6.4, any silicon in solution would be almost completely in the form of the $Si(Cat)_3^{=}$ complex rather than $Si(OH)_4$:

$$\frac{[H^+]^2[(Si(Cat)_3^{=}]}{[Si(OH)_4][H_2Cat]^3} = 3.5 \times 10^{-11}$$

$$\frac{[Si(Cat)_3^{=}]}{[Si(OH)_4]} \approx 220$$

From Eq. 1 it is clear that if we start with a slightly basic solution, the pH will decrease due to complex formation, as was, in fact, observed. It was also observed that the pH of weakly acid solutions increased to 6.4, which suggests the dissolution of magnesium trisilicate according to the reaction:

$$Mg_2Si_3O_8 \cdot 5H_2O + 4H^+ \longrightarrow 3Si(OH)_4 + 2Mg^{+2} + H_2O \qquad \text{Eq. 4}$$

The $Si(OH)_4$ will form a precipitate of hydrated silica, according to Eq. 3 if any appreciable amount of magnesium trisilicate dissolves by this mechanism.

Some of the infrared absorption bands are tabulated in Table III. One expects O-H stretching bands in the 3000-3600 cm^{-1} region. In the spectrum of $Mg[Si(Cat)_3]\cdot 9H_2O$ (see Fig. A-1, and A-2, Appendix A), there is a very broad band from 3000-3400 cm^{-1} that is characteristic of

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* The value of the equilibrium constant reported by Bartels, 3.5×10^{-11}, differs from that reported by Bauman, 4.7×10^{-12}.

strongly associated water and also sharp bands at 3531 and 3555 cm^{-1} in the region of free or weakly associated O-H groups. A single sharp O-H band is also observed at 3551 cm^{-1} in $Mg[Si(Cat)_3]\cdot 3H_2O$, 3545 cm^{-1} in $(NH_4)_2[Si(Cat)_3]\cdot H_2O$, 3570 cm^{-1} in $(CN_3H_6)_2[Si(Cat)_3]\cdot H_2O$, and at 3496 cm^{-1} in $(C_5H_6N)_2[Si(Cat)_3]$ after it has been exposed to atmospheric moisture. It is believed that this band is due to an Si-OH group. This band is absent, of course, in the spectrum of anhydrous $Mg[Si(Cat)_3]$, as are the other O-H stretching bands and the H-O-H bending near 1600 cm^{-1}.

Kelley (38) has pointed out that the C-H in-plane-bending bands of catechol show a distinct shift when the catechol is coordinated. These data are shown in Table IV. In free catechol the bands appear at 1104 and 1049 cm^{-1} and the difference is 55 cm^{-1}. When the catechol reacts with silicon the difference between the two frequencies increases to about 80 cm^{-1} due to the shift of the 1049 cm^{-1} band to $\sim$ 1020 cm^{-1}.

The bands at 632, 658, and 671 cm^{-1} (see Fig. A-4, Appendix A) could be due to either wagging, rocking, or twisting (or all three) of lattice water or water coordinated to magnesium (43, pp 166-9, 327).

Guanidinium Salt of Tris(catecholato)siliconate

Analytical data for the guanidinium salt are presented in Table V. Those data obtained in this work are from a sample that was dried under vacuum at room temperature for three more days after it had reached constant weight. These data fit the empirical formula (based on six nitrogen atoms) $C_{20.0}\ H_{25.7}\ N_{6.0}\ Si_{1.0}\ O_{7.0}$. The average values of the analytical data (three sets from Kelley's (38) and one set from this study) give an empirical formula of $C_{20.5}\ H_{25.6}\ N_{6.0}\ Si_{1.0}\ O_{7.0}$. Both

TABLE IV

COMPARISON OF SOME C-H IN-PLANE BENDING BANDS IN THE INFRARED SPECTRA OF CATECHOL-SILICON COMPLEXES

COMPOUNDS	cm^{-1}	cm^{-1}	Diff. cm^{-1}
Catechol	1104	1049	55
$(NH_4)_2[Si(Cat)_3]\cdot H_2O$	1102	1022	80
$(CN_3H_6)_2[Si(Cat)_3]\cdot H_2O$	1098 1072	1018	~80
$(C_5N\ H_6)_2[Si(Cat)_3]$	1106 1101	1021	~85
$Mg[Si(Cat)_3]\cdot 9H_2O$	1103 1096	1021 1014	~82
$Mg[Si(Cat)_3]\cdot 3H_2O$	1100	1016	84
$Mg[Si(Cat)_3]$	1100 1096	1019	~80

TABLE V

ANALYTICAL DATA FOR GUANIDINIUM TRIS(CATECHOLATO)SILICONATE

	Theory		Found				Average
	$x^a=\frac{1}{2}$	$x^a=1$	Sample 1[b]	Sample 2[b]	Sample 3[b]	Sample 4[c]	
C	49.86	48.97	50.39	48.53	49.69	49.04	49.41
H	5.23	5.34	5.24	5.01	5.27	5.27	5.20
N	17.45	17.13	17.18	16.71	16.56	17.21	16.91
Si	5.83	5.73	5.81	5.96	6.25	5.80	5.95
O[d]	21.60	22.83	21.38	23.79	22.23	22.68	22.52

a. x is the number of hydrates.

b. data were obtained by Kelley (38).

c. data were obtained in this work.

d. the values for oxygen are calculated by difference from 100%.

empirical formulas agree with $C_{20}\ H_{26}\ N_6S_1\ O_7$ for $(CN_3H_6)_2[Si(Cat)_3]\cdot H_2O$ rather than with $C_{20}\ H_{25}\ N_6\ Si_1\ O_{6.5}$ for $(CN_3H_6)_2[Si(Cat)_3]\cdot\frac{1}{2}H_2O$.

In the nmr spectrum the water and guanidinium protons appear as a single peak due to rapid exchange. The ratio between the phenyl protons and exchangeable protons would be 12:14 for $(CN_3H_6)_2[Si(Cat)_3]\cdot H_2O$ and 12:13 for $(CN_3H_6)_2[Si(Cat)_3]\cdot\frac{1}{2}H_2O$. The nmr study of this guanidinium salt in dimethylsulfoxide by Kelley (38) resulted in the ratios of 12:14.0, 12:14.4, and 12:12 and in N,N-dimethylformamide from this work: 12:13.0, 12:13.6, and 12:13.8. The overall results of these nmr studies also agree with one mole of "water of crystallization" and, therefore, the guanidinium salt is formulated as $(CN_3H_6)_2[Si(Cat)_3]\cdot H_2O$.

Structure of the Silicon-Catechol Complex

Rosenheim et al. (22) prepared the ammonium salt, $(NH_4)_2[Si(Cat)_3]\cdot 9H_2O$ and also the guanidinium salt, $(CN_3H_6)_2[Si(Cat)_3]\cdot 7H_2O$, and proposed that the silicon is octahedrally coordinated as shown in Figure 7. Flynn and Boer (36) confirmed this structure for the pyridinium salt, $(C_5H_6N)_2[Si(Cat)_3]$, by a single crystal x-ray structure determination. Barnum (23, 37) has recently repeated previous work and found that the ammonium salt is actually a monohydrate. On the basis of the tenacity with which the water molecule is held, the failure to prepare a simple anhydrous ammonium salt, and the product obtained from the reaction of catechol with silicon tetrachloride under anhydrous conditions, he suggested the structure shown in Figure 8 for this complex, as well as similar ones that contain one mole of tightly bound "water". Earlier, Rehlen et al. (44) reviewed the previous work on $K[Sb(Cat)_3]\cdot 3/2\ H_2O$,

$K_3[Fe(Cat)_3] \cdot H_2O$, and $H[As(Cat)_3] \cdot H_2O$ and concluded that one mole of water is coordinated to the metal rather than being present as lattice water. Craddock and Jones (45) proposed a similar structure for the arsenic(V)-catechol comples, $H[As(Cat)_3] \cdot H_2O$. Fairbrother _et al._ (46) came to the same conclusion regarding the "water" in niobium-catechol complexes.

Although coordination through a hydrogen bond, as shown in Figure 8, is unusual, it has been established in a nickel(II)-catechol complex, (Salen•NEt_2)(HCat)Ni(II)[*], by an x-ray diffraction structure determination (47).

One can imagine four possible structures for the silicon complex in $Mg[Si(Cat)_3] \cdot 9H_2O$ and $Mg[Si(Cat)_3] \cdot 3H_2O$ (Figures 7, 8, 9, and 10).

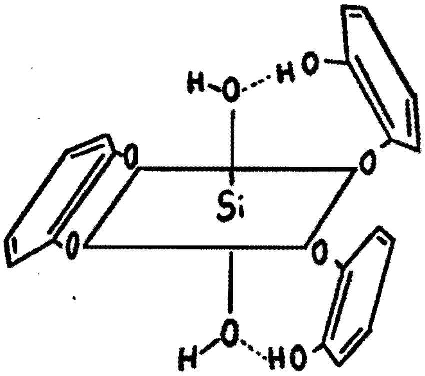

Figure 9. $[Si(OH)_2[HCat)_2(Cat)]^=$.
cis and _trans_ isomers

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[*] Salen•NEt_2 refers to $C_6H_5(OH)CN(CH_2)_2$-NEt_2, the Schiff base, derived from the condensation of salicyladehyde and N,N-diethylethylenediamine.

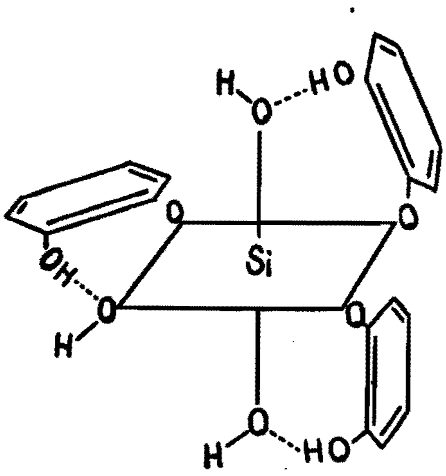

Figure 10. $[Si(OH)_3(HCat)_3]^{=}$, fac and mer isomers

The structure shown in Figure 10 is unlikely because the infrared spectrum of $Mg[Si(Cat)_3]\cdot 3H_2O$ has a band due to H-O-H bending at 1623 cm^{-1}. Also the absorption bands at 671, 658, and 632 cm^{-1} are believed to be the in-plane and out-of-plane bending mode of water coordinated to magnesium (see Fig. A-4; 43, p 327). One would expect these bands to be absent if the structure shown in Figure 10 were the correct structure. Furthermore, complex ions such as shown in Figures 9 and 10 are not known in any other cases so there is no precedent for such structures. Hydrates containing more than one mole of water were sought by Barnum (23, 37) among the ammonium salts. Although higher hydrates exist they lose water easily in vacuum giving the monohydrate, $(NH_4)_2[Si(Cat)_3]\cdot H_2O$.

The strong tendency of silicon-catechol complexes with other cations to hold only one "water" suggests that the structure shown in Figure 8 is the most probable. The fact that the magnesium salt is isolated as a trihydrate might be due to the requirement that the magnesium ion in the crystal is "solvated" or coordinated in some manner. Although the water would best satisfy this requirement, the existence of anhydrous $Mg[Si(Cat)_3]$ shows that the $Si(Cat)_3^{=}$ ion itself may contribute to the coordination sphere around magnesium.

Kelley (38) has discussed the possible structure of the guanidinium salt, $(CN_3H_6)[Si(Cat)_3]\cdot H_2O$ and concluded that the structure shown in Figure 8 is the most probable and the best formulation is $(CN_3H_6)_2[Si(Cat)_3]\cdot H_2O$.

III. REACTION BETWEEN SILICATE MINERALS AND CATECHOL IN AQUEOUS SOLUTIONS

INTRODUCTION

In Part I the reasons for believing that aromatic vic-diols might play an important role in various geochemical reactions were discussed and in Part II the case in which aqueous catechol solutions dissolved synthetic magnesium trisilicate was described. Further work carried out on some magnesium and calcium silicate minerals using conditions of temperature and pH close to those found in natural environments is presented in this part.

EXPERIMENTAL

Minerals

The description of minerals used in this study is summarized in Table VI. Mineral samples were purchased from one of the following supply houses: Southwest Mineral Supply, Santa Fe, NM; Filler's, Yucaipa, Calif; or David New-Minerals, Providence, Utah. Generally, the cleanest looking pieces were selected, crushed in a percussion mortar, ground to a fine powder, and then passed through a sieve in order to collect the fraction smaller than 325 mesh ($<48\mu$ dia). For enstatite a 200 mesh screen was used ($<78\mu$ dia). The olivine was obtained from a fist sized "bomb" that was weathered on the outside but clean and not visibly altered on the inside. It crumbled fairly easily into granules, 1-3 millimeter in diameter, of light

TABLE VI

DESCRIPTION OF MINERALS

Mineral	Formula	Sub - class	Group	Source	Reference
Olivine	$(Mg,Fe)_2SiO_4$	Nesosilicate	Olivine	Kilbourne Hole, Dona Ana Co., New Mexico	ASTM 7-79
Sepiolite	$Mg_2Si_3O_8 \cdot 2H_2O$	Inosilicate	Sepiolite-polygorskite	Riddle, Oregon	ASTM 14-1
Diopside	$CaMgSi_2O_6$	Inosilicate	Pyroxene	Jefferson, Park County, Colorado	ASTM 11-654
Augite	$Ca(Mg,Fe,Al)(Al,Si)_2O_6$	Inosilicate	Pyroxene	Barislave, near Tepice N.W. Bohemia, Czechoslovakia	a
Enstatite	$MgSiO_3$	Inosilicate	Pyroxene	Bamle, Norway. DavidNew . Minerals Hamilton, Montana	ASTM 7-216

a. I.Y. Borg and D.K. Smith, *Calculated X-ray Powder Patterns for Silicate Minerals*, The Geological Society of America in cooperation with the Mineralogical Society of American (1969), pp 249-52.

green olivine and dark green enstatite. The olivine granules were separated manually before grinding and sieving.

The identity of each mineral was checked by x-ray powder diffraction and infrared absorption.

The x-ray powder diffraction of olivine indicates that it is forsterite (Mg_2SiO_4).

The diffraction pattern of diopside has weak lines due to termolite ($Ca_2Mg_5Si_8O_{22}(OH)_2$) (see Table B-4, Appendix B) and the ir spectrum (see Figure B-3, Appendix B) also has a band of $\sim 13.2\ \mu$ due to tremolite as well as a band at $\sim 7.1\ \mu$ that may be due to calcite. The x-ray powder diffraction pattern however does not show any calcite.

The intensities of lines in diffraction pattern of augite are in poor agreement with the ASTM pattern, but this is probably because CuKα radiation was used in this work whereas the ASTM pattern was measured using FeKα radiation. The pattern is in good agreement however with that of fassaite (Al-augite) reported by Berg and Smith (48).

Both ir and x-ray patterns of sepiolite are in good agreement with β-sepiolite, which is a poorly crystallized variety (50). The sepiolite also contained some unknown dark brown impurity that was separated mechanically and its x-ray diffraction pattern is given in Table B-3, of Appendix B.

Enstatite showed some magnetite (Fe_3O_4) in its x-ray diffraction pattern. All other ir spectra and x-ray powder diffraction patterns are in good agreements with published data.

