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Catechol Effected Dissolution of Silicate Minerals

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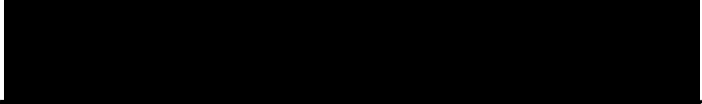
AN ABSTRACT OF THE THESIS OF James Maurice Kelley for the

Master of Arts in Chemistry presented January 25, 1972.

Title: Catechol Effected Dissolution of Silicate Minerals.

APPROVED BY MEMBERS OF THE THESIS COMMITTEE:

Raymond P. Lutz, Chairman

Gary L. Gard

Morris B. Silverman

The chemical properties of guanidinium tris(catecholato)siliconate, $[(H_2N)_2C=NH_2]_2[Si(C_6H_4O_2)_3] \cdot XH_2O$ ($0 < X \leq 1$), precipitated from an ammoniacal solution of silica and catechol by adding guanidinium hydrochloride, $(H_2N)_2C=NH \cdot HCl$, were studied, and infrared, nmr, x-ray powder diffraction, and analytical data were gathered.

This same compound was, upon addition of $(H_2N)_2C=NH \cdot HCl$, isolated from 0.25 M aqueous catechol solutions buffered at pH 10 and containing the silicate minerals albite, andradite, muscovite, pyrophyllite, talc, and wollastonite, and also from unbuffered catechol solutions containing wollastonite and andradite.

It is concluded from this work that the formation of an anionic catechol-silicon complex, $Si(C_6H_4O_2)_3^{2-}$, is largely responsible for the dissolution of the minerals mentioned above. From this conclusion, it is proposed that naturally occurring members of the class of organic compounds to which catechol belongs, the aromatic vic-diols, may play a role in chemical weathering, in the development of certain soil profiles, and in the entry and accumulation of silica in plants.

CATECHOL EFFECTED DISSOLUTION OF SILICATE MINERALS

by

JAMES MAURICE KELLEY
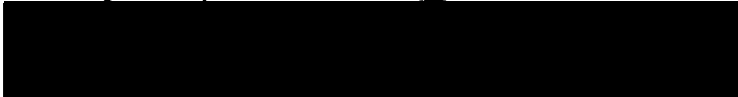
A thesis submitted in partial fulfillment of the
requirements for the degree of

MASTER OF ARTS
in
CHEMISTRY

Portland State University
1972

TO THE OFFICE OF GRADUATE STUDIES:

The members of the Committee approve the thesis of
James Maurice Kelley presented January 25, 1972.

Raymond P. Lutz, Chairman

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APPROVED:

Gary L. Gard, Head, Department of Chemistry

David T. Clark, Dean of Graduate Studies

April 7, 1972

ACKNOWLEDGEMENTS

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I. INTRODUCTION

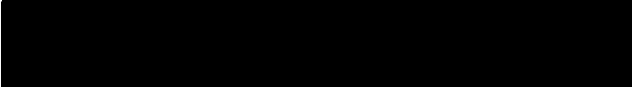Silicate minerals comprise about 90% of the earth's crust. Although a wide variety of different silicates exist, they all have as their basic structural unit the silica tetrahedron in which silicon is, or is approximately, equidistant from four oxygens.

Because of the ubiquity of silicon compounds in nature, studies dealing with the breakdown of silicates followed by the formation of secondary products constitutes a major area of research. For example, geochemists continually seek to explain various weathering phenomena by proposing mechanisms which generally incorporate well established inorganic reactions. Such mechanisms must, of course, obey the laws of chemical equilibria and also meet the criteria imposed by nature. These mechanisms are often quite satisfactory and can, in many cases, be tested in the laboratory.

Too often, though, classical mechanisms fail to provide the answers. Evans (1) points out that there are many examples where sediments like quartzites and limestones have consolidated rapidly under mild environmental conditions. In such cases, mechanisms embodying pressure and long periods of time must be ruled out, and the role which organic matter might play in geochemical events deserves serious

consideration.

Natural weathering environments usually contain organic matter originating from root secretion, decomposition of plant debris, and even the leaching of live plants. Trace amounts of organic matter are found in ancient sedimentary rocks, and Iler (2, p.3) cites an unusual example where quartz crystals have formed with inclusions of mineral oil and liquid carbon dioxide.

There is a class of organic compounds, the aromatic vic-diols,* whose presence in natural environments has recently been suggested in connection with studies dealing with water quality (3) and soil development (4,5). Compounds from this class are relatively stable against bacterial attack which increases the likelihood that they will persist in natural environments for significant periods of time. It is interesting to note, that while both of the studies cited above focused on the iron complexing properties of aromatic vic-diols, these diols also constitute the only class of organic compounds known to form water stable silicon complexes.

A wide variety of aromatic vic-diol-silicon complexes have been prepared and investigated (6,7,8,9,10). The aromatic vic-diols known to form complexes with silicon are

* A vic-diol is an organic compound with at least two hydroxy groups attached to adjacent carbons. Ethylene glycol is the simplest vic-diol, and catechol is the simplest aromatic vic-diol.

pyrogallol, alizarin, purpurin, gallic acid, quercetin, cat-
echol, tannic acid--tannic acids are found in natural sur-
face waters (11)--and several more. Quite generally, the
ratio of aromatic vic-diol to silicon is 3:1. It is fairly
certain that should one of these compounds fail to form a
complex with silicon, it would be the exception rather than
the rule.

The possible involvement of organic matter in geochem-
ical processes has not been ignored; however, thought usu-
ally centers around mineral dissolution resulting from che-
lation of metallic cations (1,12, p.47). Although mecha-
nisms involving chelation of cations show promise in resolv-
ing many chemical weathering anomalies, and help to explain
how certain soil profiles formed, mechanisms involving or-
ganic-silicon complexes have been overlooked.

The theory that aromatic vic-diols are involved in the
development of soils of the podsol* group has received con-
siderable attention by soil scientists. Bloomfield (4) has

---

* Podsols, the most widely distributed of the humid
climate soil groups, exhibit well developed A, B and C
horizons (layers). The A or eluvial (washed-out) horizon
is usually subdivided into three parts: the A_0 horizon
consists of forest litter and partially decayed organic
matter, the A_1 horizon consists of raw humus, and the A_2
horizon is a siliceous grey layer from which iron and alu-
minum have been leached. The B or illuvial (washed-in)
horizon is subdivided into two parts: the B_1 horizon con-
sists of precipitated humus, and the B_2 horizon consists
of sesquioxides (Fe_2O_3 and Al_2O_3) and colloidal clay. The
C horizon consists of weathered bedrock. Both the A and B
horizons are strongly acidic.

shown that polyphenolic extracts of forest leaves and litter effectively complexes and dissolves iron and aluminum oxides. Percolation of rain water through forest litter is believed to result in the leaching of iron and aluminum from the A2 horizon. The complexed iron and aluminum then move down the soil profile until immobilized and redeposited in the B horizon as sesquioxides. This theory is quite plausible, especially when compared with alternatives, and is gaining acceptance. It would be even more plausible if it were shown that dissolution of the parent mineral from which sesquioxides are leached is effected not only by chelation of iron and aluminum, but also by formation of polyphenol-silicon (i.e., aromatic vic-diol-silicon) complexes.

It has already been established that basic solutions containing aromatic vic-diols are effective in dissolving silica, whether it be in the form of an amorphous gel or crystalline quartz (6,7). Also Hess, Bach and Deuel (13) reported that an ammoniacal solution containing catechol was effective in dissolving permutite, a synthetic amorphous aluminum silicate, and somewhat less effective in dissolving perlite, a naturally occurring amorphous aluminum silicate. They also mentioned that under the same conditions an insoluble brown coating formed on the potash feldspar, orthoclase. They did not attempt to isolate or identify the reaction products.

Kononova et al (14) treated some silicates (i.e., lep-

idomelane, kaolinite, nepheline and plagioclase) with certain organic and inorganic substances found in soil matter. They reported that tartaric acid, catechol and humic acids were effective in dissolving these minerals. They noted that mineral dissolution was accompanied by a rise in pH. Solutions were electrophoretically fractionated and cations were detectected as organometallic compounds. There was no indication that the possible formation of silicon complexes was considered.

Silica itself is found in many forms of plant life and in some animals. Biogenically precepitated silica is almost always an amorphous variety, ranging from opaline forms secreted by radiolaria, diatoms and sponges, the gelatinous "tabisher" found in the hollow stems of bamboo. There are reports (1), though, where crystalline silica, in the form of quartz aggregates, was found in kidney stones of human beings who were treated for peptic ulcers with a synthetic silicate of zeolitic structure. Such occurrences are also reported as being common with sheep that feed on certain types of hay having a high silica content.

The manner in which silica enters and accumulates in plants is not completely understood. Siever and Scott (15) mention that although it is reasonable to attribute the accumulation of silica in most plants to the evaporation of silica rich fluids, another mechanism must operate for diatoms since they secrete silica under water. It would seem

that such a mechanism requires the involvement of a transient organic-silicon complex.