Reactions of Minerals with Aqueous Catechol Solutions

The amounts of mineral, catechol, and solvent shown in Table VII were placed in a 125-ml glass stoppered flask with a side arm and stopcock. The flask was evacuated, filled with nitrogen, and the solvent added. Solvents used were 0.05 F acetic acid, 0.05 F potassium biphthalate, water, 1.0 F ammonium chloride and 0.05 F ammonia. The contents of the flask were swirled until all of the catechol dissolved. Each mixture was kept for about 1-2 weeks in a controlled temperature water bath at 40°C with constant mechanical shaking and then stored at room temperature for an additional period of time to see if any precipitate or crystals formed. No product being formed, the unreacted mineral was filtered off under nitrogen, washed with water and dried to constant weight under vacuum. The weights of recovered mineral were compared with the initial weights and the percentages of minerals dissolved are reported in Table VIII. The pH of the filtrate (without the washings) was adjusted to 9 and then the volume of 1.0 F guanidine hydrochloride shown in Table VII was added. Generally, the dissolved silicon precipitated immediately as $(CN_3H_6)_2[Si(Cat)_3]\cdot H_2O$. In the case of enstatite the precipitate only appeared after standing about one week. To be sure precipitation was complete the solution was left two days (enstatite for two weeks) before filtering off the guanidinium salt under nitrogen. It was washed three times, dried under vacuum to constant weight, and weighed. The weights are tabulated in Table VIII. The identity of each precipitate was confirmed by both its ir spectrum and x-ray powder diffraction pattern.

TABLE VII

REACTIONS BETWEEN MINERALS AND AQUEOUS CATECHOL SOLUTIONS

Minerals	Solvent	Vol. Solvent Taken, ml	Mineral Taken		Catechol Taken		Reaction Time [b]		Vol. Guanidine hydrochloride added, ml
			Weight, g	m.mol of Si	Weight, g	m.mol	At 40°C	At Room Temp.	
Olivine (Forsterite) $(Mg_2SiO_4)^a$	0.05 F Acetic Acid	40	0.8443	6.00	6.61	60	7	12	15
	0.05 F KHP	40	0.8442	6.00	6.61	60	16	12	15
	H_2O	40	0.8442	6.00	6.61	60	16	12	15
	1.0 F NH_4Cl	40	0.8442	6.00	6.61	60	16	12	15
	0.05 F Ammonia	40	0.8443	6.00	6.61	60	16	12	15
	15 F Ammonia	40	0.8443	6.00	6.61	60	16	12	15
Sepiolite $(Mg_2Si_3O_8 \cdot 2H_2O)^a$	0.05 F KHP	40	1.7818	6.00	6.61	60	7	40	20
	H_2O	40	1.7818	6.00	6.61	60	7	40	20
	1.0 F NH_4Cl	40	1.7818	6.00	6.61	60	7	40	20
	15 F Ammonia	40	1.7818	6.00	6.61	60	7	40	20
Diopside $(CaMgSi_2O_6)^a$	0.05 F Acetic Acid	20	0.6504	3.0	3.30	30	14	7	20
	0.05 F KHP	20	0.6501	3.0	3.30	30	14	21	20
	H_2O	20	0.6502	3.0	3.30	30	14	21	20
	1.0 F NH_4Cl	20	0.6502	3.0	3.30	30	14	21	20
	0.05 F Ammonia	20	0.6501	3.0	3.30	30	14	7	20
	15 F Ammonia	20	0.6503	3.0	3.30	30	14	28	20
Augite $(CaMgSi_2O_6)^a$	0.05 F Acetic Acid	20	0.6504	3.0	3.30	30	14	7	10
	0.05 F KHP	20	0.6501	3.0	3.30	30	14	7	10
	H_2O	20	0.6502	3.0	3.30	30	14	7	10
	1.0 F NH_4Cl	20	0.6503	3.0	3.30	30	14	7	10
	0.05 F Ammonia	20	0.6502	3.0	3.30	30	14	7	10
	15 F Ammonia	20	0.6504	3.0	3.30	30	14	7	10
Enstatite $(MgSiO_3)^a$	0.05 F Acetic Acid	20	0.3033	3.0	3.30	30	(c)	18 mo	15
	0.05 F KHP	20	0.3033	3.0	3.30	30	(c)	12 mo	15
	H_2O	20	0.3045	3.0	3.30	30	(c)	12 mo	15
	1.0 F NH_4Cl	20	0.3033	3.0	3.30	30	(c)	12 mo	15
	0.05 F Ammonia	20	0.3034	3.0	3.30	30	(c)	12 mo	15
	15 F Ammonia	20	0.3033	3.0	3.30	30	-	5 mo	15

a. These formulas were used through out in this study.
b. The reaction time is in "days", except those expressed in "mo", months.
c. The reactions were refluxed for about 15 min. before storing at room temperature .

TABLE VIII

RESULTS FROM REACTIONS OF MINERALS WITH AQUEOUS CATECHOL SOLUTIONS

Mineral	Solvent	pH of[a] Reaction Mixture	% Mineral Dissolved, g	Guanidinium Salt[b] Recovered	
				Weight, g	% Recovery
Olivine (Forsterite) (Mg_2SiO_4)	0.05 F Acetic Acid	5.80	16	0.2452 (0.49 m.m)	8
	0.05 F KHP	6.10	17	0.4183 (0.86 m.m)	14
	H_2O	6.85	9	0.2071 (0.42 m.m)	7
	1.0 F NH_4Cl	6.50	11	0.2487 (0.51 m.m)	8
	0.05 F Ammonia	7.50	8	0.2390 (0.49 m.m)	8
	1.0 F Ammonia	11.30	c	0.5456 (1.11 m.m)	19
Sepiolite ($Mg_2Si_3O_8 \cdot 2H_2O$)	0.05 F KHP	6.05	17	0.4818 (0.98 m.m)	5
	H_2O	6.30	14	0.8845 (1.80 m.m)	10
	1.0 F NH_4Cl	6.50	30	1.5566 (3.17 m.m)	18
	15 F Ammonia	d	e	0.6397 (1.03 m.m)	6
Diopside ($CaMgSi_2O_6$)	0.05 F Acetic Acid	5.05	11	0.0331 (0.07 m.m)	1
	0.05 F KHP	6.50	5	0.0760 (0.16 m.m)	5
	H_2O	6.35	f	0.0122 (0.02 m.m)	0.3
	1.0 F NH_4Cl	6.50	f	0.0865 (0.18 m.m)	3
	0.05 F Ammonia	7.40	f	0.0851 (0.18 m.m)	3
	15 F Ammonia	d	c	0.2083 (0.42 m.m)	7
Augite ($CaMgSi_2O_6$)	0.05 F Acetic Acid	4.15	d	0.0161 (0.03 m.m)	0.5
	0.05 F KHP	4.75	3	0.0139 (0.03 m.m)	0.5
	H_2O	5.55	6	0.0599 (0.12 m.m)	2
	1.0 F NH_4Cl	5.70	d	0.0551 (0.11 m.m)	2
	0.05 F Ammonia	7.20	3	0.1299 (0.26 m.m)	4
	15 F Ammonia	d	e	0.2895 (0.59 m.m)	10
Enstatite ($MgSiO_3$)	0.05 F Acetic Acid	d	d	0.0214 (0.04 m.m)	1
	0.05 F KHP	4.20	d	0.0202 (0.04 m.m)	1
	H_2O	5.50	d	g	g
	1.0 F NH_4Cl	d	d	g	g
	0.05 F Ammonia	7.15	d	0.0160 (0.03 m.m)	0.5
	15 F Ammonia	d	h	h	h

a. In each case, the pH of the reaction was measured at the end of the reaction.
b. Guanidinium salt is $(CN_3H_6)_2[Si(Cat)_3] \cdot H_2O$.
c. Some small crystals were formed along with the residue and were identified as the ammonium salt, $(NH_4)_2[Si(Cat)_3] \cdot H_2O$
d. The values were not collected
e. Some small crystals were formed along with the residue and were identified as the combination of two ammonium salts, $(NH_4)_2[Si(Cat)_3] \cdot H_2O$ and $(NH_4)_2[Si(Cat)_3] \cdot H_2O \cdot H_2Cat$.
f. A gelatineous product was formed along with the residue which possibly was $Ca(HCat)_2 \cdot XH_2O$, or $Ca[Si(Cat)_3] \cdot XH_2O$, or the mixture of both.
g. In each case, about 5 mg of guanidinium salt was obtained.
h. The mineral dissolved was calculated to be 10 % and the dissolved product was recovered as the ammonium salt, $(NH_4)_2[Si(Cat)_3] \cdot H_2O$, which contained a small amount of $(NH_4)_2[Si(Cat)_3] \cdot H_2O \cdot H_2Cat$.

When 15 F ammonia was used for the solvent, crystals had formed before the unreacted mineral was filtered off. In most cases a small amount of the crystalline product, uncontaminated by unreacted mineral, could be separated mechanically for identification by ir and x-ray powder diffraction method. Upon drying this product to constant weight under vacuum, the crystals crumbled to a white powder which was subsequently identified as $(NH_4)_2[Si(Cat)_3]\cdot H_2O$. Often some of the catechol solvate, $(NH_4)_2[Si(Cat)_3]\cdot H_2O\cdot H_2Cat$, was present as an impurity.

Preparation of Magnesium Tris(catecholato)siliconate Trihydrate from Sepiolite and Olivine

Two attempts were made to obtain the magnesium salt, $Mg[Si(Cat)_3]\cdot 3H_2O$, from the reaction between sepiolite and aqueous catechol. In both cases 1.78 g of sepiolite (18 m·moles of Si)*, 6.61 g of catechol (60 m·moles), and 40 ml each of water and .05 F ammonia were used. The reaction was carried out in water by refluxing for about 2 hours and then storing at room temperature for 3 months. The second reaction was carried out at 40°C for one week with mechanical shaking. For olivine, 0.97 g (6.5 m·moles of Si) and 5.51 g of catechol with 20 ml of water were used. The reaction was kept at room temperature for 4 months. Crystals of $Mg[Si(Cat)_3]\cdot 9H_2O$ did not form in any of these mixtures as they did in the case of magnesium trisilicate, $Mg_2Si_3O_8\cdot 5H_2O$.

The unreacted minerals were filtered off and the filtrates were evaporated to dryness under vacuum. The residues were then extracted seven times with small portions of diethyl ether to remove excess

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* Based upon the formula $Mg_2Si_3O_8\cdot 2H_2O$.

catechol and dried in vacuum at room temperature to constant weight. The yields were about 0.3 g of light brown product from sepiolite and about 0.6 g of violet product from olivine.

Both the ir spectrum and the powder diffraction pattern of these products were identical with that of $Mg[Si(Cat)_3]\cdot 3H_2O$, except that the powder diffraction pattern had an additional strong peak at d = 12.2 Å which occassionally, in previous preparations from magnesium trisilicate was observed as a very small peak. It was not ascertained whether impurity or the way the product was formed caused this additional peak. However, both ir and powder diffraction showed that most of the product is $Mg[Si(Cat)_3]\cdot 3H_2O$.

RESULTS

Nearly neutral solutions of catechol were shaken with various minerals for 1-2 weeks at 40°C and then allowed to stand for an additional 2-3 weeks at room temperature. Partial dissolution of the minerals occurred due to the formation of a silicon-catechol complex, $Si(Cat)_3^{=}$, which was precipitated as the insoluble guanidinium salt, $(CN_3H_6)_2[Si(Cat)_3]\cdot H_2O$. The extent of dissolution was measured not only by the weight of silicon-catechol complex recovered, but also by the loss in weight of mineral. These data are summarized in Table VIII.

It will be seen in Table VIII that the recovery of silicon as the guanidinium salt is generally less than the percentage of mineral dissolved would indicate. This is expected because the solubility of the guanidinium salt in water is too large for quantitative recovery, i.e. 0.5 g/100 ml (38). Thus, the primary quantity to be considered should be the percentage of mineral dissolved.

Although quantitative data on the solubility of minerals is almost non-existent, it is possible to make a rough comparison between the solubility in pure water and the solubility in neutral catechol solutions. Thus, augite was reported to be soluble to the extent of 0.057-0.097 % (53) whereas as much as 6 % went into solution in the presence of catechol. Bolton (54) reported that augite and olivine were not dissolved by dilute mineral acids or by dilute carboxylic acids. Sepiolite is gelatinized by hydrochloric acid (53, pp 427-49). It is also reported that the water lost at the lower temperature can be resorbed reversibly (55). However, neither the extent of gelatinization nor solubility in water is mentioned. Diopside and augite were reported to be insoluble in hydrochloric acid (56). Enstatite is more resistent to weathering than olivine (57). It may, therefore, be concluded that the catechol either increases the solubility of the mineral or greatly enhances the rate of dissolution.

The data for diopside and enstatite in Table VIII require further comment.

The extent of reaction with enstatite was very small, even though the solutions stood in contact with the mineral for 12-18 months compared with 3-5 weeks for the other minerals. Although the particle size of the enstatite sample was greater ($< 75\ \mu$ diameter as compared with $<48\ \mu$ for other minerals in Table VII), the difference is probably not enough to account for the slower reaction. Therefore, of the minerals investigated, enstatite is the most stable against attack by catechol solution. Furthermore, the fact that so little silicon-catechol complex was recovered from this reaction is good evidence that much larger recoveries in the other cases were due to the reaction with the mineral rather than with the glass reaction vessel.

The results for diopside are uncertain. All of the minerals were examined by ir and powder diffraction before and after reaction with catechol. Those reactions with diopside using water, 1.0 F ammonium chloride, or 0.05 F ammonia as the solvent gave a gelatinous precipitate along with unreacted diopside. Both the ir and the powder diffraction pattern of the gel agree with an unidentified "Compound A" isolated by Kelley (38) from the reaction of aqueous catechol with wollastonite. The substance has not been isolated in pure form, but apparently contains catechol, silicon, and calcium. Kelley suggested that it may be $Ca[Si(Cat)_3]\cdot xH_2O$, or $Ca(HCat)_2\cdot xH_2O$, or a mixture of both. Also, the ir spectrum of the starting diopside has a broad band at $\sim 7.1\ \mu$ which disappeared upon reaction with aqueous catechol. These spectra are compared and shown in Figure B-3, Appendix B. It is not unusual to find that calcite, diopside, and tremolite are associated and it is possible that the bands at ~ 7.1 and $\sim 13.2\ \mu$ are due to the presence of calcite and tremolite, respectively. Hence, the observed loss in weight of diopside as well as the recovery of the guanidinium silicon-catechol complex may be due to reaction with the impurities.

The ir spectra of the residues from the reactions of olivine in 0.05 F acetic acid and 0.05 F potassium biphthalate showed the presence of silica along with unreacted olivine. Probably in these two cases, the pH of the solution was not sufficiently high to keep the silicon complexed; i.e. the complex decomposed according to Eq. 2 and 3 in Part II.

The ir spectra of the residues remaining from the reactions of sepiolite showed additional weak bands at approximately 6.5 and 7.2 μ and the shoulders at about 8 and 13 μ in the starting material were broadened. This was probably due to absorption of catechol on the surface, since sepiolite has a porous structure that can absorb other substances.

All other residues from the reactions were checked by ir and powder diffraction pattern and were found to be identical with their starting minerals. The reaction of aqueous catechol with synthetic amorphous magnesium trisilicate, $Mg_2Si_3O_8 \cdot 5H_2O$, gave crystals of $Mg[Si(Cat)_3] \cdot 9H_2O$ after about one month at room temperature (see Part II). This reaction was also attempted with olivine and sepiolite. Crystals of the magnesium salt were not formed spontaneously as they were with magnesium trisilicate. However, by filtering off the unreacted mineral, evaporating to dryness, extracting excess catechol with diethyl ether, and taking to constant weight under vacuum, magnesium tris(catecholato)siliconate trihydrate was obtained. It gave about 6 % and 20 % recoveries from sepiolite and olivine, respectively.

The reaction carried out in 15 F ammonia caused even more mineral to dissolve than reaction in nearly neutral solutions. The reaction is similar to that with various forms of hydrated silica and catechol in concentrated ammonia that was reported earlier by Barnum (23, 38). In each case, crystals of an ammonium salt were formed $(NH_4)_2[Si(Cat)_3]\cdot xH_2O\cdot yNH_3$ which had to be separated manually from unreacted mineral. Upon drying to constant weight under vacuum at room temperature, the crystals crumbled to a white powder which was identified by its powder diffraction pattern as $(NH_4)_2[Si(Cat)_3]\cdot H_2O$, or in the cases of enstatite, sepiolite, and augite a mixture was obtained which also contained some catechol solvate, $(NH_4)_2[Si(Cat)_3]\cdot H_2O\cdot H_2Cat$.

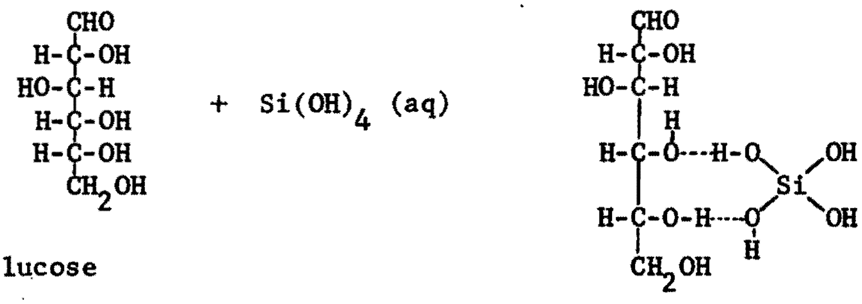
No evidence was found in this work that the glass reaction vessels were attacked by aqueous catechol solutions. In no case was any etching observed, even after four years in a flask containing 2.5 F catechol in 15 F ammonia. In fact, the results with enstatite constitute a sort of blank. There was only 5-21 mg of silicon complex (depending on the solvent) obtained whereas all the other minerals gave substantially greater recoveries.

Some of the minerals in Table VII contain iron(III), (i.e., enstatite, olivine) or aluminium (i.e., augite) and these metals are also complexed by catechol (58, 59, 69, 61, 62). The complexes are strong enough that in the presence of catechol, $Fe(OH)_3$ and $Al(OH)_3$ do not precipitate from slightly basic solution (63). Those minerals containing iron, either as a principal constituent or as an impurity, became highly colored (violet or deep red depending on pH) as the mineral decomposed. No aluminium complexes were isolated although they must have been formed under the conditions used. The fate of Ca^{++} and Mg^{++} is more uncertain as these ions can form insoluble catecholate salts; $Ca(HCat)_2$ and $Mg(HCat)_2$. Indeed, in the case of diopside the reaction with catechol gave an insoluble product that may be the calcium catecholate, but no corresponding magnesium catecholate such as $Mg(HCat)_2 \cdot xH_2O$ was isolated from reactions of magnesium containing minerals with aqueous catechol solutions.

DISCUSSION

Interaction between silicon and naturally occurring "organic matter" has been known for a long time. For example, a particularly thorough review article "One the Geological Action of the Humic Acids" was published (64) in 1879. It was pointed out that 1) a high silicon content in natural waters is generally associated with a high content of organic matter, 2) silicon is tightly bound to certain "black acids" of the soil, and 3) the assimilation of silicon by plants depends greatly on the amount of humus present in the soil. Since that time many other workers have commented on the interaction between natural organic matter and silicon but very little has been accomplished in explaining the nature of the interactions.

Two proposals are often seen in the literature. One is that silicic acid monomers in solution are strongly attached to sugars, cellulose, and other poly-hydroxy compounds through hydrogen bonds. For example:



glucose

glucose - silicic acid complex

The other proposal is that the silica is present as colloidal particles and the organic matter acts as a protective colloid that prevents coagulation.

There is a third proposal, however, that has received almost no attention. Hess _et_ _al_. (24) have suggested that aromatic _vic_-diols are capable of attacking silicate minerals and in the process form water stable silicon complexes. This idea is relatively new and requires more complete investigation.

Although the present work was only done with catechol, one expects other aromatic _vic_-diols to react in the same manner. Thus Weiss _et_ _al_. (23) prepared silicon complexes with catechol, methylcatechol, 3,4-dihydroxybenzaldehyde, 3,4-dihydroxybenzoic acid, 2,3-dihydroxybenzoic acid, 2,3-dihydroxynaphthalene, pyrogallol, gallic acid, alizarin, purpurin, quercetin, and tannic acid. Also, formation constants for various complexes of the form $Si(diol)_3^{=}$ have been measured by Bartels (41) and by Baumann (42) and these are tabulated in Table IX. It may be concluded that any aromatic _vic_-diol will form a silicon complex unless prevented from doing so by steric repulsion. It is also evident from the formation constants that strong electron withdrawing groups in the ring cause a decrease in stability but those _vic_-diols that exist in natural waters, ground water, etc., probably do not contain such groups.

That abundant sources of aromatic _vic_-diols exist in nature was already discussed in the Introduction (Part I).

Hess _et_ _al_. (24) obtained unconvincing evidence that aromatic _vic_-diols can play a role in geochemical reactions. Their solutions were strongly ammoniacal and therefore did not correspond to any conditions found in nature. Furthermore, only permutite (a synthetic, amorphous aluminosilicate) and perlite (an amorphous aluminosilicate) gave a clear-cut reaction; they observed no reaction with montmorillonite, and only formation of a brown coating on orthoclase. The reactions run in this work as well as those done earlier by Kelley and others are summarized in Table X. Of particular interest in this table is the column headed "% Mineral Reacted". It will be seen that substantial reaction has occurred in most cases. Also, examination of the reaction conditions reveals that some minerals, especially quartz, sepiolite, wollastonite, olivine, and pyrophyllite, are attacked and dissolved in nearly neutral solutions at ~25°C; i.e., under conditions of temperature and pH very close to those which occur in natural waters, soils, and weathering environments. The main difference, however, is the concentration of catechol, which was on the order of 0.01-1.5 F whereas one might expect something on the order ot 10^{-5} F or less in a neutral environment.

In order to evaluate the effect of concentration of free *vic*-diol and pH, a stability diagram was calculated for the catechol complex using Bartels' value (41) for the formation constant:

$$10^{-10.45} = \frac{[H^+]^2\,[Si(Cat)_3^=]}{[H_2Cat]^3[Si(OH)_4]}$$

Conditions of $[H^+]$ and $[H_2Cat]$ were calculated such that

$$[Si(Cat)_3^=] = [Si(OH)_4]$$

TABLE IX

EQUILIBRIUM CONSTANTS OF SOME AROMATIC VIC-DIOLS WITH SILICIC ACID[a]

vic-diol	pK	Ref.
Catechol	11.33, 10.45	b,c
4-methylcatechol	10.87	c
Dihydroxyphenylalanine	10.38	b
Pyrogallol	9.92	c
Adrenaline	9.76	b
4-chlorocatechol	8.54	c
4-nitrocatechol	5.13	c
Catechol-3,5-disulfonic acid	4.81	c
3-nitrocatechol	4.73	c

a. For the reaction at 25°C:

$$Si(OH)_4 + H_2diol \rightleftharpoons 2H^+ + Si(Cat)_3^= + 4H_2O$$

b. Baumann (42).

c. Bartels (41).

TABLE X

SUMMARY OF REACTIONS OF MINERALS WITH AQUEOUS CATECHOL SOLUTIONS

Mineral	Formula	Ref.	Particle Size, µ	Reaction Temp., °C	Conc. Catechol, F	pH	Reaction Time	Mineral Reacted, %
Quartz	SiO_2	(a)	< 7	~ 25	"conc"	8.2	60 days	35
Silica, hydrated	$SiO_2 \cdot xH_2O$	(b)	Powder	~ 25	0.91	15F NH_3	2-16 hrs	100
Magnesium Trisilicate	$Mg_2Si_3O_8 \cdot 5H_2O$ (synthetic, amorphous)	(c)	Powder	~ 25	1.5	5.4-7.8	~30 days	30-50
		(c)	Powder	~ 25	1.5	15F NH_3	~30 days	100
Sepiolite	$Mg_2Si_3O_8 \cdot 2H_2O$	(c)	< 48	(d)	1.5	~ 6-8	(d)	14-30
Enstatite	$MgSiO_3$	(c)	< 78	(e)	1.5	~ 6-8	12-18 mo	1
		(c)	< 78	~ 25	3.0	15F NH_3	5 months	10
Olivine	Mg_2SiO_4	(c)	< 48	(f)	1.5	~ 6-8	(f)	8-17
		(c)	< 48	(f)	1.5	15F NH_3	(f)	19
Augite	$Ca(Mg,Fe,Al)(Al,Si)_2O_6$	(c)	< 48	(g)	1.5	~ 6-8	(g)	3-6
Diopside	$CaMgSi_2O_6$	(c)	< 48	(h)	1.5	~ 6-8	(h)	(h)
Wollastonite	$CaSiO_3$	(i)	< 74	~ 25	0.24	10	13 months	24
		(i)	< 74	~ 25	0.24	4	13 months	38
		(i)	< 74	~ 100	0.24	~ 7	90 hrs	21
Andradite	$Ca_3Fe_2(SiO_4)_3$	(i)	< 74	~ 25	0.24	10	13 months	53
		(i)	< 74	~ 100	0.52	6-6.8	142 hrs	18
Albite	$NaAlSi_3O_8$	(i)	< 74	~ 25	0.24	10	13 months	24
Muscovite	$KAl_2(AlSi_3O_{10})(OH)_2$	(i)	< 74	~ 25	0.24	10	13 months	49
Talc	$Mg_3Si_4O_{10}(OH)_2$	(i)	< 74	~ 25	0.24	10	13 months	33
Pyrophyllite	$Al_2Si_4O_{10}(OH)_2$	(i)	< 74	~ 25	0.24	10	13 months	30
		(i)	< 74	~ 25	0.24	4	13 months	12
Lepidomelane	$KFe_3\ Si_3(Al,Fe)O_{10}\ (OH)_{10}$	(j)	< 100	~ 25	0.012	5.81-8.0	10 days	2
Plagioclase	$(Ca,Na)(Al,Si)AlSi_2O_8$	(j)	< 100	~ 25	0.012	5.13-8.0	10 days	0.2
Nepheline	$Na(AlSiO_4)$	(j)	< 100	~ 25	0.012	5.13-6.81	10 days	0.5
Kaolinite	$Na(AlSiO_4)$	(j)	< 100	~ 25	0.012	5.81-4.85	10 days	< 0.2

a. Weiss *et al.* (24)
b. Barnum (37)
c. This work
d. 7 days 40°C followed by 40 days at room temperature
e. refluxed for about 15 min. followed by 12- 18 months at room temperature
f. 7-16 days at 40°C followed by 12 days at room temperature
g. 14 days at 40°C followed by 7 days at room temperature
h. 14 days at 40°C followed by 7-21 days at room temperature. The result was ambiguous. The apparent reaction may be due to the impurities in diopside.
i. Kelley (38). The % mineral dissolved was calculated from m.moles of silicon used and m.moles of silicon dissolved which were recovered as the guanidinium salt.
j. Kononova *et al.*(2). The % mineral dissolved was calculated from the weight difference between the initial and final weights of Al_2O_3, or Fe_2O_3, or both, of the mineral.

and the result is plotted in Figure 11. The dash lines set off a transition region in which the relative amount of $Si(Cat)_3^=$ ranges from 1% to 99%. Most natural waters have pH values on the order of 5-8 and it will be seen in the figure that a concentration of aromatic vic-diol on the order of 10^{-3} - 10^{-1}M will be required in order to affect appreciable complex formation. Unfortunately, no data at all are available on the concentrations of aromatic vic-diols to be expected in natural waters. Probably it would be quite variable depending on rainfall, microbial activity, redox potential, etc., but values as high as 10^{-3} - 10^{-1}M would not be expected and the silicon must therefore be present as $Si(OH)_4$. Still, such high concentration might occur in certain local microvolumes such as the immediate vicinity of plant root rhizomes, colonies of fungi, etc..

One may note from the stability constants in Table IX that catechol forms one of the weaker complexes with silicon. Armoatic vic-diols occurring in natural environments, are likely to contain methoxy or other hydroxyl groups and these might form more stable complexes.

Another important aspect of Figure 11 is that formation of the silicon complex is influenced more by changes in concentration of vic-diols than by changes in pH. For example, it takes approximately a 100 fold change in hydrogen ion concentration to cross the transition region, but only a 20 fold change in the concentration of free vic-diol. This could result in the attack and dissolution of minerals in regions or times of relatively high concentration of complexing agent and then transport, and precipitation as hydrated silica, quartz, or other minerals when the concentration of complexing agent decreased.

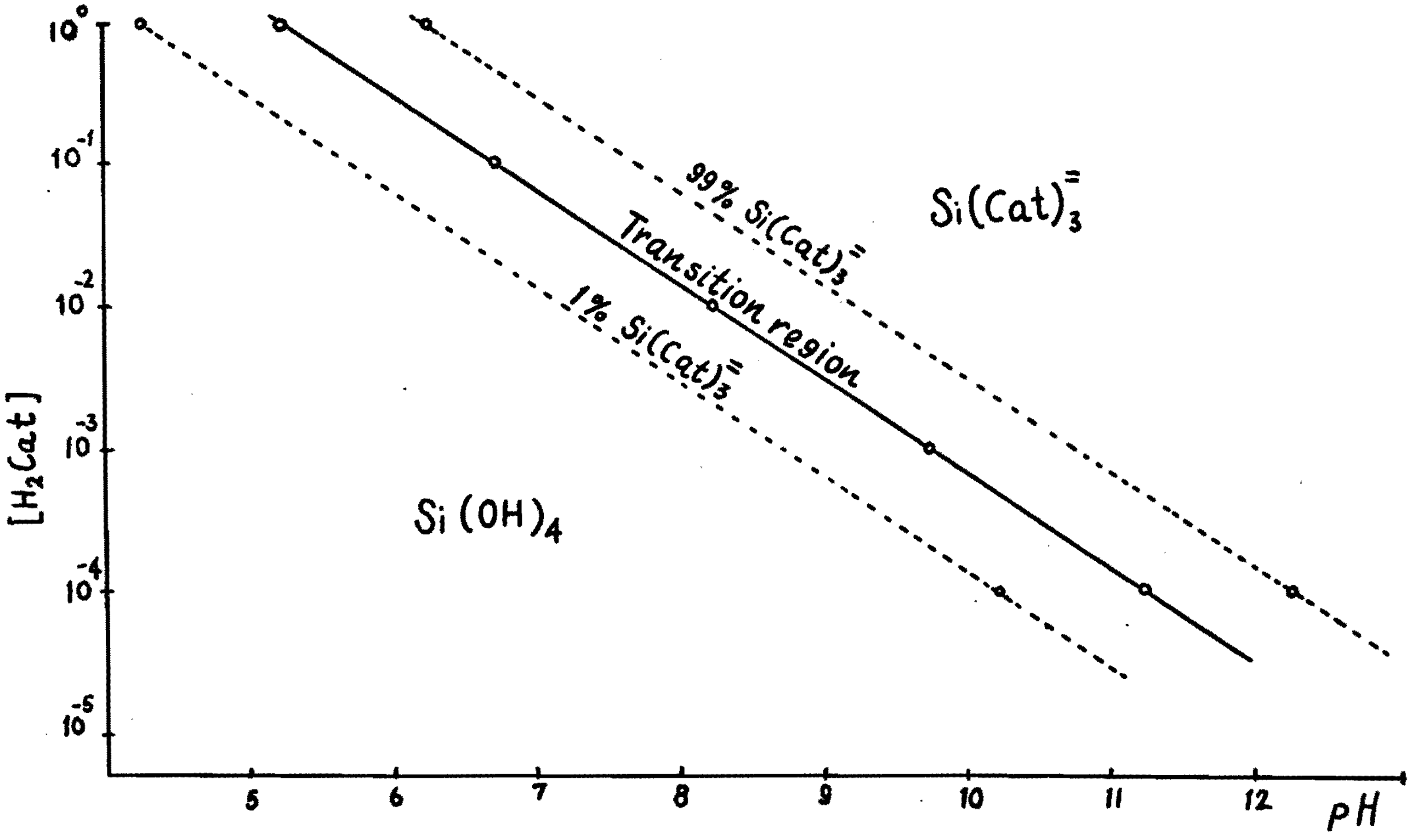


Figure 11. Stability Diagram for Silicon-Catechol Complex

The solid line represents conditions of pH and $[H_2Cat]$ for which $[Si(Cat)_3^=] = [Si(OH)_4]$. The dashed lines set off the approximate transition region where 1-99% silicon is represented as $Si(Cat)_3^=$.