Iler (2, p.290) recounts an investigation of the mechanism by which silica is brought into solution by the roots of rye and sunflower. Silica accumulates in the shoots and leaves of these plants indicating that soluble silica moves along the transpiration stream—it does this with most plants which accumulate silica. When the rye and sunflower were grown in clay, the roots secreted a substance which brought silica into solution. It was speculated that soluble silicic acid was then absorbed by the plants. Since the root secretion apparently dissolved the clay silicate, it likely did so by chelation of metallic constituents. It can be speculated, however, that silicon itself also could have been complexed and perhaps absorbed by the plant as a complex rather than as silicic acid. Iler aptly points out that this study furnishes an excellent example of the role of plants in weathering of rocks and formation of soils. In this case it is a dual role involving mechanical breakdown of rocks as plants grow and roots spread, and chemical breakdown as root secretions dissolve minerals allowing the removal of soluble silica.

This work is a continuation of the attempt to demonstrate the effectiveness of organic matter in dissolving silicate minerals. However, emphasis is placed upon the importance of the formation of silicon complexes. Since, as

was mentioned, aromatic vic-diols are the only organic com-
pounds known to form water soluble complexes with silicon,
the simplest one, catechol, was chosen for these studies.

The guanidinium salt of the catechol-silicon complex
was characterized since it was chosen to be isolated in sub-
sequent reactions of catechol with silicate minerals. fol-
lowing initial studies of the solubilization of silicate
minerals by catechol in buffered aqueous media, reactions
with the minerals wollastonite and andradite were investi-
gated in more detail.

II. PREPARATION, PROPERTIES, AND STRUCTURE OF GUANIDINIUM TRIS(CATECHOLATO)SILICONATE, $[(H_2N)_2C=NH_2]_2[Si(Cat)_3] \cdot XH_2O^*$

INTRODUCTION

The guanidinium salt of the catechol-silicon complex was first prepared by Rosenheim et al (6). A solution containing an excess of freshly precipitated silica, SiO_2, was treated with catechol and sodium hydroxide, the unreacted silica was filtered off, and guanidinium hydrochloride, $(H_2N)_2C=NH \cdot HCl$, was added to the filtrate. A guanidinium salt, which was reported to be a seven-hydrate, precipitated.

Weiss et al (7) reported the preparation of a dimeric tetrahydrated guanidinium salt, $[(H_2N)_2C=NH_2]_4[Si_2(Cat)_6] \cdot 4H_2O$, from an analogous ammonium salt, $[NH_4]_4[Si_2(Cat)_6] \cdot 9H_2O$. The guanidinium salt was precipitated from an aqueous solution of the ammonium salt at a pH between 6.0 and 6.5 by adding aqueous guanidinium carbonate, $(H_2N)_2C=NH \cdot H_2CO_3$. The recovered product was washed with ether.

The degree of hydration of the guanidinium salt prepared in the present work is uncertain; it does not, however,

* The following abbreviations will be used to represent catechol and its ions in this paper:
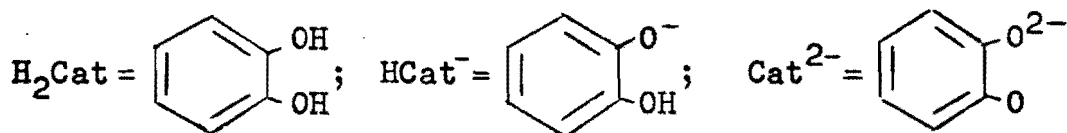
contain more than one mole of water. X-ray, infrared, and nmr studies of this salt are included in this paper.

EXPERIMENTAL

Preparation of $[(H_2N)_2C=NH_2]_2[Si(Cat)_3] \cdot XH_2O$ From Silicic Acid

Since catechol is easily oxidized, especially in basic media, it is necessary to carry out this preparation in a nitrogen atmosphere. Introduce 15 g of catechol into a 250-ml round bottom flask to which a side arm with a straight bore stopcock is attached. Insert a ground glass stopper into the neck of the flask, evacuate the flask through the side arm and then bleed in nitrogen. Prepare an ammoniacal solution of silica by adding 2-3 g of silicic acid to about 200 ml of concentrated (15 M) ammonium hydroxide. Stir for about one hour and then filter off the undissolved silica. Fit a rubber serum cap to the side arm of the round bottom flask and, using a hypodermic syringe, introduce 175 ml of the filtered ammoniacal silica solution through the serum cap and open bore of the stopcock. Stir thoroughly until all of the catechol dissolves. Then, in the same manner, introduce 35 ml of 4 M guanidinium hydrochloride solution. A precipitate begins to form within a few minutes. After one hour, precipitation appears to be complete. Filter the precipitate under nitrogen, wash with small portions of cold 1 M ammonium hydroxide, and dry to constant weight in a vacu-

um at room temperature. The yield is about 1½ g.*

Properties of [(H$_2$N)$_2$C=NH$_2$]$_2$[Si(Cat)$_3$]·XH$_2$O

The dry guanidinium salt is a white powder which is

somewhat hygroscopic. It begins to discolor in air after

about one month. Thus, it can be handled in air but should

be stored under nitrogen. The guanidinium salt is only

slightly soluble in water; the solubility was found to be

0.50 g/100 cc.** It is soluble in DMSO to the extent of at

least 12 g/100 cc. It is considerably less soluble in eth-

anol than in water and is insoluble in diethyl ether and

acetone. In dilute aqueous acid solutions, the guanidinium

salt decomposes to regenerate catechol and silica; the cate-

chol goes into solution and the silica precipitates.

Analytical data obtained for [(H$_2$N)$_2$C=NH$_2$]$_2$[Si(Cat)$_3$]·XH$_2$O

prepared from silicic acid and also from the silicate min-

eral wollastonite (the preparation of the guanidinium salt

___

* Equilibrium studies by Baumann (10) show that under
the basic conditions of this reaction, dissolved silica is
quantitatively converted to the anionic catechol-silicon
complex. Therefore, since a large excess of guanidinium
ions were present, and the guanidinium salt of the catechol-
silicon complex is only very slightly soluble, it is likely
that if the yield is not quantitative with respect to the
amount of silica present, it is very high. However, the
amount of silica present in the concentrated ammonia solu-
tion depends upon the rate of dissolution, and thus varies
with the amount of silica added, its specific surface area,
and the time and temperature of stirring.

** Measured in a pH 7.5 H$_2$CO$_3$/HCO$_3^-$ buffer solution;
ionic strength = 0.05.

from wollastonite is described in Part IV) are presented in Table I. The high molecular weight of the catechol-silicon complex makes any decision regarding the degree of hydration somewhat uncertain. Nevertheless, the data agree best with a salt containing one half mole of water. A salt containing more than one mole of water can almost be ruled out. The disagreement between the degree of hydration of the salt prepared in this work with that of salts prepared by Rosenheim and Weiss arises because neither Rosenheim nor Weiss dried their products to constant weight under vacuum.

X-ray powder diffraction data are presented in Table A-1, Appendix A. There is no detectable difference between the powder patterns of the salt prepared from silicic acid and the salt prepared from wollastonite.

The infrared spectrum of $[(H_2N)_2C=NH_2]_2[Si(Cat)_3]\cdot XH_2O$ is shown in Figure A-1, Appendix A. The bands at 2.95 μ and 3.18 μ are believed to be due to symmetric and asymmetric N-H stretching modes and are well resolved compared to the corresponding bands for most guanidinium salts (e.g., guanidinium hydrochloride, $(H_2N)_2C=NH\cdot HCl$, exhibits a relatively broad band centered at about 3.0 μ with a barely visible shoulder at 3.18 μ). Upon close examination of the N-H stretching bands, two shoulders are seen—one at about 2.8 μ and the other at about 3.1 μ. A high resolution spectrum (not shown) reveals distinct absorption bands where the

TABLE I

ANALYTICAL DATA FOR $[(H_2N)_2C=NH_2]_2[Si(Cat)_3]\cdot XH_2O$

	Theory				Prep. from Silicic Acid	Prep. from Wollastonite[1]	
	$X=0$	$X=1/2$	$X=1$	$X=3/2$			
C	50.84	49.86	48.97	48.09	50.39	48.53	49.69
H	5.12	5.23	5.34	5.45	5.24	5.01	5.27
N	17.78	17.45	17.13	16.82	17.18	16.71	16.56
Si	5.94	5.83	5.73	5.62	5.81	5.96	6.25
O[2]	20.32	21.60	22.83	24.02	(21.38)	(23.79)	(22.23)

[1] The samples prepared from wollastonite contained traces of iron complexed with catechol which might influence the analytical data slightly; the data obtained for the pure guanidinium salt prepared from silicic acid should be quite reliable.