REFERENCES

1. M. M. Konova, Soil Organic Matter, Pergamon Press, New York (1961).

2. M. M. Konova, I. V. Aleksandrova, and N. A. T. tova, Pochvovedenie, 1-12. 1964.

3. S. Chaberek and A. E. Martell, Organic Sequestering Agents, Wiley, (1959).

4. S. M. Manskaya and T. V. Drozdova, Geochemistry of Organic Substances, English trans. by L. Shapiro and I. A. Breger, Pergamon (1968).

5. A. Schatz, J. Argric. Food Chem., 11, 112-8 (1963).

6. J. Shapiro, J. Am. Water Works Assoc., 56, 1062-82 (1964).

7. M. Ghassemi and R. F. Christman, Limnology and Oceanography, 13, 583-97 (1968).

8. R. F. Christman and M. Ghassemi, J. Am. Water Works Assoc., 58, 723-41 (1966).

9. J. E. Zajic, Microbial Biogeochemistry, Academic Press, New York (1969).

10. R. Siever and R. A. Scott, "Organic Geochemistry of Silica", Internat. Ser. of Monographs on Earth Sciences, 16, Organic Geochemistry, ed. I. A. Breger, MacMillan, New York (1963).

11. R. K. Iler, The Colloid Chemistry of Silica and Silicates, Cornell University Press, Ithaca (1955).

12. F. J. Stevenson, "Organic Acids in Soil", Chapt. 5 in Soil Biochemistry, ed. by A. D. McLaren and G. H. Peterson, Marcel Dekker, N. Y. (1967) 119-46.

13. V. Vancura and A. Hovadik, Plant and Soil, 22, 21-5 (1965).

14. A. D. Rovira, "Plant Root Exudates and Their Influence Upon Soil Microorganisms", Ecology of Soil-Borne Plant Pathogens, K. F. Baker and W. C. Snyder, eds., Univ. of California Press (1965), 170 *et seq*.

15. D. M. Grodzinskii, Ukr. Biokhim, Zhur., 16, No. 2, 30-8 (1959). Chem. Abst. 51:16556d.

16. E. I. Parfenova and E. A. Yarilova, *Pochvovedenie* No. 4, 38-42, (1956). Chem. Abst. 51:8353b.

17. E. I. Sokolova, *Geokhim.*, No. 7, 111-41, (1966). Chem. Abst. 65:1743.

18. J. W. Muir, J. Logan, and C. J. Brown, *J. Soil Sci.*, *15*, 226-37 (1964).

19. I. I. Ginzburg, V. V. Belyatskii, L. A. Matveeva, T. S. Nuzhdenovskaya, and Z. S. Rozhdestvenskaya, Eksp. Issled. Razlozheniya, *Miner. Org. Kislotami*, 18-65 (1965). Chem. Abst. 72:123792d.

20. H. M. Hurst and N. A. Burges, "Lignin and Humic Acids", Chapt. 11 in *Soil Biochemistry*, ed. by A. D. McLaren and G. H. Peterson, Marcel Dekker, N. Y. (1967) 260-83.

21. J. F. Slowey, L. M. Jeffrey, and D. W. Hood, *Nature*, *214*, 377-8 (1967).

22. A. Rosenheim, B. Raibmann, and G. Schendel, *Z. Anorg. Allgem. Chem.*, *196*, 160-76 (1931).

23. D. W. Barnum, *Inorg. Chem.* (1972) in press.

24. A. Weiss, G. Reiff, and A. Weiss, *Z. Anorg. Allgem. Chem.*, *311*, 151-79 (1961).

25. R. Hess, R. Bach, and H. Deuel, *Experientia*, *16*, 38-40 (1960).

26. J. B. Hemwall, "The Absorption of 4-tert-butylpyrocatechol by Soil Clay Minerals" in *Internat. Clay Conf.*, Stockholm, 1963, ed. by I. Th. Rosenqvist and P. Graff-Peterson, Pergamon Press (1963) 319-28.

27. S. A. Gordon, K. Yu. Volkov and M. A. Menkovskii, *Geokhimiya*, No. 4 384-8 (1958). Chem. Abst. 53:1679b.

28. V. M. Ershov, *Geokhimiya*, 605-6 (1958). Chem. Abst. 53:6000e.

29. J. F. Thorpe and M. A. Whiteley, *Thorpe's Dictionary of Applied Chemistry*. Fourth ed., Vol. XI, 390-405, Longman (1961).

30. C. B. Coulson, R. I Davies, and D. A. Lewis, *J. Soil Sci.*, *11*, No. 1, 20-29 (1960).

31. P. C. Stobbe and J. R. Wright, *Soil Sci. Soc. Am. Proc.*, *23*, 161-4 (1959).

32. C. Bloomfield, *J. Soil Sci.*, *4*, No. 1, 5-15 (1953), *4*, No. 1, 17-23 (1953), *5*, No. 1, 39-45 (1954).

33. F. J. Hingston, *Aust. J. Soil Res.*, *1*, 63-73 (1963).

34. J. M. Bremner, "Organic Nitrogen in Soils", Chapt. 5, in *Soil Nitrogen*, ed. by W. V. Bartholomew and F. E. Clark, Am. Soc. of Agronomy, Vol. 10, Madison, Wis. (1965), 93-149.

35. C. Steelink and G. Tollin, "Free Radicals in Soil", Chapt. 6 in *Soil Biochemistry*, ed. by A. D. McLaren and G. H. Peterson, Marcel Dekker (1967), 147-69.

36. J. J. Flynn and F. P. Boer, *J. Am. Chem. Soc.*, *91*, 5756-61 (1969).

37. D. W. Barnum, *Inorg. Chem.*, *9*, 1942-3 (1970).

38. J. M. Kelley, M. S. Thesis, Portland State University, 1972.

39. S. Herzog, J. Dehnert, and K. Luhder, "An Expedient Method for Preparative Procedure in an Inert Atmosphere", *Technique of Inorganic Chemistry*, Vol. VII, ed. by H. B. Jonasen and A. Weissberger, Interscience (1968) 119-49.

40. F. T. Mackenzie and R. M. Garrels, *Science*, *150*, 57-8 (1965).

41. H. Bartels, *Helv. Chim. Acta*, *47*, 1605-9 (1964).

42. H. Baumann, *Beitr. Silikose-Forsch.*, S-Bd Grundfragen Silikoseforsch., *4*, 43-50 (1960).

43. K. Nakamota, *Infrared Spectra of Inorganic and Coordination Compounds*, Second ed., Wiley-Interscience (1970).

44. Rehlen, A. Sapper, and G. A. Kall, *Z. Anorg. Chem.*, *144*, 218-24 (1925).

45. J. H. Craddock and M. M. Jones, *J. Am. Chem. Soc.*, *83*, 2893-43 (1961).

46. F. Fairbrother, N. Ahmed, K. Edgard, and A. Thompson, *J. Less-Common Metals*, *4*, 466-75 (1962).

47. L. Sacconi, P. L. Orioli, and M. Di Vaira, *Chem. Comm.*, 849-50 (1957).

48. I. Y. Borg and D. K. Smith, *Calculated X-Ray Powder Patterns for Silicate Minerals*, The Geological Society of American in cooperation with the Mineralogical Society of America (1969) 249-52.

49. R. J. Launer, *Am. Miner.*, *37*, 764-84 (1952).

50. R. Otsuka, H. Hayashi, and S. Shimoda, *Mem. Sch. Sci. Eng., Waseda Univ.*, *32*, 13-24 (1968).

51. J. Hunt, M. P. Wisherd, and L. C. Bonham, Anal. Chem., 22, 1478-1497 (1950).

52. K. Omori, Am. Miner., 56, 1607-16 (1971).

53. J. W. Mellor, A Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol. VI, p 820, Longmans, Green, and Co., London (1953).

54. H. C. Bolton, Ann. N. Y. Acad. Sci., 1, 153-159, (1878-1879).

55. S. Caillere and S.Henin, "Sepiolite", The X-Ray Identification and Crystal Structure of Clay Minerals", G. Brown, ed., Mineralogical Soc., London (1961) 325-41.

56. J. W. Deer, R. A. Howie, and J. Zussiman, Rock Forming Minerals, Longmans (1962), Vol. 1, 2.

57. M. L. Jackson and G. D. Sherman, "Chemical Weathering of Minerals in Soils", Adv. in Agronomy, 5, 219-318 (1953), Academic Press, N. Y.

58. R. F. Weinland and K. Binder, Ber., 45, 148-54 (1912).

59. R. F. Weinland and K. Binder, Ber., 45, 1113-24 (1912).

60. R. F. Weinland and K. Binder, Ber., 46, 874-85 (1913).

61. R. C. Mehrotra and R. K. Mehrotra, J. Indian Chem. Soc., 39, 635-40 (1962).

62. S. N. Dubey and R. C. Mehrotra, J. Inorg. Nuclear Chem., 26, 1543-50, (1964).

63. R. F. Weinland and W. Denzel, Ber., 47, 737-50 (1914).

64. A. A. Julian, Poc. Amer. Assoc. Adv. Sci., 28, 311-410 (1879).

APPENDIX A

INFRARED AND NMR SPECTRA, AND X-RAY POWDER DIFFRACTION PATTERNS OF MAGNESIUM AND GUANIDINIUM SALTS OF TRIS(CATECHOLATO)SILICONATE

The infrared spectra were measured with a Perkin-Elmer 137 B Infracord and with a Beckman IR-12, and the x-ray powder diffraction patterns with a General Electric XRD 5 spectrogoniometer using copper Kα radiation with a nickel filter.

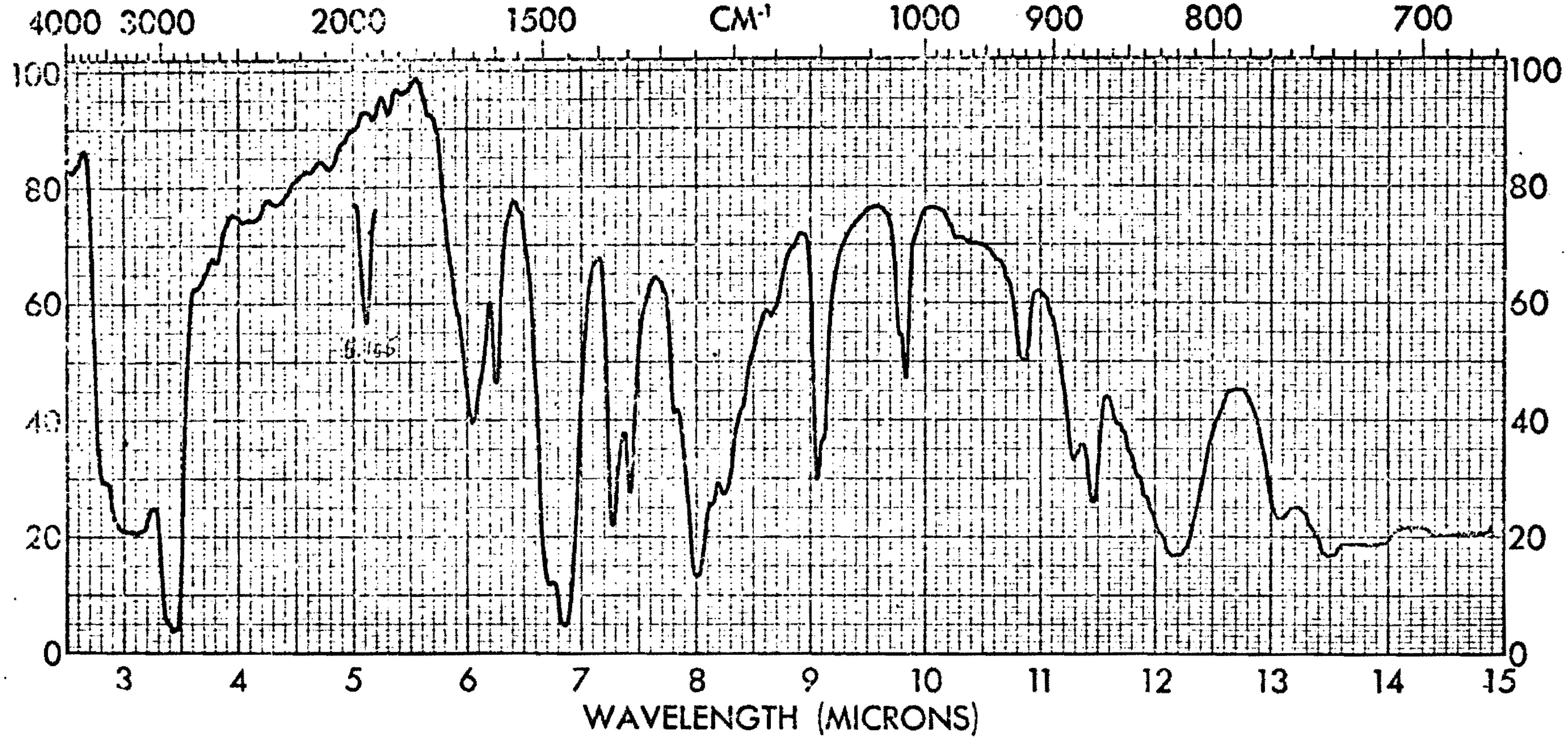
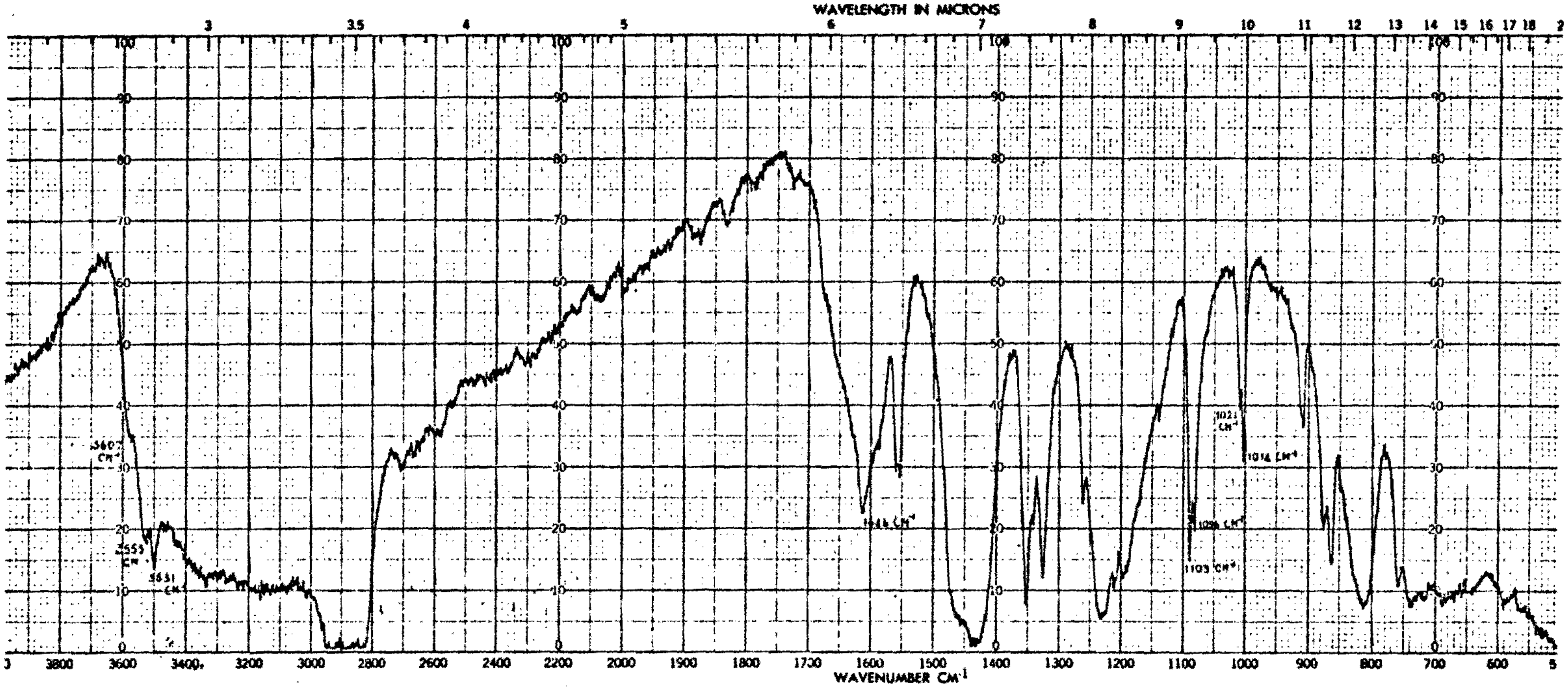


Figure A-1. Infrared Spectrum of Magnesium Tris(catecholato)siliconate Nonahydrate, $Mg[Si(Cat)_3] \cdot 9H_2O$.
(Nujol Mull)



<u>Figure A-2.</u> Infrared Spectrum of Magnesium Tris(catecholato)siliconate Nonahydrate,
(Nujol Mull)
$Mg[Si(Cat)_3]\cdot 9H_2O$

Note: The scale of the spectrum is <u>not</u> correct. The written values of wave numbers of some bands are calibrated against the spectrum of polystyrene.

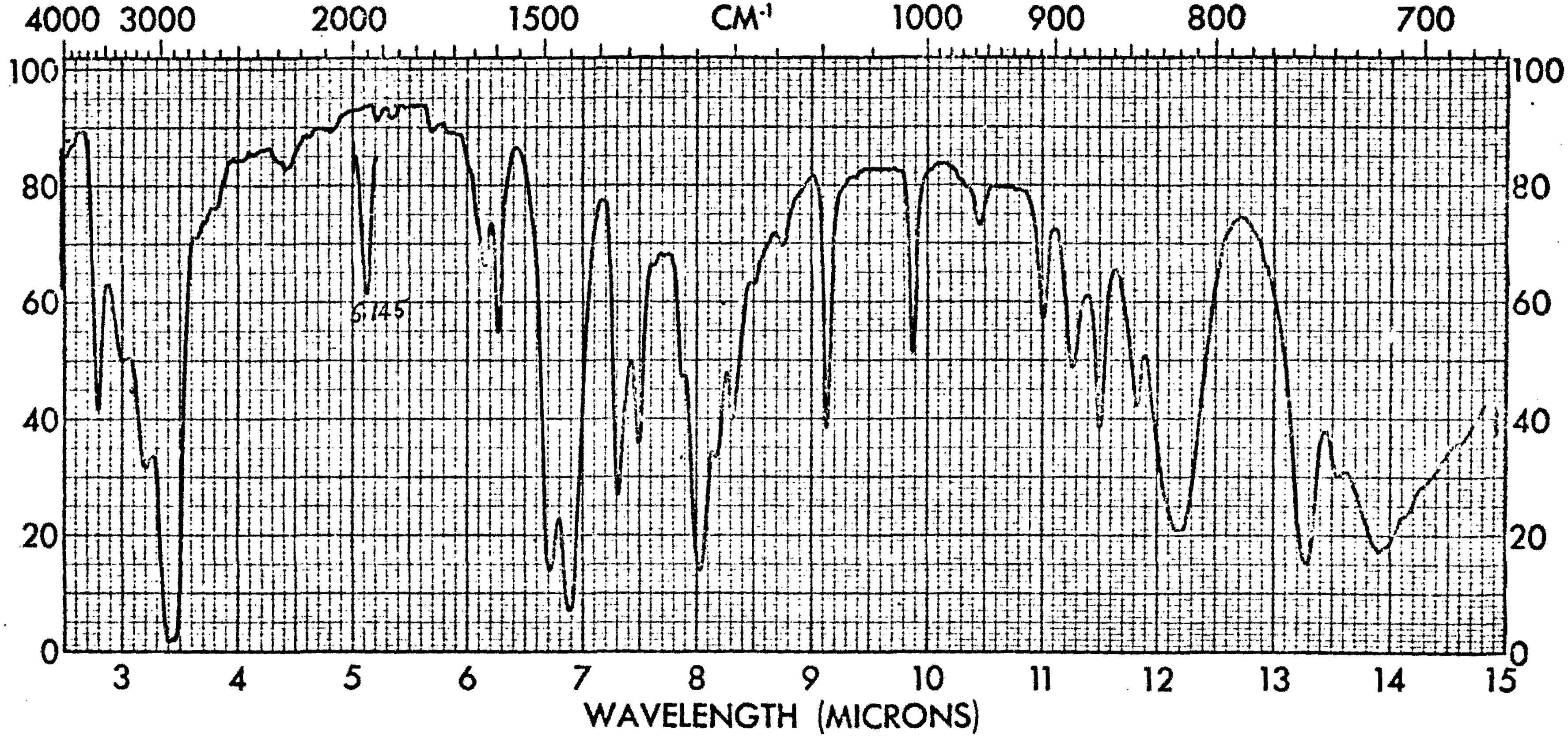
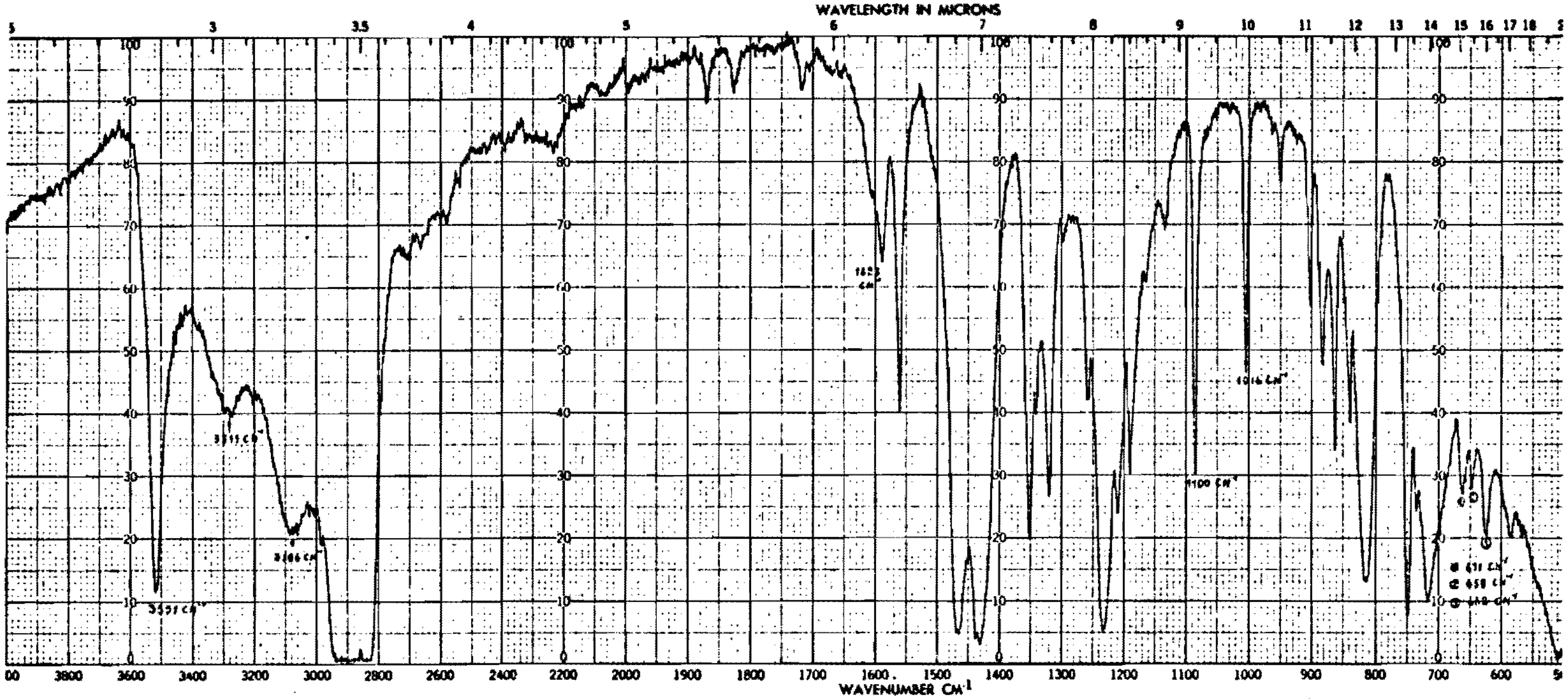
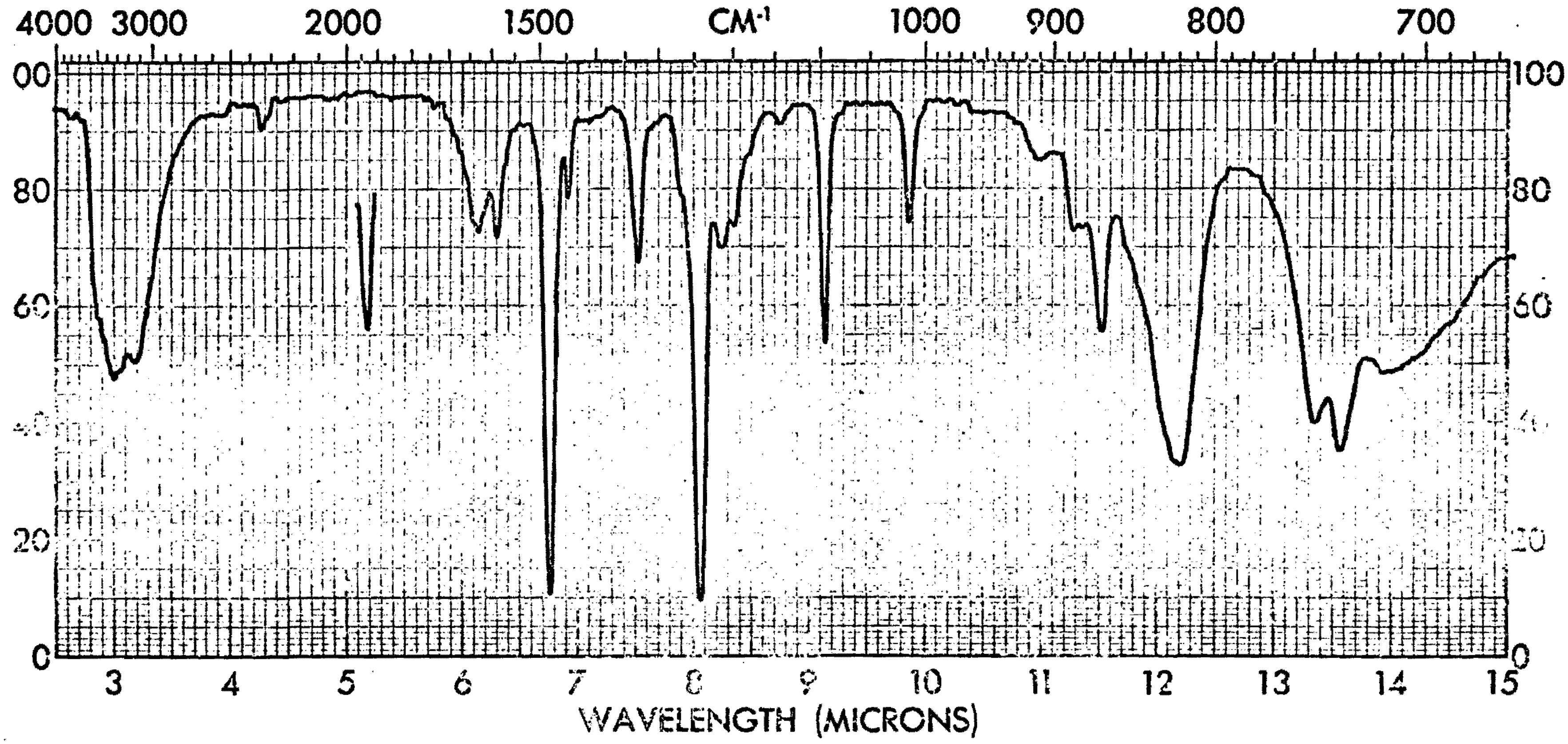


Figure A-3. (Nujol Mull) Infrared Spectrum of Magnesium Tris(catecholato)siliconate Trihydrate, $Mg[Si(Cat)_3] \cdot 3H_2O$.



<u>Figure A-4.</u> (Nujol Mull) Infrared Spectrum of Magnesium Tris(catecholato)siliconate Trihydrate, $Mg[Si(Cat)_3] \cdot 3H_2O$.

(See <u>Note</u> on Fig. A-2).