[2] Values for oxygen in parentheses are calculated by difference from 100%.

shoulders appear in the lower resolution spectrum.* These
bands very possibly arise from intra- and intermolecular
hydrogen bonding O-H groups which exhibit stretching bands
at 2.78-2.86 µ and 2.94-3.13 µ respectively; the aromatic
C-H stretching band should appear at a higher wavelength
(~3.3 µ) and would not necessarily be seen (i.e., the C-H
stretching band is likely hidden in the N-H stretching band
at 3.18 µ).

Two absorption bands are seen in the C-H in-plane
bending region--one at 9.14 µ and the other at 9.82 µ. The
location of these bands is an important feature of the in-
frared spectrum of the catechol-silicon complex since the
shifts from positions at 9.10 and 9.59 µ found for catechol
itself provide evidence that a chelate is formed; similar
shifts have been observed for three other salts of the 3:1
catechol-silicon ester.** A spectrum run from a nujol mull
preparation reveals that the band at 9.14 µ is, for the
guanidinium salt of the complex, actually a closely spaced
doublet (see Figure A-2, Appendix A).

The nmr spectrum of $[(H_2N)_2C=NH_2]_2[Si(Cat)_3] \cdot XH_2O$ in

* The author wishes to thank Mr. Boonthong Poocharoen
for providing a high resolution infrared spectrum of
$[(H_2N)_2C=NH_2]_2[Si(Cat)_3] \cdot XH_2O$.

** Infrared spectra of salts of the catechol-silicon
complex have not been published. However, shifts of infra-
red bands located between 9 and 10 µ (believed to be associ-
ated with aromatic C-H in-plane bending) have been observed
upon formation of pyridinium, ammonium and magnesium salts
prepared in this laboratory by the author and coworkers.

deuterated DMSO is shown in Figure A-3, Appendix A. Two peaks are observed—one at τ 3.72 ppm and the other at τ 3.45 ppm.

If small quantities of guanidinium hydrochloride are added to the sample, the peak at τ 3.45 ppm will shift downfield and approach τ 2.75 ppm—the location of the proton peak for guanidinium hydrochloride itself. If, however, microliter amounts of water are successively introduced, the peak at τ 3.45 ppm will move upfield towards the residual DMSO proton peak. As the water concentration increases, hydrogen bonding becomes important and the peak begins to move back downfield approaching τ 5.25 ppm. Clearly, the peak at τ 3.45 ppm is due to guanidinium protons which are quite capable of undergoing rapid exchange with hydroxylic protons. Hence, even if the complex should be a hydrate, the hydroxylic protons would be averaged with the guanidinium protons. The resultant peak would appear at a concentration-dependent, intermediate position. The fact that the peak at τ 3.45 ppm is upfield from τ 2.75 ppm suggests that guanidinium protons could be exchanging either with free water protons or Si-OH protons.

There is, however, another explanation for the upfield location of the guanidinium proton peak. Conductivity studies clearly reveal ion-pair formation in DMSO at concentrations as low as 10^{-4} M (see Figure A-4, Appendix A). Hence, the possibility of ring current shielding of the

guanidinium protons is not unlikely. In fact, the field generated by the very mobile π electrons of the guanidinium ion might in turn be shielding phenyl protons. The phenyl proton peak at τ 3.72 ppm is upfield from τ 3.29 ppm where the peak is found for catechol. Also, while catechol exhibits a symmetrical A_2B_2 splitting pattern, the complexed catechol shows just a single peak.

Even without ion-pair formation, though, the chemical shift of the phenyl protons of the complex would be expected to differ from that of the free catechol protons. Assuming that the complex is hydrated, all factors just discussed are likely operating to establish the shift positions observed for this spectrum.

The nmr spectrum of $[(H_2N)_2C=NH_2]_2[Si(Cat)_3]\cdot XH_2O$ prepared from wollastonite exhibits only a single peak at τ 3.72 ppm. The absence of the guanidinium proton peak was shown to be due to a spin-lattice relaxation effect resulting from a trace amount of paramagnetic iron. When 1.0 μl of a DMSO solution containing 2.3% of iron(III) was introduced into an nmr tube containing an 8.4% DMSO solution of the complex prepared from silicic acid, the guanidinium proton peak disappeared completely. The electron magnetic moment is more than one thousand times greater than nuclear magnetic moments, and so it is not surprising that such a drastic reduction of the spin-lattice relaxation time for the exchanging guanidinium protons is observed. As substan-

tially larger quantities of iron(III) are introduced, the phenyl proton peak begins to broaden.

In some preparations from wollastonite, the guanidinium proton peak was actually detected; however, it was very broad. This shows that iron was present only in trace quantities. If not observed, the guanidinium proton peak will emerge if a few microliters of water are added. The resultant peak will, of course, be broad and shifted slightly upfield.

An anhydrous guanidinium salt of the catechol-silicon complex would exhibit a phenyl to guanidinium proton ratio of 12:12, while a monohydrate would show peaks which should integrate 12:14. Two spectra run in freshly distilled DMSO integrated 12:14.03 and 12:14.38. A third spectrum which was run in deuterated DMSO integrated 12:14.27. However, a spectrum of the deuterated solvent itself revealed that water was present. The integral of the water proton peak was compared to that of the residual DMSO proton peak. From this relationship, it was possible to subtract the contribution of water originally present in the solvent from the integral of the guanidinium-water proton peak. The result was a ratio of 12:11.97. These conflicting results, coupled with the dubious reliability of integrals taken on closely spaced peaks, makes it necessary to admit that the integral data are inconclusive and do not reveal the degree of hydration of the salt prepared in this work.

STRUCTURE OF $[(H_2N)_2C=NH_2]_2[Si(Cat)_3] \cdot XH_2O$

Silicon is normally thought of as having a coordination number of four. A familiar exception is the hexacoordinated fluorosilicate ion, SiF_6^{2-}. Iler (2, p.18) prefers to think of the silicon atom as having a coordination number of six in basic solutions. He states that in this way it is easier to visualize the probable mechanism by which polymerization of silica occurs. He further points out that while silica and silicates contain tetracoordinated silicon, the picture changes when the coordinating oxygens are present as hydroxyl groups. The reason given is that the OH^- ion resembles the F^- ion because of penetration of the O^{2-} electron cloud by the H^+ ion. In this way, the diameter of the OH^- ion is reduced by polarization. It is true that F^- ions often replace OH^- ions in many silicate minerals. Iler reasons that since the ion SiF_6^{2-} exists, $Si(OH)_6^{2-}$ should also exist.

Flynn and Boer (16) furnish examples of some less common compounds in which silicon is believed to have a coordination number of six. Among these are silicon acetylacetonates, silicon imidodiphosphinates and fluorosilicate-like compounds, SiF_5R^{2-}. They also furnish references to x-ray studies on a number of pentacoordinated silicon compounds of which I is an example.

$$\left[\bigcirc\!\!-\!Si\!\left(\!\!\begin{array}{c} O \\ O \end{array}\!\!\bigcirc\!\!\right)_2 \right]^{-} \qquad I$$
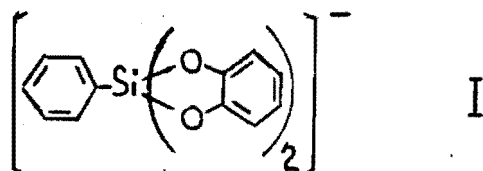
Rosenheim (6), who first prepared the guanidinium salt of the catechol-silicon complex (as well as other salts), concluded that silicon was hexacoordinated by three catechol groups to form a monomeric anion as depicted by II.

$$\left[Si\!\left(\!\!\begin{array}{c} O \\ O \end{array}\!\!\bigcirc\!\!\right)_3 \right]^{2-} \qquad II$$
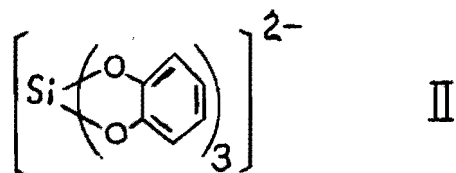
Weiss (7) proposed some more complicated dimeric structures; however, his arguments have been challenged by Barnum (17), Frye (18) and Flynn (16). As a matter of fact, Flynn's single crystal x-ray study undertaken on an anhydrous pyridinium salt, $[C_5H_5NH]_2[Si(Cat)_3]$, has quite convincingly shown that the complex is monomeric with silicon octahedrally coordinated by three catecholate groups as shown in III.

$$\left[\ \cdots Si \cdots \ \right]^{2-} \qquad III$$
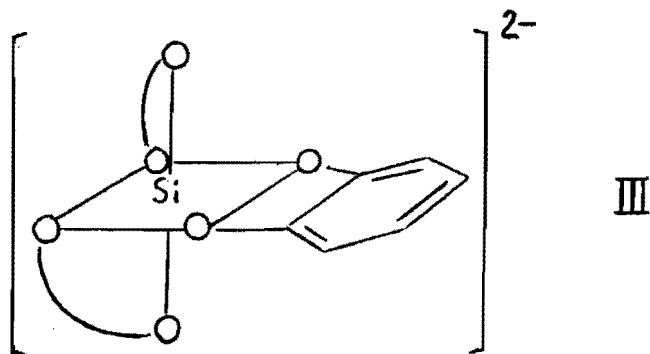
That the guanidinium salt prepared in this work is probably hydrated is, as was pointed out earlier, suggested by the analytical data, the infrared spectrum and, to a lesser extent, by the nmr spectrum. It would be tempting to say, on the basis of the analytical data, that the complex contains one half mole of water as an occlusion in the crystal lattice. However, Barnum (17) reported preparing an ammonium salt according to the directions given by Rosenheim and Sorge (8) in which the product was recovered from an ethanol solution with water rigorously excluded. The purpose was to isolate an anhydrous salt. However, the recovered salt, $[NH_4]_2[Si(OC_2H_5)(HCat)(Cat)_2]$, contained a mole of "ethanol" believed to be present as $Si\text{-}OC_2H_5$ and $H\text{-}Cat$ groups. Upon contact with air, the ethoxy compound is converted to a monohydrate. Furthermore, the water from $[NH_4]_2[Si(Cat)_3]\cdot H_2O$ cannot be removed even after heating to $60^{\circ}C$ in a vacuum for two weeks. The conclusion was that a simple water of hydration was not involved, but instead the "water" was incorporated as an $Si\text{-}OH$ group plus a phenolic hydrogen as depicted in structure IV. Barnum (19) also

IV
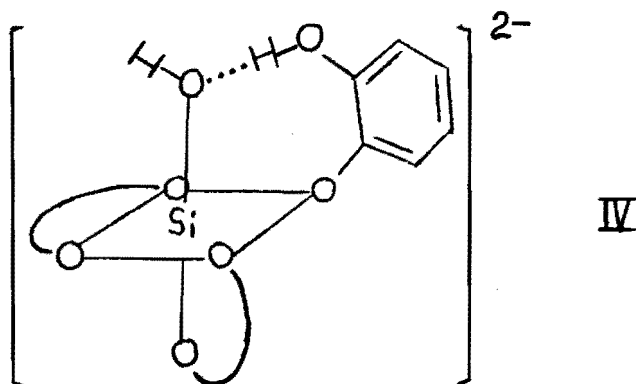
points out that the ammonium salts of analogous complexes (i.e., $[NH_4]_2[M(Cat)_3] \cdot H_2O$, where M can be germanium, tin or niobium as well as silicon), and different salts of octahedrally coordinated arsenic, tin and iron complexes of catechol all contain a mole of strongly held water.

All of the samples prepared in this work were taken to constant weight in a vacuum. Some samples remained in a vacuum for as long as three days. If the guanidinium salt prepared here is hydrated, it is probably a monohydrate which would be best represented by structure IV and best formulated as $[(H_2N)_2C=NH_2]_2[Si(OH)(HCat)(Cat)_2]$.

III. REACTIONS BETWEEN SILICATE MINERALS AND CATECHOL IN BUFFERED AQUEOUS MEDIA

INTRODUCTION

The possible involvement of aromatic vic-diols in weathering and soil formation was discussed in Part I. The work described in this section was undertaken to determine whether aqueous solutions containing catechol will attack silicate minerals. Albite, andradite, muscovite, pyrophyllite, talc and wollastonite were treated with aqueous catechol solutions buffered at pH 10; in addition, wollastonite and pyrophyllite were treated with pH 4 catechol solutions. These minerals were chosen for this investigation because they are available in relatively pure form and represent four of the six silicate mineral subclasses (i.e., the tekto-, neso-, phyllo-, and inosilicates).

EXPERIMENTAL

Description of Minerals

The minerals used in this work are described in Table II. They were crushed in a percussion mortar and further ground in an agate mortar until the powder passed a 200-mesh (74 μ) sieve.

X-ray powder diffraction patterns were obtained in

TABLE II

DESCRIPTION OF MINERALS

Mineral	Formula[1]	Subclass	Group (or Series)	Source	ASTM X-Ray PDF[3] Reference; Remarks
Albite	$NaAlSi_3O_8$	Tektosilicate	Plagioclase	Bancroft, Ontario, Canada	9-466 Some discrepancy
Andradite	$Ca_3Fe_2(SiO_4)_3$	Nesosilicate	Garnet	Eagle Mts., Riverside Co., California	10-288 Good agreement
Muscovite	$KAl_2(AlSi_3O_{10})(OH)_2$	Phyllosilicate	Mica	Spruce Pine, Mitchell Co., N. Carolina	6-0263 Some discrepancy
Pyrophyllite	$Al_2Si_4O_{10}(OH)_2$	Phyllosilicate	---	Tres Cerritos, Mariposa Co., California	2-0613 Some discrepancy
Talc	$Mg_3Si_4O_{10}(OH)_2$	Phyllosilicate	---	Unknown[2]	13-558 General agreement
Wollastonite	$CaSiO_3$	Inosilicate	Pyroxenoid	Calico, San Bernadino Co., Calif.	10-487 General agreement

[1] These formulas represent hypothetical "ideal" minerals in which ion substitution does not occur; in reality, this is rarely the case.

[2] It was intended to study the mineral tremolite here. The mineral which was ordered was labled tremolite and its source was listed as San Jacinto Mt., Riverside Co., California. However, the mineral was apparently misidentified, since x-ray and infrared data show conclusively that is was actually talc.

[3] The ASTM x-ray pdp references listed here are those which best agree with the x-ray patterns obtained for the minerals used in this work. The remarks refer to comparisons of the patterns. Both the ASTM patterns and those obtained in this work are tabulated in Appendix B.

order to verify that the minerals were properly identified and reasonably pure. Since a variety of methods are used to estimate line intensities, and since some minerals studied here are known to exhibit varying degrees of substitution depending upon their origin (e.g., albite of the plagioclase series), most of the powder patterns obtained in this work do not agree exactly with those published in the ASTM file. For this reason, the x-ray data for the minerals used in this study are listed in Tables B-1 through B-6, Appendix B. The ASTM powder patterns best agreeing with the lattice spacings and line intensities found in this work are also included in these tables. To further verify that the minerals were properly identified, infrared spectra were compared with published spectra (20); good agreement was found for all six minerals.

The x-ray powder diffraction pattern of the wollastonite, $CaSiO_3$, used in this work exhibits lines at d = 4.247, 3.320, 1.811, and 1.537 $\overset{o}{A}$ suggesting that small amounts of quartz might be present (see Table B-6, Appendix B). Quartz contamination of wollastonite is not uncommon. In order to show conclusively that the mineral contained quartz, an x-ray powder pattern of a silica residue recovered after dissolving the wollastonite in concentrated hydrochloric acid was obtained and found to be identical to ASTM 5-0490, the powder pattern of α-quartz. Since pure wollastonite dissolves in concentrated acids to form only amorphous silica,

the quartz had to be present originally. An attempt to re-move the quartz from the wollastonite by a heavy liquid den-sity separation was unsuccessful; apparently the densities of the two minerals ($\rho = 2.65$ and 2.9 respectively) are so similar, that the techniques used in this work were inade-quate. However, a small quantity of magnetite, Fe_3O_4, sepa-rated from the wollastonite.

A density separation performed on andradite, $Ca_3Fe_2(SiO_4)_3$, yielded only magnetite and andradite itself. If quartz or amorphous silica were present, they should have separated since their densities are considerably less than that of andradite. The x-ray powder pattern of the andra-dite used in this work (see Table B-2, Appendix B) agrees very well with ASTM 10-288 and does not indicate the pres-ence of any quartz. The mineral did, however, contain con-siderably more magnetite than did the wollastonite mineral. Still, the quantity of magnetite was small and the x-ray pattern does not reveal its presence.

It was possible to separate trace quantities of mag-netite from the other four minerals by means of a magnet, and the x-ray powder pattern of pyrophyllite, $Al_2Si_4O_{10}(OH)_2$, reveals the presence of a small amount of quartz (see Table B-4, Appendix B).

Initiation of Reactions

A pH 4.0 buffer solution was prepared by dissolving

16.5 ml of glacial acetic acid and 4.1 g of sodium acetate in 500 ml of deionized water. The pH was measured and adjusted to 4.0 by adding 0.1 N sodium hydroxide. A pH 10.0 buffer solution was prepared by dissolving 9.0 g of sodium bicarbonate along with 5.3 g of sodium carbonate in 500 ml of deionized water. The pH was adjusted to 10.0 with 0.1 N sodium hydroxide.