<u>Figure A-5.</u> Infrared Spectrum of Magnesium Tris(catecholato)siliconate Trihydrate, $Mg[Si(Cat)_3]\cdot 3H_2O$.
(KBr Pellet)

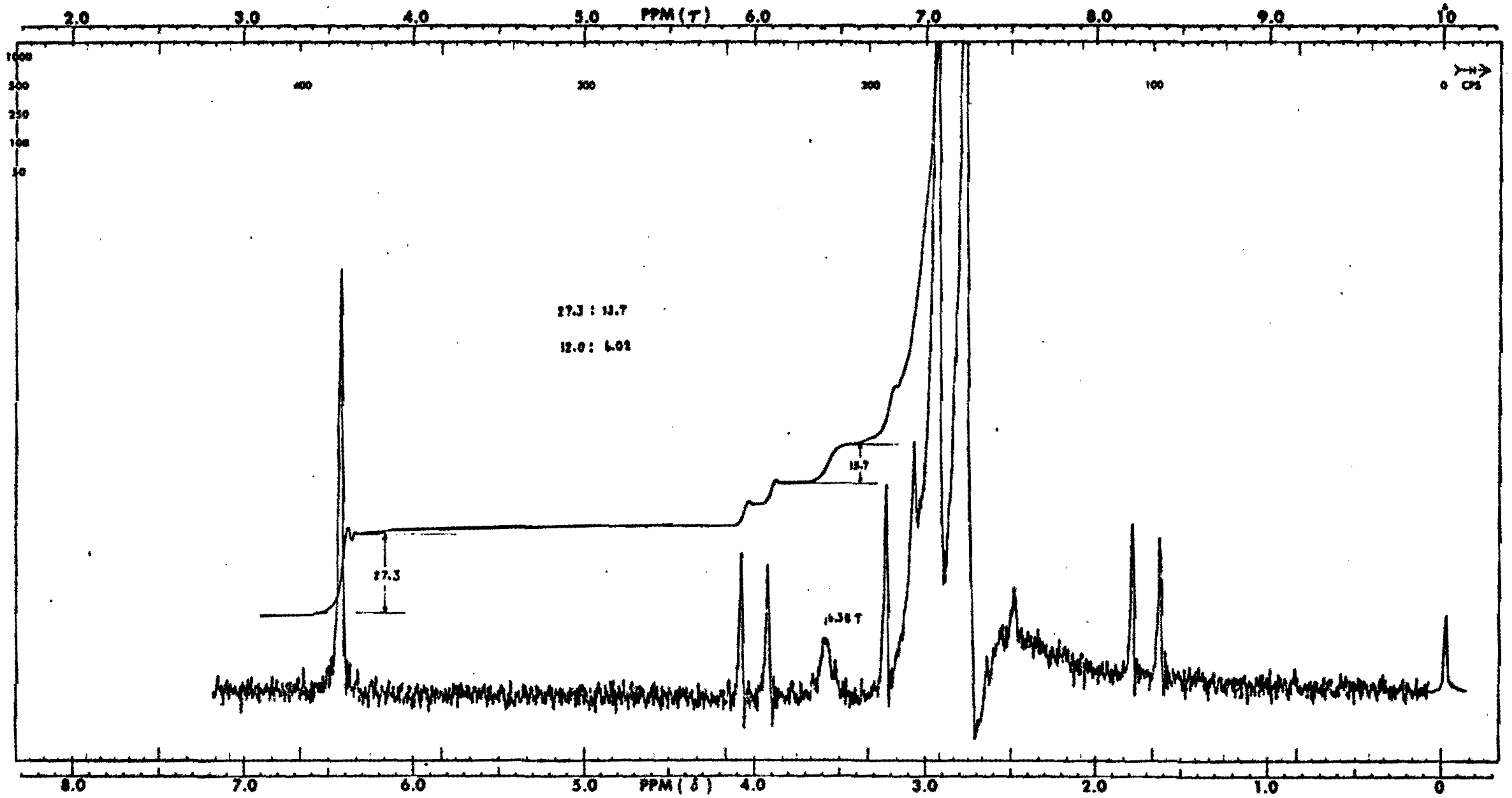
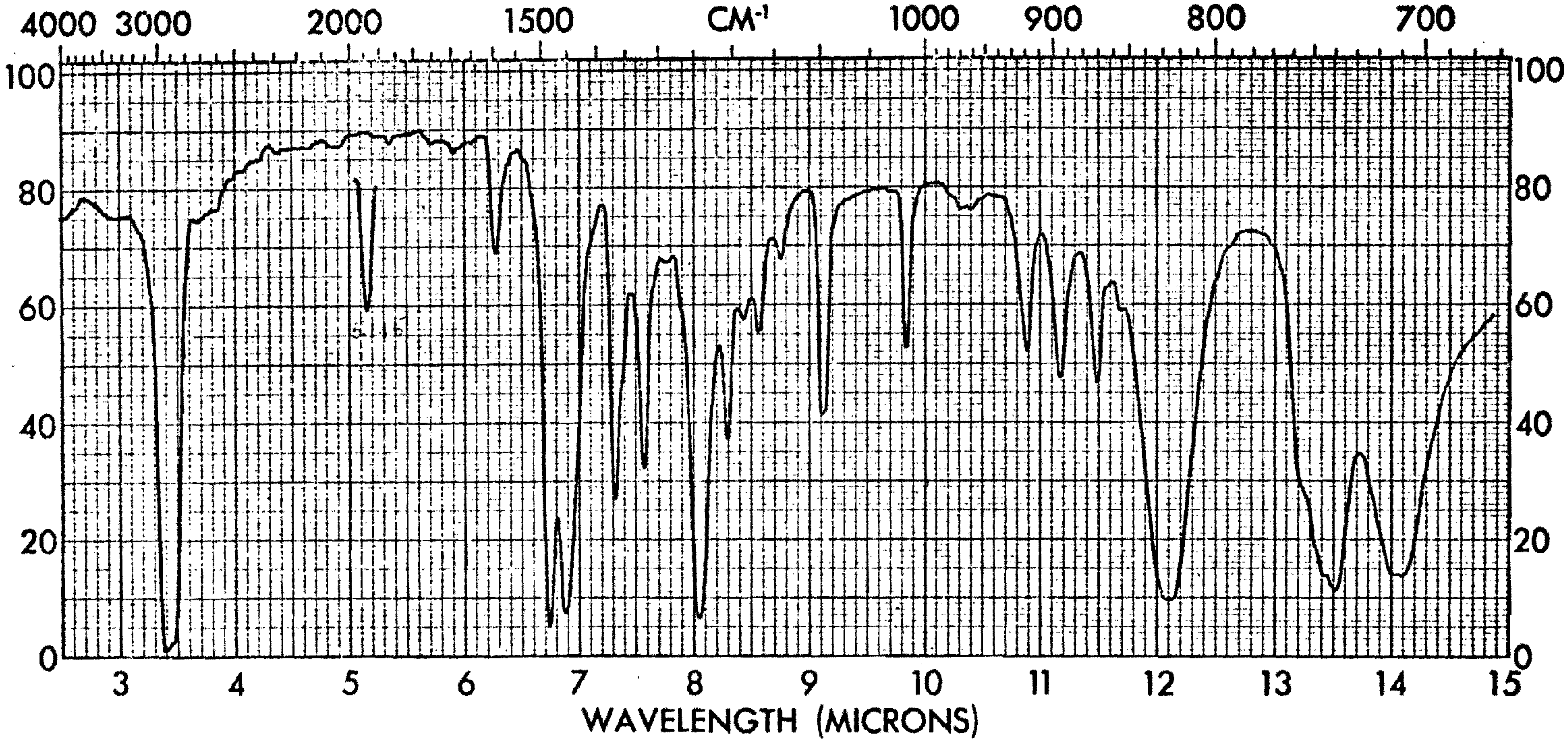
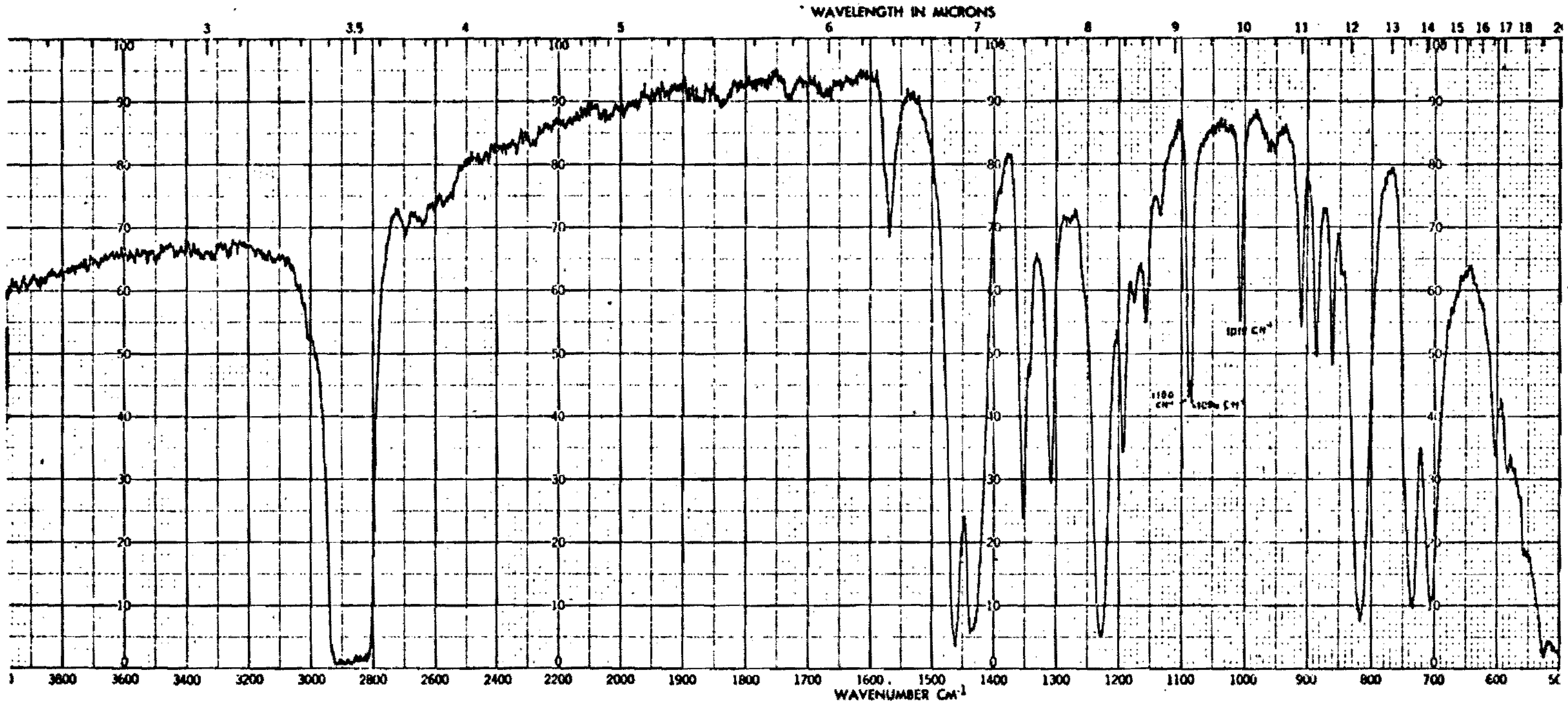


Figure A-6. NMR Spectrum of $Mg[Si(Cat)_3]\cdot 3H_2O$ in N,N-Dimethylformamide (~2.7 % solution).



<u>Figure A-7</u>. Infrared Spectrum of Magnesium Tris(Catecholato)siliconate, Mg[Si(Cat)$_3$]. (Nujol Mull)



<u>Figure A-8</u>. Infrared Spectrum of Magnesium Tris(catecholato)siliconate, Mg[Si(Cat)$_3$].
(Nujol Mull)

(See Note on Fig. A-2)

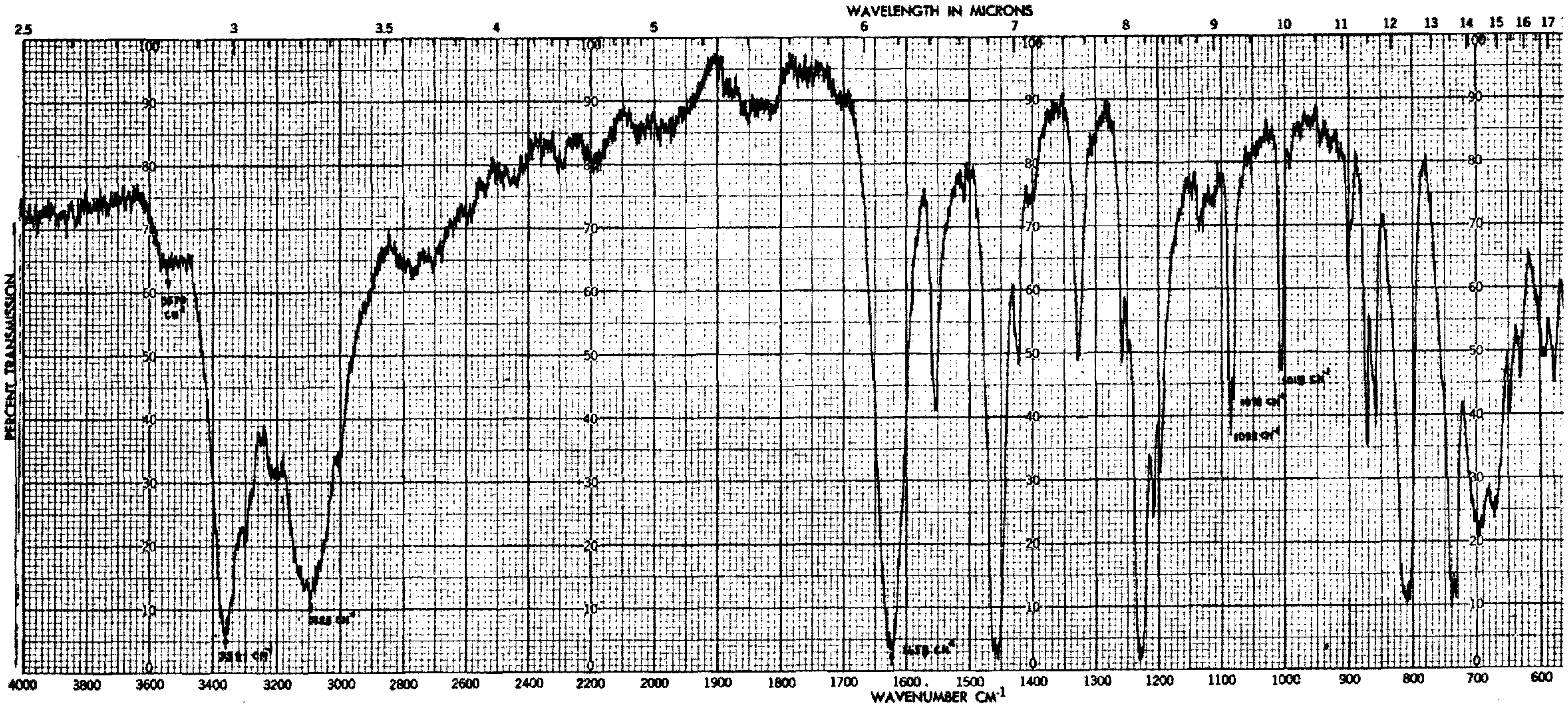


Figure A-9. (KBr Pellet) Infrared Spectrum of Guanidinium Tris(catecholato)siliconate Monohydrate, $(CN_3H_6)_2[Si(Cat)_3] \cdot H_2O$.