Two sets of reaction mixtures were prepared in a nitrogen atmosphere:

Set 1. Quantities of albite, andradite, muscovite, pyrophyllite, talc and wollastonite such that 2.08 mmoles of silicon would be present (the quantities were based on the ideal formulas listed in Table II) were introduced into 50-ml erlenmeyer flasks along with 6.2 mmoles (0.69 g) of practical grade catechol. The ratio of catechol to silicon was 3:1. The flasks were fitted with one-hole rubber stoppers into which short lengths of pyrex tubing were inserted. Rubber serum caps were fitted to the tubing and then each flask was swept with nitrogen for twenty minutes; nitrogen entered and departed through syringe needles inserted into the serum caps. Next, 25.0 ml of pH 10.0 buffer solution was introduced into each flask by means of a hypodermic syringe. Two additional reactions with pyrophyllite and wollastonite were initiated in the same manner except pH 4.0, instead of pH 10.0, buffer solution was introduced.

After about twenty four hours, the six reaction mix-

tures buffered at pH 10.0 began to develop a red-brown color while the pH 4.0 reaction mixtures began to develop a violet color. After a couple of months, the reaction mixtures buffered at pH 10.0 darkened. Apparently the basic catechol solutions were oxidizing--quite likely because air leaked into the flasks, but possibly, since each mineral contained traces of magnetite, Fe_3O_4, because iron(III) might have been reduced to iron(II). The eight Set 1 reaction mixtures were set aside for a total of thirteen months.

Set 2. This set of reactions was carried out with albite, andradite, muscovite, talc and wollastonite--pyrophyllite was excluded. The same quantities of starting materials were used here as in Set 1. Catechol and mineral were introduced into 100-ml round bottom flasks to which side arms fitted with serum caps were attached. A reflux condenser connected by rubber tubing to a bubbler trap was fitted to the neck of each flask. Nitrogen was passed through each flask via a syringe needle inserted into the serum cap. After purging for twenty minutes, 25.0 ml of pH 10.0 buffer solution was introduced. Each reaction mixture was then refluxed for six hours under a slow steady stream of nitrogen.

During the reflux period, the reaction mixtures developed a red-brown color. After refluxing, the five flasks were allowed to cool, then were stoppered and set aside for thirteen months. These reaction mixtures appeared to have

been protected from the atmosphere better than those of
Set 1; oxidation was not as noticeable.

Treatment of Reaction Mixtures

Set 1. When thirteen months had passed (thirteen
months was a convenient, and not necessarily important,
period of time), each reaction mixture in Set 1 was suction
filtered under nitrogen. The residues were washed with wa-
ter followed by acetone and allowed to dry in the atmos-
phere. Then they were weighed. The weights obtained are
reliable only to about ±5 mg since the residues were not
collected very quantitatively.

The filtrates from Set 1 were treated with 15.0 ml of
1.0 M guanidinium hydrochloride, $(H_2N)_2C=NH \cdot HCl$, which was
introduced with a hypodermic syringe. After a few minutes,
precipitates began to form in the filtrates obtained from
the pH 10.0 reaction mixtures which originally contained
wollastonite, pyrophyllite and albite. The precipitates
were filtered under nitrogen, washed with small portions of
cold water, dried in a vacuum and weighed. The filtrates
from the pH 10.0 muscovite, andradite and talc reaction mix-
tures were badly oxidized and no precipitates were obtained.
Nor did the filtrates from the pH 4.0 wollastonite and pyro-
phyllite reaction mixtures yield precipitates.

Set 2. Precipitate formation upon addition of guani-
dinium ions to the filtrates of the pH 10.0 wollastonite,

pyrophyllite and albite reaction mixtures of Set 1 implied that these three minerals react with catechol. Therefore, it was only necessary to treat the muscovite, andradite and talc reaction mixtures of Set 2. After filtering and introducing guanidinium hydrochloride, just as was done for Set 1, precipitates formed in all three filtrates. These were collected and treated, as were the reaction residues, in the same way that they were for Set 1.

RESULTS

Table III summarizes the results of this study. Infrared spectra showed conclusively that the precipitates recovered by treating the filtrates with guanidinium ions were, in all six cases, the guanidinium salt of the catechol-silicon complex, $[(H_2N)_2C=NH_2]_2[Si(Cat)_3] \cdot XH_2O$. Infrared spectra also revealed that reaction residues with the exception of those collected from reactions with wollastonite consisted mainly of unreacted starting material.

X-ray powder diffraction patterns of the residues obtained from the pH 10 albite, andradite, muscovite, talc and pyrophyllite reaction mixtures are compared with corresponding starting mineral and ASTM powder patterns in Tables B-1 through B-5, Appendix B. A diffractometer was used to obtain the powder patterns of the original minerals, whereas the patterns of the residues were viewed on photographic films. Diffractometer line intensities fall off rather rap-

TABLE III

SUMMARY OF THE RESULTS FOLLOWING REACTIONS OF SILICATE MINERALS WITH
CATECHOL IN BUFFERED AQUEOUS MEDIA

Mineral	pH of Reaction Mixture	Weight of[2] Mineral Starting Material (g)	Weight of[3] Residue (g)	Quantity of[4] Mineral Dissolved (mmoles Si)	Residue			Weight of[6] Recovered Guanidinium Tris(catecholato)-siliconate (g)
					I.R.	X-Ray PDP[5]	Comments	
Albite $NaAlSi_3O_8$	10.0	0.1828	0.148	0.40	Albite	Albite (Table B-1)	The pdp generally agrees with that of the starting mineral.	0.2746 (0.506 mmoles)
Andradite[1] $Ca_3Fe_2(SiO_4)_3$	10.0	0.3537	0.318	0.21	Andradite	Andradite (Table B-2)	The pdp agrees with that of the starting mineral.	0.5419 (1.105 mmoles)
Muscovite[1] $KAl_2(AlSi_3O_{10})(OH)_2$	10.0	0.2756	0.222	0.40	Muscovite	Muscovite (Table B-3)	The pdp line intensities differ considerably from those of the starting mineral. However, the pdp agrees as well with ASTM 6-0263 as does that of the original mineral.	0.4954 (1.010 mmoles)
Talc[1] $Mg_3Si_4O_{10}(OH)_2$	10.0	0.2117	0.183	0.30	Talc	Talc (Table B-5)	Most of the original pdp lines are present. Their intensities differ in some cases. Some new lines are present.	0.3362 (0.685 mmoles)
Pyrophyllite $Al_2Si_4O_{10}(OH)_2$	10.0	0.1876	0.163	0.27	Pyrophyllite	Pyrophyllite (α-quartz) (Table B-4)	The pdp shows some change. However, it agrees as well with ASTM 2-0613 as does that of the starting mineral. The quartz lines are more intense in the residue pdp than in the original mineral pdp.	0.3095 (0.631 mmoles)
	4.0	0.1568	0.165	---	Pyrophyllite	---	A pdp was not run.	None
Wollastonite $CaSiO_3$	10.0	0.2413	0.205	---	Calcite ($CaCO_3$)	Calcite (α-quartz) (Table B-7)	The residue is definitely calcite. Some α-quartz is also present.	0.2492 (0.508 mmoles)
	4.0	0.2432	0.150	---	Silica	α-Quartz (Wollastonite) (Table B-8)	The residue is definitely silica. The pdp agrees with ASTM 5-0490, the pdp for -quartz. Some wollastonite is also present.	None

[1] The reaction mixture was refluxed for six hours prior to setting aside for thirteen months.

[2] These weights correspond to 2.08 mmoles of silicon.

[3] The residues were not collected very quantitatively. These numbers are probably not better than ± 5 mg.

[4] The quantity of mineral that dissolved, reported here as mmoles of Si in solution, was calculated from the weight difference between starting material and residue. It is based on the not necessarily valid assumption that the residue consists entirely of unreacted mineral.

[5] The residue pdp tables listed in parentheses are located in Appendix B. The minerals listed in parentheses are present in trace quantities.

[6] The number of mmoles of guanidinium tris(catecholato)siliconate in parentheses were calculated assuming a monohydrate formulation.

idly with increasing angle (i.e., decreasing d-spacing) and the intensities of lines viewed on films were only visually estimated; consequently, comparisons of intensities can only be expected to be qualitative. Nevertheless, the x-ray, like the infrared, data show that these five pH 10 reaction residues consisted mainly of unreacted starting mineral. However, they also show that at least some mineral alteration may have occurred--especially with muscovite and to a lesser extent with talc and pyrophyllite. That alteration may have occurred is inferred from the fact that in some cases line intensities have changed drastically, and in other cases new lines have appeared. None of the new lines were identified and the investigation of the residues was not further pursued. An x-ray powder pattern of the pH 4 pyrophyllite reaction residue was not obtained.

Examination of the residues obtained from the pH 4 and pH 10 reaction mixtures of wollastonite revealed that little, if any, of the original mineral remained. Calcite, $CaCO_3$, formed in the pH 10 reaction mixture (a carbonate buffer), and silica formed in the pH 4 mixture. The x-ray pattern of the pH 10 residue (Table B-7, Appendix B) shows some weak quartz lines along with the calcite lines, and the pattern of the pH 4 residue (Table B-8, Appendix B) shows quartz lines only.

DISCUSSION

The data in Table III reveal that in every case the

original quantity of mineral provided 2.08 mmoles of silicon, the amounts of silicon recovered in the form of the guanidinium salt ranged from 0.506 to 1.105 mmoles (assuming that the salt is a monohydrate), and the weight differences between residues and mineral starting materials ranged from 24 to 54 mg. Assuming that every residue consisted of unreacted starting mineral, in each case the amount of mineral which reacted does not account for all of the product obtained (compare columns 5 and 9, Table III).

It is not possible, on the basis of the work performed here, to rationalize such an anomaly with any certainty. Nevertheless, reaction residues might have contained quantities of water--either surface adsorbed or incorporated in structurally disrupted outer margin alteration layers with the original mineral structure preserved in the inner zone-- which would have the effect of minimizing the apparent extent of mineral dissolution. Such an explanation is not inconsistent with the x-ray data which, as was pointed out earlier, reveals that with each residue except those obtained from wollastonite reaction mixtures some alteration may have occurred even though the original mineral is still present.

Another explanation for the fact that the apparent quantity of mineral which dissolved does not account for all of the product obtained lies in considering the glass reaction vessels as sources of silicon. Weiss (7) has shown that the reaction rate of catechol with various forms of

silica decreases drastically as the specific surface area decreases. The specific surface area of the 50-ml glass reaction vessels used in this work is minute compared to that of the finely divided minerals, and no etching of vessels was detected. Nevertheless, alkaline solutions are known to attack glass, and, since a control reaction was not run, such a possibility cannot be ignored.

Regardless of what the explanation might be, this study clearly reveals that in the presence of catechol at least some mineral dissolves; in the case with wollastonite, most if not all of the mineral dissolves; and as each mineral dissolves, the catechol-silicon ester forms (i.e., except in acid media).

Catechol will react slowly with finely divided quartz. Weiss (7), for example, demonstrated that after sixty days, approximately 32% of a sample of quartz particles which were smaller than 7 μ dissolved in a "concentrated" catechol solution at pH 8.2. Larger particles of quartz react at a much slower rate.

It was mentioned earlier that the wollastonite and pyrophyllite used in these reactions contained small amounts of quartz and that the andradite did not contain any detectable quantities. Although the albite, muscovite and talc used here might have contained trace quantities of quartz, x-ray powder patterns do not reveal its presence.

The x-ray powder patterns of the pyrophyllite and wol-

lastonite reaction residues revealed quartz lines which were even more intense than the corresponding lines in the patterns of the original minerals. The conclusion is that the catechol-silicon complex isolated in these reactions originated primarily from dissolution of the minerals themselves rather than from reactions with quartz contaminants.

Wollastonite dissolves in both concentrated acid and concentrated base solutions with the separation of silica. It has been reported (21, p.357) that wollastonite is soluble in water to the extent of 0.01 g/l; how long it takes to attain equilibrium was not mentioned. Although the conditions under which the reactions between catechol and wollastonite were carried out were quite mild, the mineral still dissolved almost completely.

In the presence of catechol at pH 10, silica did not form--the complex did. And, in the carbonate-bicarbonate buffer solution, calcium precipitated as calcite:

$$\text{CaSiO}_3 + 3\text{H}_2\text{Cat} \xrightarrow{\text{CO}_3^{2-}} \text{SiCat}_3^{2-} + \text{CaCO}_3\downarrow + 3\text{H}_2\text{O}$$
(Wollastonite)   (Calcite)
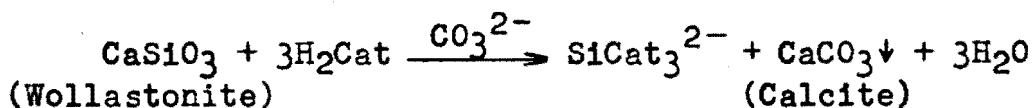
Baumann (10) showed, in connection with some quite · thorough studies of the three-way equilibrium between silica, $\text{SiO}_2\cdot X\text{H}_2\text{O}$, silicic acid, Si(OH)_4, and the catechol-silicon complex, SiCat_3^{2-}, that at pH 4 the concentration of complex is extremely small ($\sim 10^{-8}$ M) when the catechol concentration is only 0.25 M as it was with the reactions carried out in this work. His findings are consistent with the fact

that the guanidinium salt of the complex, as well as other salts, decompose in acid media to form silica. So the recovery of the complex from the pH 4 wollastonite reaction mixture was not realized; however, silica formed:

$$CaSiO_3 + 3H_2Cat \xrightarrow{\underset{?}{pH\ 4}} SiCat_3^{2-} + 3H_2O + Ca^{2+}$$

(Wollastonite)

$$CaSiO_3 \xrightarrow[\quad ?\quad]{2H_3O^+} SiO_2\downarrow + 3H_2O + Ca^{2+} \quad (Silica)$$

$$SiCat_3^{2-} \xrightarrow{2H_3O^+} SiO_2\downarrow + 3H_2Cat \quad (Silica)$$
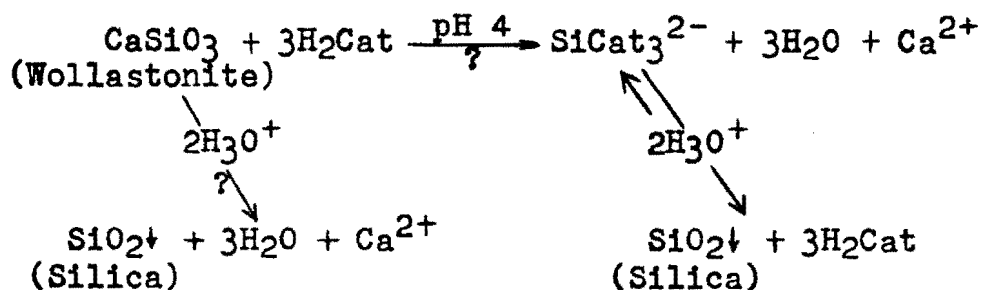
An important question is whether catechol actually effected the dissolution of the minerals studied in this work, or whether they would have dissolved even if catechol had not been present. Mellor (21) indicates that andradite, albite and talc are insoluble in concentrated acid solutions, but that pyrophyllite is slightly affected by concentrated hydrochloric acid. He also points out that pyrophyllite is slightly attacked by sodium carbonate solutions. However, most reports dealing with the dissolution of the minerals studied here focus on hydrothermal decomposition. It may be considered highly probable but, since control reactions were not run, not absolutely conclusive that catechol played the major role in dissolving these silicate minerals. This conclusion is supported by the fact that even muscovite, which is extremely persistent in weathering environments and was reported (21, p.618) to be insoluble in carbonated water even

after one year, reacted to form the complex.

The reaction mixtures were not adequately protected from the atmosphere in this experiment. The fact that catechol-silicon esters were not recovered from the oxidized muscovite, andradite and talc reaction mixtures of Set 1, yet were from the better protected Set 2 reaction mixtures, supports this statement. Negative results for reactions undertaken with the minerals diopside, white beryl, kaolinite, orthoclase and zircon were not described since, with the exception of kaolinite, serious oxidation of the reaction mixtures rendered such results inconclusive. It is not unlikely that some of these minerals will also react with catechol.*

* Recently, the catechol-silicon complex was isolated as the guanidinium salt from a reaction between catechol and diopside, $CaMgSi_2O_6$, in this laboratory by Boonthong Poocharoen.

IV. REACTIONS BETWEEN SILICATE MINERALS AND CATECHOL IN UNBUFFERED AQUEOUS MEDIA

INTRODUCTION

It was shown in Part III that aqueous catechol solutions buffered at pH 10 will attack the silicate minerals albite, andradite, muscovite, pyrophyllite, talc and wollastonite to form a catechol-silicon complex. Since the environmental pH represents mainly the effect rather than the cause of chemical weathering (12, p.vii), reactions described in this section were carried out in unbuffered aqueous media with the pH monitored. The purpose was to react minerals (i.e., wollastonite, andradite, talc, white beryl and diopside) under pH conditions satisfying natural environmental criteria, to react them in quantities sufficient to dispel doubts that catechol effected dissolution might be insignificant, and to further show that the minerals themselves react rather than reaction vessel surfaces or contaminants. In addition, an effort to isolate a possible calcium salt of the catechol-silicon complex, $Ca[Si(Cat)_3]$, from a reaction mixture of catechol and wollastonite, $CaSiO_3$, is described.

EXPERIMENTAL

Description of Minerals

The wollastonite used in these reactions was ground to pass a 325-mesh (43 μ) sieve; the andradite, talc, white beryl and diopside were ground to pass a 200-mesh (74 μ) sieve. The x-ray powder diffraction patterns of the andradite, talc and wollastonite are shown in Tables B-2, B-5 and B-6, Appendix B, respectively. The wollastonite contains a small amount of quartz. The powder pattern of the white beryl, $Be_3Al_2(SiO_3)_6$, used here agrees well with ASTM 9-430. The diopside, $CaMgSi_2O_6$, powder pattern shows reasonable agreement with ASTM 11-654; a trace of quartz might be present. It was possible to remove traces of magnetite, Fe_3O_4, from all five of these minerals by means of a magnet.