(See Note on Fig. A-2)

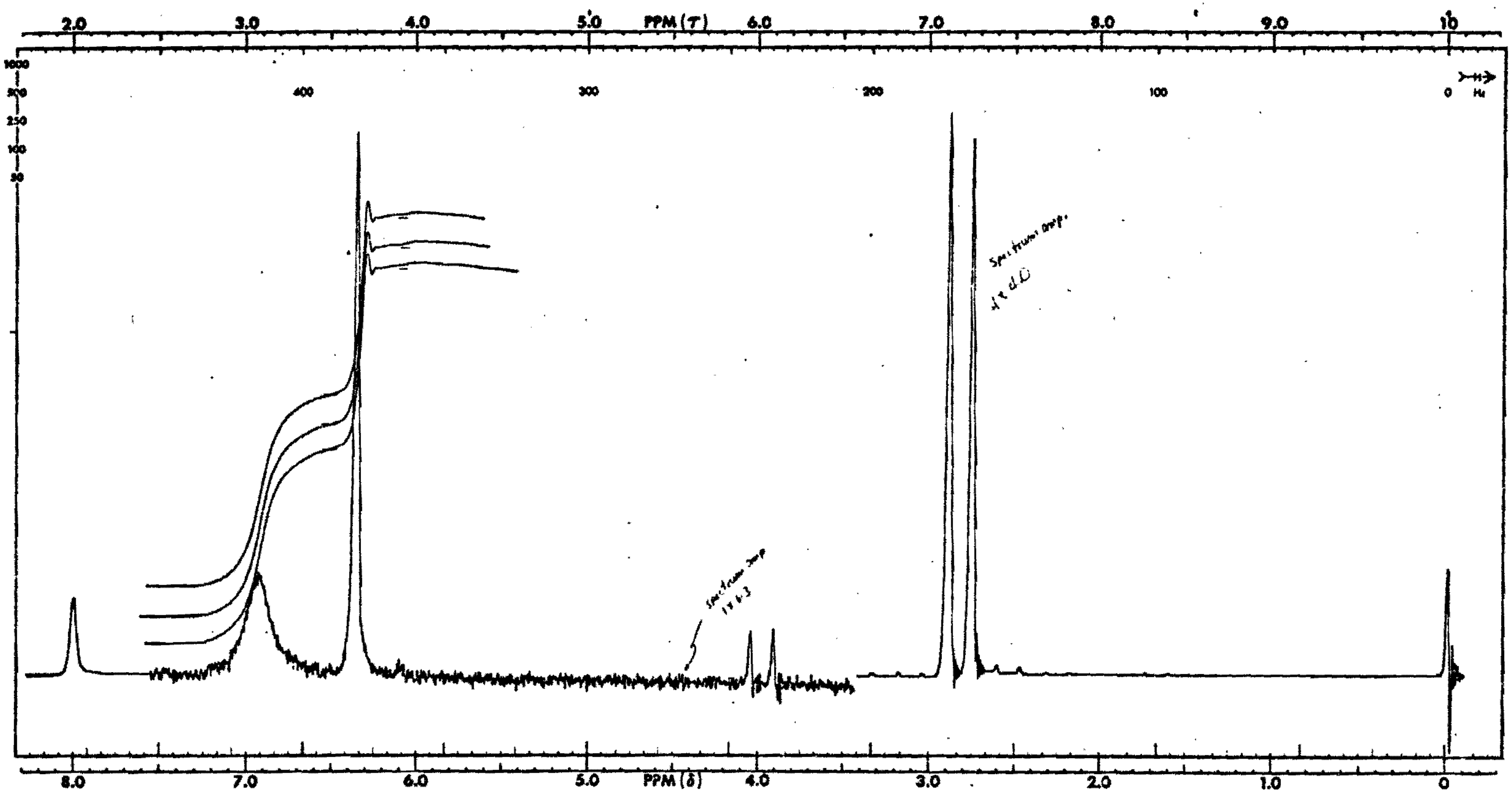


Figure A-10. NMR Spectrum of Guanidinium Tris(Catecholato)siliconate Monohydrate, $(CN_3H_6)_2[Si(Cat)_3]\cdot$

TABLE A-1

X-RAY POWDER DIFFRACTION PATTERN OF $Mg[Si(Cat)_3]\cdot 9H_2O$

Radiation: CuKα

I/Io: Diffractometer

d,Å	I/Io
11.2	90
8.5	65
8.1	80
7.6	25
6.30	20
5.90	12
5.52	36
5.06	34
4.83	100
4.66	48
4.53	60
4.40	11
4.25	25
4.02	20
3.840	27
3.666	4
3.559	16
3.512	16
3.424	37
3.140	8
3.023	25
2.966	14
2.932	10
2.882	10
2.733	12
2.704	12
2.660	15
2.596	27
2.460	5
2.395	10
2.252	10
2.231	17
2.118	7
2.106	7
2.014	11
1.894	5
1.857	5

TABLE A-2

X-RAY POWDER DIFFRACTION PATTERN OF $Mg[Si(Cat)_3]\cdot 3H_2O$*

Radiation: CuKα $\quad$ I/I_o: Diffractometer

d,Å	I/I_o	d,Å	I/I_o
11.1	100	3.48	4
10.3	46	3.348	7
7.46	14	3.184	7
6.41	57	3.087	6
6.23	43	2.910	12
5.93	37	2.855	6
5.68	13	2.738	6
5.55	43	2.704	6
5.41	29	2.598	5
5.14	8	2.477	4
4.85	25	2.371	3
4.77	13	2.328	2
4.61	8	2.301	2
4.56	8	2.283	2
4.44	10	2.250	1
4.31	9	2.215	2
4.21	21	2.230	5
4.00	12	1.916	3
3.63	25	1.812	3

---

* The diffraction pattern changes on exposure to air for more than ½ hour due to its hygroscopic nature. For example, the 11.1 Å line will move to 11.4 Å, the 10.3 Å line will be more intense, and the 7.46 Å line will disappear. Several other lines also shift or their intensities change slightly.

TABLE A-3

X-RAY POWDER DIFFRACTION PATTERN OF ANHYDROUS $Mg[Si(Cat)_3]$*

Radiation: CuKα, Debye-Scherrer camera,
I/I_o: vission

d,Å	I/I_o	
10.4	20	broad
9.3	100	
8.3	100	
7.5	1	
7.0	2	
6.64	1	
5.10	90	
4.72 4.04	10	broad
3.52	3	
2.92	1	broad
2.64	2	
2.03	1	
1.76	2	

* All the lines are broad.

TABLE A-4

X-RAY POWDER DIFFRACTION PATTERN OF GUANIDINIUM SALT, $(CN_3H_6)_2[Si(Cat)_3].H_2O$

Radiation: CuKα

I/Io: Diffractometer

d,Å	I/Io	d,Å	I/Io
11.1	11	4.10	100
10.1	>100	4.05	90
8.9	36	3.87	7
8.0	56	3.69	12
7.54	30	3.54	16
6.93	18	3.48	31
6.67	16	3.37	16
6.24	21	3.32	28
5.32	15	3.222	8
5.16	31	3.106	4
5.00	85	2.947	6
4.86	10	2.886	15
4.62	14	2.838	12
4.53	11	2.642	7

APPENDIX B

INFRARED SPECTRA AND X-RAY POWDER DIFFRACTION PATTERNS OF SILICATE MINERALS, AND X-RAY POWDER DIFFRACTION PATTERN OF THE GELATINOUS PRODUCT FROM THE REACTION OF DIOPSIDE WITH CATECHOL IN 1.0 F AMMONIUM CHLORIDE

The infrared spectra were measured with a Perkin-Elmer 137 B Infracord and the x-ray powder diffraction patterns with a General Electric XRD 5 spectrogoniometer using copper Kα radiation with a nickel filter.

Figure B-1. Infrared

Spectra of:

Top - Olivine (Forsterite)

Bottom - Sepiolite

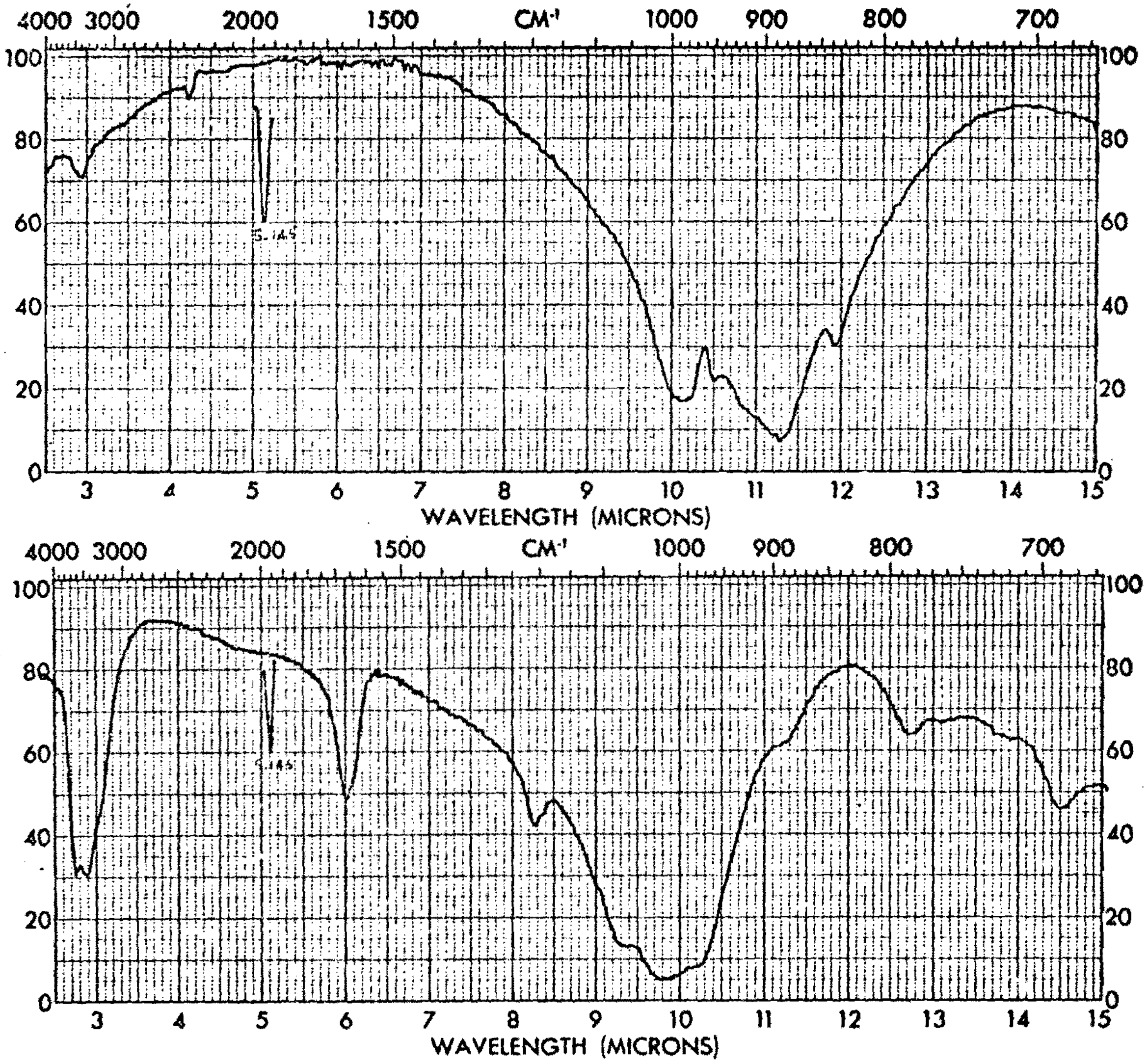


Figure B-2. Infrared Spectra of:

Top - Enstatite

Bottom - Augite

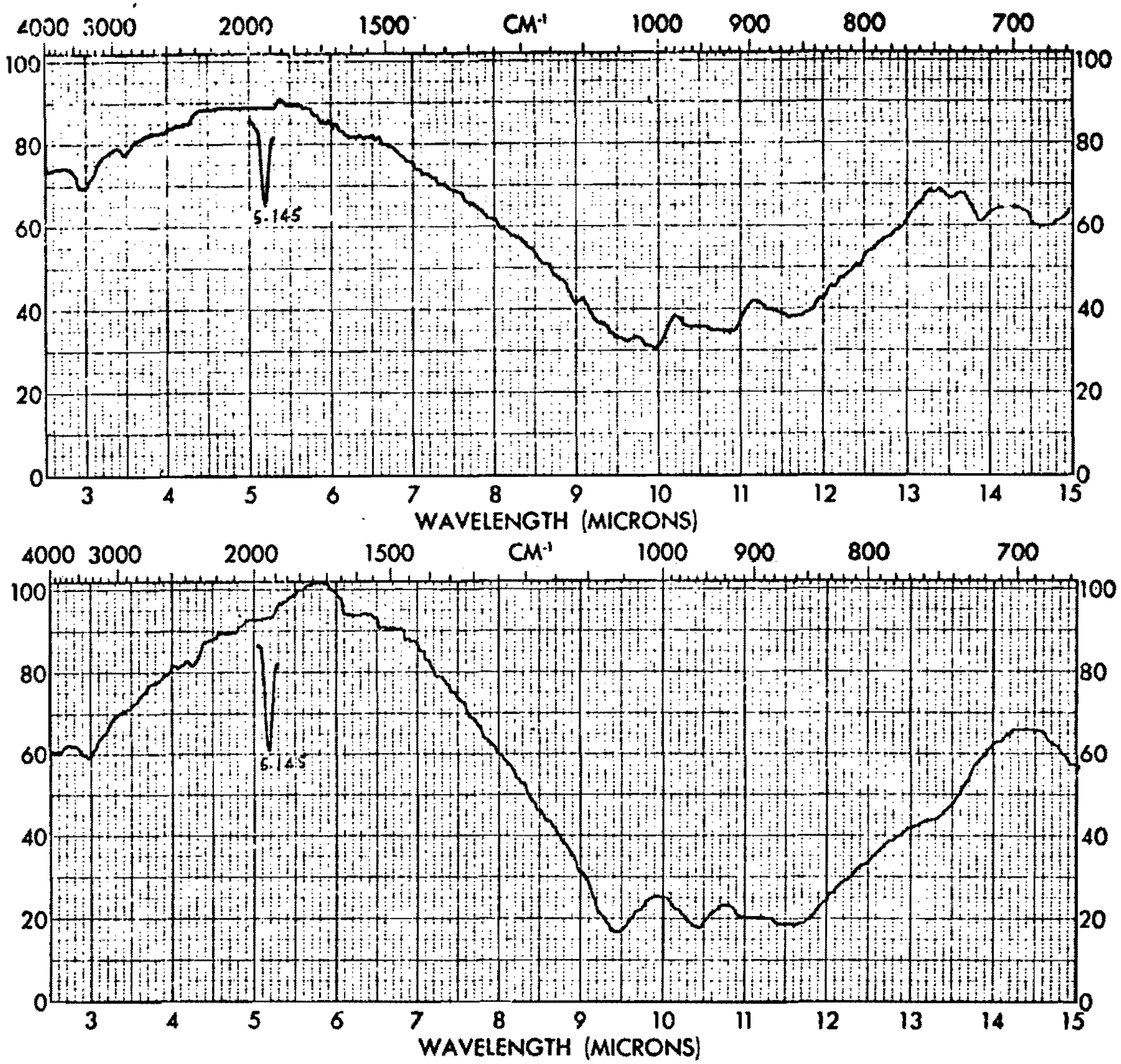


Figure B-3. Infrared

Spectra of:

Top - Diopside, Starting Mineral

Bottom - The Reaction Residue from the Reaction of Diopside with Catechol in 0.05 F Potassium Biphthalate