Preparation of $[(H_2N)_2C=NH_2]_2[Si(Cat)_3] \cdot XH_2O$ from Wollastonite

Method 1. 1.5 g of catechol, 0.5 g of wollastonite, $CaSiO_3$, and 1.0 g of guanidinium hydrochloride, $(H_2N)_2C=NH \cdot HCl$, were introduced into a 125-ml erlenmeyer flask. The flask was purged with nitrogen and 50 ml of water was added. After about twenty four hours, long needle-like crystals of $[(H_2N)_2C=NH_2]_2[Si(Cat)_3] \cdot XH_2O$ began to grow upward from the unreacted wollastonite. However, the guanidinium salt has not been recrystallized in this work and so the preparation described below (Method 2), in which the product is free of mineral, is typical of several reactions which were carried out.

Method 2. A reaction mixture consisting of 14.72 g of

catechol and 3.89 g of wollastonite in 400 ml of water was refluxed under nitrogen for ninety hours. Occasionally during the reflux period, the reaction mixture was cooled, a calomel-glass combination electrode was inserted into the solution, and the pH was checked; it remained at 7.0 throughout the course of the reaction. After refluxing, the unreacted mineral was filtered off under nitrogen--21% (0.83 g corresponding to 7.2 mmoles) of the wollastonite dissolved-- and 50 ml of 1.0 M guanidinium hydrochloride was introduced into the dark red-brown filtrate. The precipitate which formed was filtered, washed with several portions of cold 1 M ammonium hydroxide and dried to constant weight in a vacuum at room temperature. The yield was 2.16 g (4.5 mmoles), or 63% with respect to the quantity of mineral which dissolved. Infrared, x-ray, nmr and analytical data confirmed that the precipitate, which had a slight pink tinge due to a trace of iron impurity, was guanidinium tris(catecholato)-siliconate.

Preparation of $[(H_2N)_2C=NH_2]_2[Si(Cat)_3] \cdot XH_2O$ from Andradite

A reaction mixture consisting of 20.0 g of catechol and 5.14 g of andradite in 350 ml of water was refluxed under nitrogen for 142 hours. Prior to refluxing, the pH of the reaction mixture was 6.8. After the reflux period, the pH was found to be 6.0. Initially, the reaction mixture was a red-brown color but became dark violet as the pH dropped.

Following the filtration of the reaction mixture--11% (0.56 g, corresponding to 3.3 mmoles of silicon) of the andradite dissolved--90 ml of 1.0 M guanidinium hydrochloride was added to the filtrate. Whereas a precipitate began to form within a few minutes after the introduction of guanidinium ions to the filtrate obtained from the wollastonite reaction mixture, such wasn't the case with the andradite reaction. When no precipitate was observed, the pH of the filtrate was raised to 7.5 by adding 5 ml of 1.0 N sodium hydroxide. Small lustrous red-violet crystals formed overnight. It is not known whether the addition of base was really necessary. After washing and then drying to constant weight, a light red-violet powder was left. X-ray and infrared data showed this powder to be guanidinium tris(catecholato)siliconate. A yield of 0.39 g (0.80 mmoles), or 24% with respect to the quantity of mineral which dissolved, was realized.

Reactions of Diopside, Talc and White Beryl with Catechol

Reactions of catechol with diopside, talc and white beryl, which were initiated in a similar manner as the reaction of catechol with andradite, were unsuccessful. These three minerals did not dissolve to any significant extent. They hydrolyzed to form acid reaction mixtures (i.e., diopside, pH = 5.1; white beryl, pH = 5.4; talc, pH = 5.6).

Preparation of an Unidentified Calcium Salt, Compound A, from Wollastonite

<u>Method 1</u>. 26.04 g of catechol and 4.61 g of wollas-
tonite in 400 ml of water was refluxed under nitrogen for
157 hours. During the reflux period, the pH of the reaction
mixture was maintained between 7.5 and 8.0 by adding about
8 ml of 1.0 N sodium hydroxide. When the reaction mixture
had cooled and sat for a few days, aggregates of dark red-
violet crystals, Compound A, formed. The crystals were
mixed with unreacted wollastonite.

<u>Method 2</u>. The identical compound was prepared by re-
fluxing 11.0 g of catechol and 5.0 g of wollastonite in 65 ml
of water. Under these conditions, the "apparent pH" of the
reaction mixture, as determined using a calomel-glass elec-
trode, remained at 7.5 without adding base. Dark red-violet
crystals began to grow in the hot reaction mixture after a
few days of refluxing. After refluxing for twenty days, a
portion of one of the crystals (the crystals were very large
by then) was removed from the cooled reaction mixture,
washed off with a little cold water and dried to constant
weight in a vacuum at room temperature. As it dried, it
disintegrated to a light pink powder.

<u>Anal</u>. Found: C, 51.50; H, 4.74; Si, 7.38, 8.26;
Ca, 8.49, 8.15. The x-ray powder diffraction pattern of
Compound A is shown in Table C-1, Appendix C. The infrared
spectrum is shown in Figure C-1, Appendix C, and the nmr
spectrum in deuterium oxide is shown in Figure C-3. The nmr
spectrum in DMSO (not shown), though poorly resolved,

reveals a peak at Υ 3.33 ppm and another at Υ 3.64 ppm.

Compound A is only slightly soluble in water and even less soluble in DMSO. If allowed to stand in ethyl ether for about one half hour, it forms a sticky green resinous mass which disintegrates to a green powder when the ether evaporates. When dry, it is stable in the atmosphere for short periods of time. However, after two days of exposure to air, the light pink powder begins to develop a greyish cast.

DISCUSSION OF RESULTS

The Dissolution of Silicate Minerals

The observed losses in weight of mineral starting materials (21% of the original 3.89 g of wollastonite and 11% of the original 5.14 g of andradite dissolved) resulting from treatment with aqueous catechol shows that the minerals themselves were reacting rather than impurities or glass surfaces of reaction vessels (i.e., it has been shown that the andradite contained no detectable quantities of silica of any kind).

Two main factors contributing to the greater effectiveness exhibited by catechol in attacking wollastonite as compared to the other minerals described in this section are believed to be: The wollastonite had a greater specific surface area since the particle size was ≤ 43 μ whereas the other minerals were ground to ≤ 74 μ; and the wollastonite

reaction mixture remained neutral while the other minerals hydrolyzed to form acid solutions--a factor which might explain why the catechol-silicon complex was not isolated from the talc, white beryl and diopside reaction mixtures which experienced pH drops to about 5.5. The fact that talc and diopside react with catechol under more favorable conditions (i.e., higher pH and/or catechol concentration) has already been established.

Balanced reactions describing the dissolution of the silicate minerals studied in this work cannot, from these studies, be written with certainty. However, the fact that neutral or slightly acid solutions are formed can be rationalized in a qualitative manner.

Consider, for example, the dissolution of andradite in aqueous catechol to form a pH 6 solution. The balanced reaction cannot be written since the nature of the cationic species is highly speculative. Therefore, the reaction will be written in a stepwise manner with andradite dissolving to form the catechol-silicon complex,

$$Ca_3Fe_2(SiO_4)_3 + 9H_2Cat \longrightarrow 3Ca^{2+} + 2Fe^{3+} + 3Si(Cat)_3^{2-} + 6OH^- + 6H_2O$$
(Andradite)
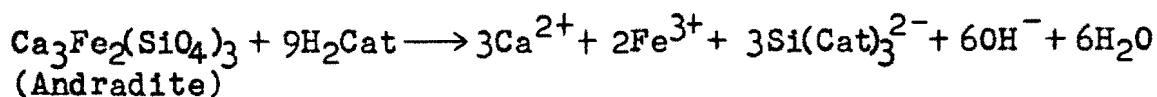
and then the ultimate fate of Ca^{2+} and Fe^{3+} will be considered.

Since both Ca^{2+} and Fe^{3+} hydrolyze in water to form acid solutions, the OH^- ions shown to form in the above reaction would immediately be consumed--explaining in part why an

acid solution actually formed.

e.g., $$Ca^{2+} + OH^- \rightleftharpoons CaOH^+$$

However Fe^{3+}, besides hydrolyzing to form $Fe(OH)^{2+}$, $Fe(OH)_2^+$, or perhaps even precipitating as $Fe(OH)_3$ (no attempt was made to detect $Fe(OH)_3$ in reaction residues), is also very likely reacting with catechol to form a complex.