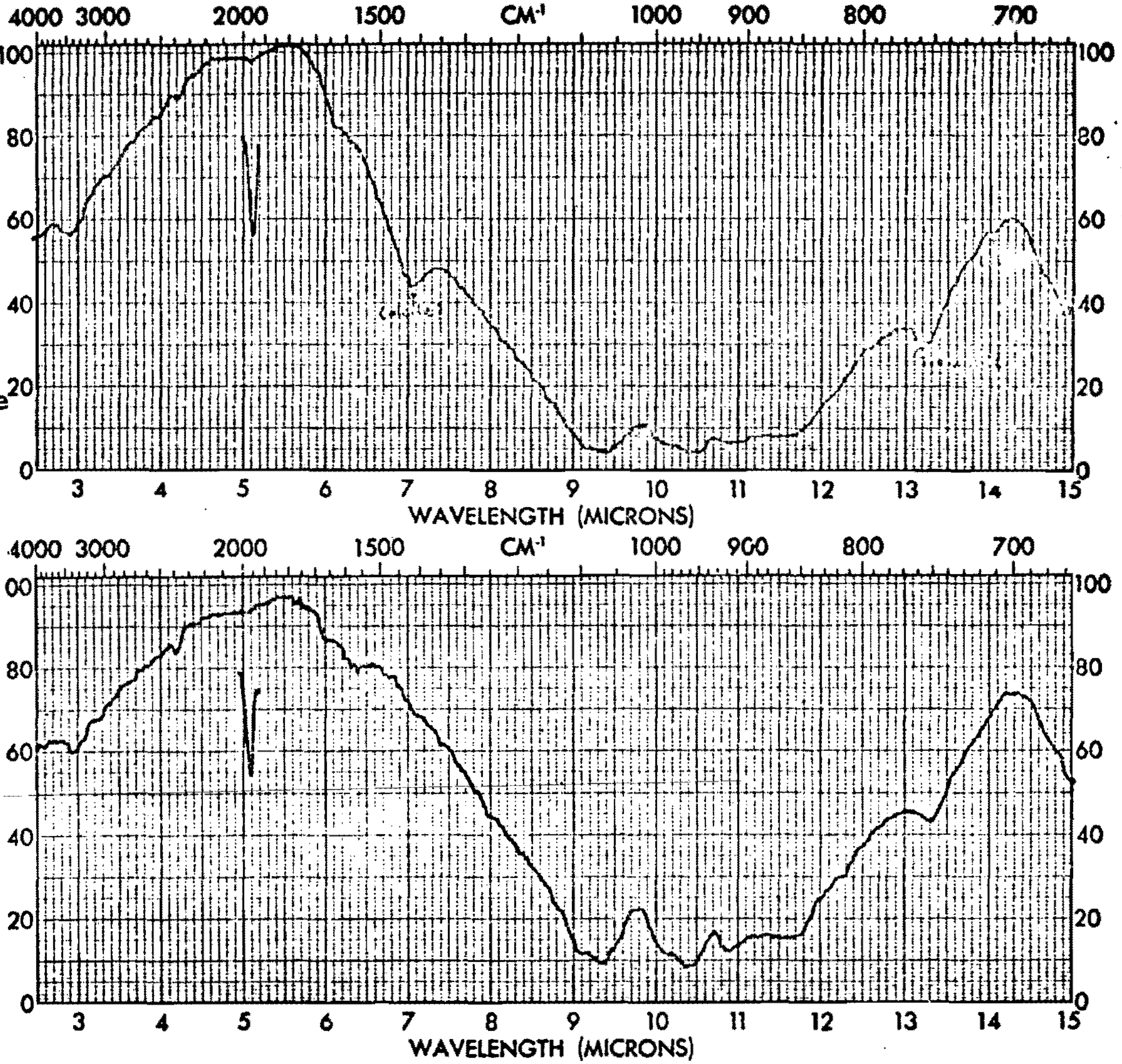


TABLE B-1

X-RAY POWDER DIFFRACTION PATTERN OF OLIVINE

Radiation: CuKα		Radiation: CuKα	
I/Io: Diffractometer		I/Io: Diffractometer	
Starting Olivine		**ASTM 7-79, Forsterite (Olivine)**	
d,Å	I/Io	d,Å	I/Io
6.66	10		
6.43	11		
6.29	9		
5.97	8		
5.87	8		
5.32	6		
5.13	48	5.10	50
		4.32	10
3.88	61	3.884	60
3.71	14	3.722	10
		3.500	20
3.488	24	3.481	10
		3.010	10
2.988	22	2.994	10
2.768	100	2.770	100
2.512	68	2.514	100
2.459	72	2.460	80

TABLE B-1 (CONTINUED)

Starting Olivine		ASTM 7-79, Forsterite (Olivine)	
d, Å	I/I_o	d, Å	I/I_o
2.349	17	2,350	20
		2.318	10
2.270	30	2.271	40
2.248	35	2.251	30
2.158	21	2.162	10
2.083	7		
2.031	7	2.034	5
1.939	7		
1.875	14	1.879	10
1.856	7		
1.810	10		
1.802	7		
1.790	8		
1.779	8		
1.748	48	1.751	40
		1.741	10
		1.733	10
1.670	9	1.672	10
1.637	20	1.639	10
		1.633	10
1.618	13	1.620	20
1.589	6	1.591	5
1.570	10		

TABLE B-1 (CONTINUED)

Starting Olivine		ASTM 7-79, Forsterite (Olivine)	
d,Å	I/Io	d,Å	I/Io
1.514	7		
1.506	7		
1.496	27	1.498	20
1.480	26	1.481	20
1.395	13	1.396	10
		1.390	5
1.351	10	1.352	20
1.323	6		
1.313	10	1.317	10
1.296	8		

TABLE B-2

X-RAY POWDER DIFFRACTION PATTERN OF SEPIOLITE

Radiation: CuKα			Radiation: CuKα	
I/Io: Diffractometer			I/Io: Diffractometer	
Starting Sepiolite			ASTM 14-1, Sepiolite	
d,Å	I/Io		d,Å	I/Io
12.5	100		12.3	100
			7.6	10
4.5	9	broad	4.9	10_B
			4.5	35
4.28	10	broad	4.3	
3.72	6	broad	3.746	35_B
			3.49	10
3.33	14	broad	3.34	35_B
			2.98	
3.18	9			
2.579	11		2.67	60_B
2.554	11		2.49	
2.427	3		2.43	20
			2.36	
2.252	5		2.24	35_B
			2.08	10_B
			1.69	10_B
			1.58	10
			1.551	20
			1.517	20

TABLE B-3

IMPURITIES IN SEPIOLITE*

Debye-Scherrer Camera Radiation: CuKα

I/Io by vision

d,Å	I/Io		d,Å	I/Io	
14.1	5	broad	1.812	30	
7.28	50	broad	1.666	3	
4.56	7		1.608	1	
4.25	10		1.538	30	
3.693	20	broad	1.498	1	
3.628			1.478	1	
3.359	100	broad	1.447	1	
3.305			1.379	3	
2.523	5		1.369	15	
2.485	4		1.285	1	
2.466	10		1.253	2	
2.331	8		1.195	2	broad
2.227	4		1.178	2	broad
2.119	5		1.088	1	
1.971	2				

---

* Those dark brown particles which were separated from starting sepiolite manually.

TABLE B-4

X-RAY POWDER DIFFRACTION PATTERN OF DIOPSIDE

Debye-Scherrer Camera

I/Io by vision

I/Io: Photometer

Radiation: CuKα

Starting Diopside		ASTM 11-654, Diopside	
d,Å	I/Io	d,Å	I/Io
8.4	10*		
		4.69	1
		4.47	3
		4.41	3
		3.66	3
		3.35	11
3.24	12*	3.23	25
3.13	10*		
2.998	100	2.991	100
2.959	12	2.952	25
2.899	12	2.893	30
		2.837	1
2.807	1*		
2.714	8*		

* Possible tremolite

TABLE B-4 (CONTINUED)

Starting Diopside		ASTM 11-654, Diopside	
d,Å	I/Io	d,Å	I/Io
2.569	7	2.566	20
2.530	80	2.528	40
		2.518	30
		2.392	3
2.311	5	2.304	15
2.220	3	2.218	13
2.203	2	2.200	11
2.161	5	2.157	9
2.135	10	2.134	15
2.114	3	2.109	7
		2.077	1
2.043	3	2.043	13
2.017	10	2.016	9
1.972	5	1.970	7
		1.862	3
1.840	6	1.838	5
		1.832	3
		1.815	3
		1.777	1
1.755	12	1.755	11
		1.720	1
		1.685	1
		1.674	5

TABLE B-4 (CONTINUED)

Starting Diopside		ASTM 11,654, Diopside	
d,Å	I/Io	d,Å	I/Io
		1.659	5
1.628	40	1.625	25
		1.618	5
		1.588	3
		1.565	3
1.552	1	1.551	3
		1.529	1
1.527	3	1.526	9
1.506	8	1.504	11
1.490	2	1.494	1
		1.488	3
		1.468	1
		1.463	1
1.440	2	1.447	3
1.425	20	1.424	13
1.410	5	1.410	7
1.393	1	1.391	3
		1.374	1
		1.345	1
1.331	5	1.330	7
		1.327	3
		1.317	3
		1.288	7

TABLE B-4 (CONTINUED)

Starting Diopside d,Å	Starting Diopside I/Io	ASTM 11.654, Diopside d,Å	ASTM 11.654, Diopside I/Io
1.285	5	1.282	7
1.266	2	1.265	5
1.250	3	1.249	3

TABLE B-5

X-RAY POWDER DIFFRACTION PATTERN OF AUGITE

Radiation: CuKα		Radiation: CuKα	
Debye-Scherrer Camera		Debye-Scherrer Camera	
I/I_o by vision,			
Starting Augite		Fassaite (Al-Augite)*	
d,Å	I/I_o	d,Å	I/I_o
3.221	15	6.471	2
		4.710	4
		4.453	3
		3.689	1
		3.359	2
3.221	15	3.236	16
2.989	100	3.002	100
2.946	20	2.961	32
2.898	20	2.909	28
2.567	10	2.568	32
		2.561	1
2.534	60	2.558	48

---

[*] I. Y. Borg and D. K. Smith, Calculated X-Ray Powder Patterns for Silicate Minerals, The Geogolical Society of American in Cooperation with Mineralogical Society of America (1969), 249-52.

TABLE B-5 (CONTINUED)

Starting Augite		Fassaite (Al-Augite)	
d,Å	I/Io	d,Å	I/Io
2.510	60	2.528	51
		2.395	1
		2.355	1
2.297	12	2.316	17
2.216	8	2.239	16
		2.220	1
2.200	5	2.218	11
2.148	8	2.157	13
2.131	12	2.115	17
2.107	7		
		2.082	1
2.038	10	2.042	23
		2.032	19
2.020	7	2.027	14
2.007	6	1.9809	11
1.968	6	1.9526	2
		1.9044	1
1.852	1	1.8659	4
		1.8447	4
		1.8431	8
		1.8247	4
1.804	6	1.8026	1
		1.7833	2

TABLE B-5 (CONTINUED)

Starting Augite		Fassaite (Al-Augite)	
d,Å	I/Io	d,Å	I/Io
1.745	20	1.7502	24
		1.7315	2
1.670	3	1.6824	3
		1.6794	11
		1.6769	10
1.664	4	1.6413	34
1.627	25	1.6295	29
1.612	2	1.6178	11
		1.5906	4
1.558	2	1.5699	8
1.544	2	1.5493	13
		1.5391	12
1.531	1	1.5354	15
		1.5318	7
1.521	2	1.5173	2
1.506	20	1.5170	30
		1.4988	2
1.480	1	1.4843	10
		1.4801	1
		1.4653	2
		1.4622	1
		1.4546	4

TABLE B-5 (CONTINUED)

Starting Augite		Fassaite (Al-Augite)	
d,Å	I/Io	d,Å	I/Io
		1.4516	4
1.419	40	1.4281	41
		1.4255	4
1.415	10	1.4124	24
1.409	12	1.4113	10
1.406	12	1.4035	13
1.390	10	1.3834	4
		1.3821	2
		1.3538	3
1.331	12	1.3380	17
		1.3359	1
		1.3352	2
1.324	10	1.3332	12
		1.3305	3
1.320	10	1.3262	10
1.292	5	1.3030	11
		1.3024	1
		1.3021	5
		1.2842	7
1.278	10	1.2838	15
		1.2806	5
1.276	5	1.2789	9

TABLE B-5 (CONTINUED)

Starting Augite		Fassaite (Al-Augite)	
d,Å	I/Io	d,Å	I/Io
		1.2656	3
		1.2640	4
		1.2630	1
1.246	10	1.2522	21
1.243	3	1.2348	5
		1.2315	1
		1.2307	2
		1.2292	2
		1.2217	2
1.210	1	1.2139	7
		1.1914	2
		1.1793	3
1.169	1		
1.151	5	1.1591	11
		1.1582	2
		1.1572	3
1.148	4	1.1477	2
		1.1394	2
		1.1195	5
		1.0893	9
1.072	5	1.0776	15
		1.0771	3
		1.0768	3

TABLE B-5 (CONTINUED)

Starting Augite		Fassait (Al-Augite)	
d,Å	I/Io	d,Å	I/Io
1.069	20	1.0737	21
		1.0684	5
		1.0679	4
1.066	5	1.0655	15
1.062	5	1.0590	13

TABLE B-6

X-RAY POWDER DIFFRACTION PATTERN OF ENSTATITE

Radiation: CuKα

Debye-Scherrer Camera

I/I_o = Vision

Radiation: CuKα

I/I_o = Vision

Starting Enstatite			ASTM 7-216 Enstatite	
d,Å	I/I_o		d,Å	I/I_o
9.3	2			
8.2	2			
			6.33	21
			4.41	14
4.01	2			
3.323	5		3.303	35
3.179	100	broad	3.167	100
3.122	2			
3.039	2			
2.953	15		2.941	44
2.878	30		2.872	87
2.832	10		2.825	23
2.709	10		2.706	26
2.542	15		2.534	43
2.501	40		2.494	51
2.477	13		2.471	31

TABLE B-6 (CONTINUED)

Starting Enstatite		ASTM 7-216 Enstatite	
d, Å	I/Io	d, Å	I/Io
2.393	2		
		2.358	7
		2.280	5
2.252	2	2.252	7
		2.232	7
2.119	20	2.114	24
2.098	18	2.096	21
2.060	8	2.058	13
2.025	5	2.019	10
1.989	10	1.984	13
1.965	20	1.958	24
1.888	2	1.887	6
1.842	2	1.854	3
		1.800	7
1.789	5	1.786	10
		1.773	7
1.737	7	1.732	8
1.704	7	1.702	9
		1.698	8
1.685	2	1.679	9
		1.649	7
1.613	15*	1.603	20

* Magnetite

TABLE B-6 (CONTINUED)

Starting Enstatite		ASTM 7-216 Enstatite	
d,Å	I/Io	d,Å	I/Io
1.592	5	1.588	10
1.530	5	1.525	7
1.522	5	1.520	14
1.489	50*	1.485	34
1.475	15*	1.470	22
1.425	5		
1.400	2		
1.396	10		
1.382	2		
1.366	2		
1.361	2		
1.342	5		
1.310	8		
1.300	5		
1.297	5		
1.271	5		
1.232	2		
1.212	2		
1.188	2		

* Magnetite

TABLE B-7

X-RAY POWDER DIFFRACTION PATTERN OF IMPURITIES IN ENSTATITE

Radiation: CuKα

Debye-Scherrer Camera

$^{I}/_{Io}$ by vision

d,Å	$^{I}/_{Io}$		
9.2	10		
3.167	50	enstatite	
3.110	10		
2.946	10		magnetite
2.865	50	enstatite	
2.528	100		magnetite
2.089	15		magnetite
2.023	100		magnetite
1.786	5	enstatite	
1.612	50		magnetite
1.480	100		magnetite
1.390	10	enstatite	
1.166	10		
1.091			magnetite

TABLE B-8

X-RAY POWDER DIFFRACTION PATTERN OF THE GELATINOUS PRODUCT FROM REACTION OF DIOPSIDE WITH CATECHOL IN 1.0 F NH_4Cl

Debye-Scherrer Camera		Diffractometer	
I/I_o = Vision			
Gelatinous Product*		Kelley's Compound A**	
d,Å	I/I_o	d,Å	I/I_o
11.3	3	11.70	8
10.6	100	10.64	100
9.5	100	9.55	25
8.9	5	8.83	13
8.4	4	8.58	7
		8.07	12
6.6	4		
		6.39	4
6.16	3	6.21	6
5.98	2		
5.60	3	5.71	2
5.43	2		

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* After excluding all other diopside lines

** J. M. Kelley, M. S. Thesis, Portland State University (1972).

TABLE B-8 (CONTINUED)

Gelatineous Product			Kelley's Compound A	
d,Å	I/I_o		d,Å	I/I_o
5.20	10			
5.06	8		4.99	6
4.82	10	broad	4.831	16
4.47	8			
4.37			4.350	10
4.23	10			
			4.149	6
4.08	10			
3.99	15			
3.883	5			
3.698	2			