In this work, mineral reaction mixtures were red-brown above pH 6.5 and violet below this value, which is explained by Weinland (22) who found that deep red alkaline solutions of iron and catechol contain $Fe(Cat)_3^{3-}$, while violet acid solutions contain $Fe(Cat)_2^-$. Also, traces of iron complex were present whenever $[(H_2N)_2C=NH_2]_2[Si(Cat)_3]\cdot XH_2O$ was isolated from reactions of minerals with catechol. Iron, inherent in the mineral itself or present in an impurity (i.e., present as magnetite, Fe_3O_4), reacting with catechol would lower the pH of a reaction mixture.

e.g., $$Fe^{3+} + 2H_2Cat \xrightarrow{pH \leq 6.5} Fe(Cat)_2^- + 4H^+$$
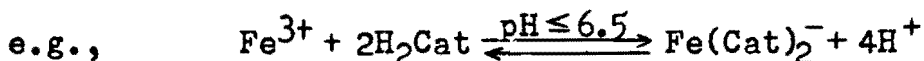
Description of Compound A

Quite possibly Compound A is a mixture consisting mainly of $Ca[Si(Cat)_3]\cdot XH_2O$, but also containing $Ca(HCat)_2\cdot XH_2O$ and some wollastonite, $CaSiO_3$. That $Ca[Si(Cat)_3]$ should form under the reaction conditions employed in this work follows from the fact that the magnesium analog, $Mg[Si(Cat)_3]$, has

been prepared under similar circumstances.* However, conditions of high pH and high catechol concentration shown by Baumann (10) to favor catechol-silicon ester formation also favor formation of the metal catecholates (e.g., $Ca(HCat)_2$) described by Scholder and Wolf (23). In this work it was found that when adding base to reaction mixtures of catechol and wollastonite in order to precipitate $Ca[Si(Cat)_3]$, as the pH approached 9, $Ca(HCat)_2 \cdot XH_2O$ precipitated exclusively.

The rather large discrepancies between the two calcium and two silicon analyses which were performed on the same sample imply that the mixture, Compound A, is non-homogeneous--possibly because of occluded wollastonite, the presence of which is confirmed by the x-ray powder diffraction pattern of Compound A (Table C-1, Appendix C).

The infrared spectrum of Compound A (Figure C-1, Appendix C) exhibits several bands also seen in the spectrum of $Ca(HCat)_2 \cdot XH_2O$ (Figure C-2, Appendix C), but those in the aromatic C-H in-plane bending region are particularly revealing: The absorption band at 9.10 μ likely arises both from $Ca(HCat)_2 \cdot XH_2O$ and $Ca[Si(Cat)_3] \cdot XH_2O$, the band at 9.72 μ from the former compound only, and the band at 9.85 μ from the latter. That these absorption bands are not associated with catechol itself is clearly revealed by viewing a spec-

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* Mr. Boonthong Poocharoen prepared $Mg[Si(Cat)_3]$ in this laboratory from a synthetic magnesium silicate, $Mg_2Si_3O_8 \cdot 5H_2O$. He also recovered a substance identical to Compound A from a reaction mixture of diopside, $CaMgSi_2O_6$, and catechol.

trum of Compound A admittedly contaminated with catechol (Figure C-2, Appendix C) which shows an additional band at 9.59 μ and a shoulder at 9.10 μ.

The nmr spectrum of a saturated solution of Compound A in deuterium oxide (Figure C-3, Appendix C) shows two phenyl proton peaks. The one at τ 3.25 ppm (τ 3.64 ppm in DMSO) corresponds to the position of the phenyl proton peak of $Ca(HCat)_2 \cdot XH_2O$. The peak at τ 3.0 ppm (τ 3.33 ppm in DMSO) possibly arises from the phenyl protons of $Ca[Si(Cat)_3] \cdot XH_2O$; although catechol, which could have formed as a hydrolysis product, exhibits an A_2B_2 splitting pattern at about the same location.

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APPENDIX A

X-RAY POWDER DIFFRACTION PATTERN, INFRARED AND NMR SPECTRA, AND EQUIVALENT CONDUCTANCE OF GUANIDINIUM TRIS(CATECHOLATO)SILICONATE

A Perkin-Elmer 137 B INFRACORD spectrophotometer was used to obtain infrared spectra. The nmr spectrum was obtained by using a Varian A-60 nmr spectrometer.

The powder diffraction pattern was measured with a General Electric XRD-5 x-ray spectrometer using a copper target and a nickel filter. I/I_0 = relative intensity on a scale running from 0 to 100; d Å = distance, in angstrom units, between crystal planes.

TABLE A-1

X-RAY POWDER DIFFRACTION PATTERN OF
$[(H_2N)_2C=NH_2]_2[Si(Cat)_3] \cdot XH_2O$

Radiation: CuK_α I/I_0: Diffractometer

d Å	I/I_0	d Å	I/I_0
14.0	8	3.735	14
13.4	6	3.682	23
11.11	12	3.552	30
10.04	100	3.477	64
8.93	45	3.373	27
8.04	84	3.312	30
7.525	36	3.223	14
6.992	27	3.118	4
6.883	25	2.957	10
6.627	24	2.887	21
6.254	36	2.846	18
5.712	4	2.572	12
5.320	28	2.469	8
5.166	54	2.348	6
5.007	60	2.215	7
4.805	14	2.023	8
4.619	23	1.995	9
4.525	17	1.940	6
4.227	7	1.809	6
4.101	100	1.760	4
4.037	97	1.720	8
3.864	15		

4000 3000   2000   1500   CM⁻¹   1000   900   800   700

WAVELENGTH (MICRONS)

Figure A-1. IR Spectrum of $[(H_2N)_2C=NH_2]_2[Si(Cat)_3]\cdot XH_2O$
(KBr Pellet).

5.43 μ
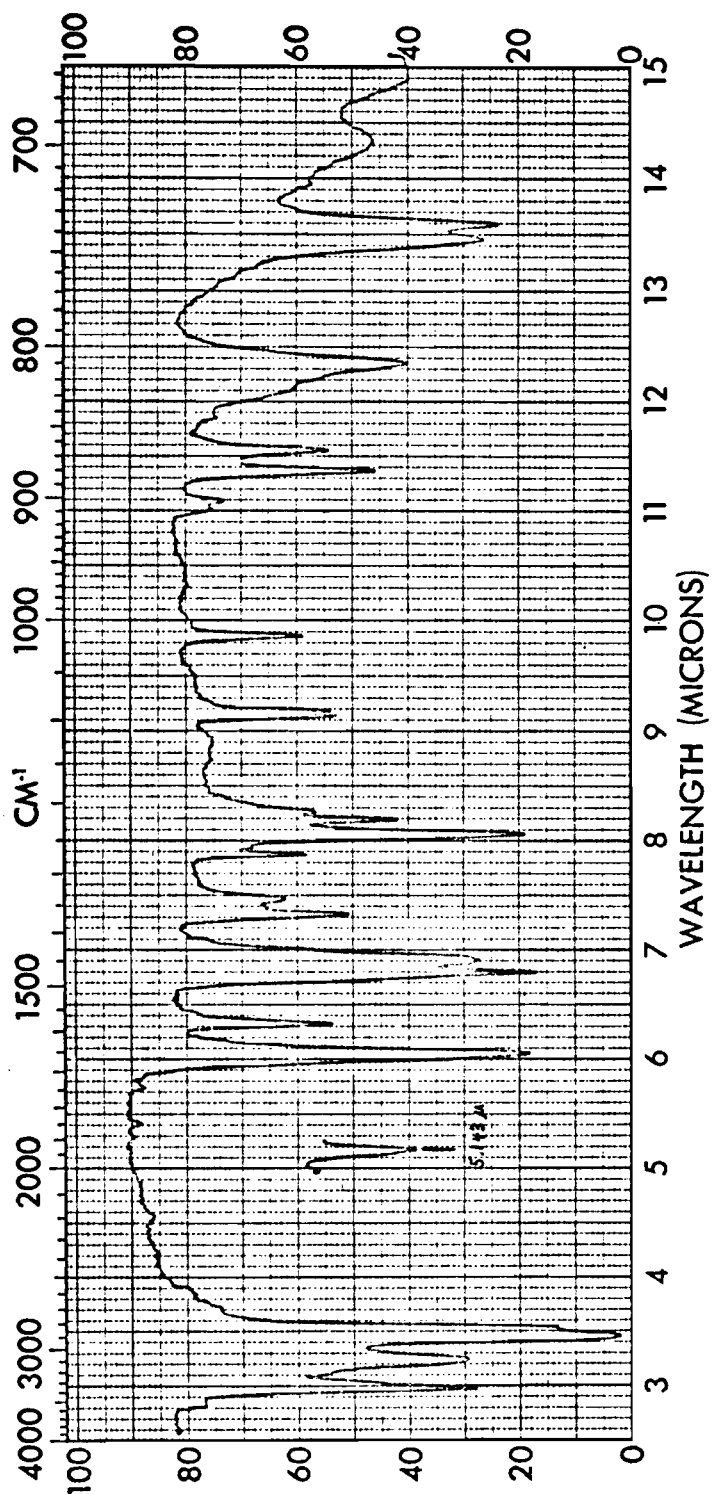
Figure A-2. IR Spectrum of [(H₂N)₂C=NH₂]₂[Si(Cat)₃]·XH₂O (Nujol Mull).
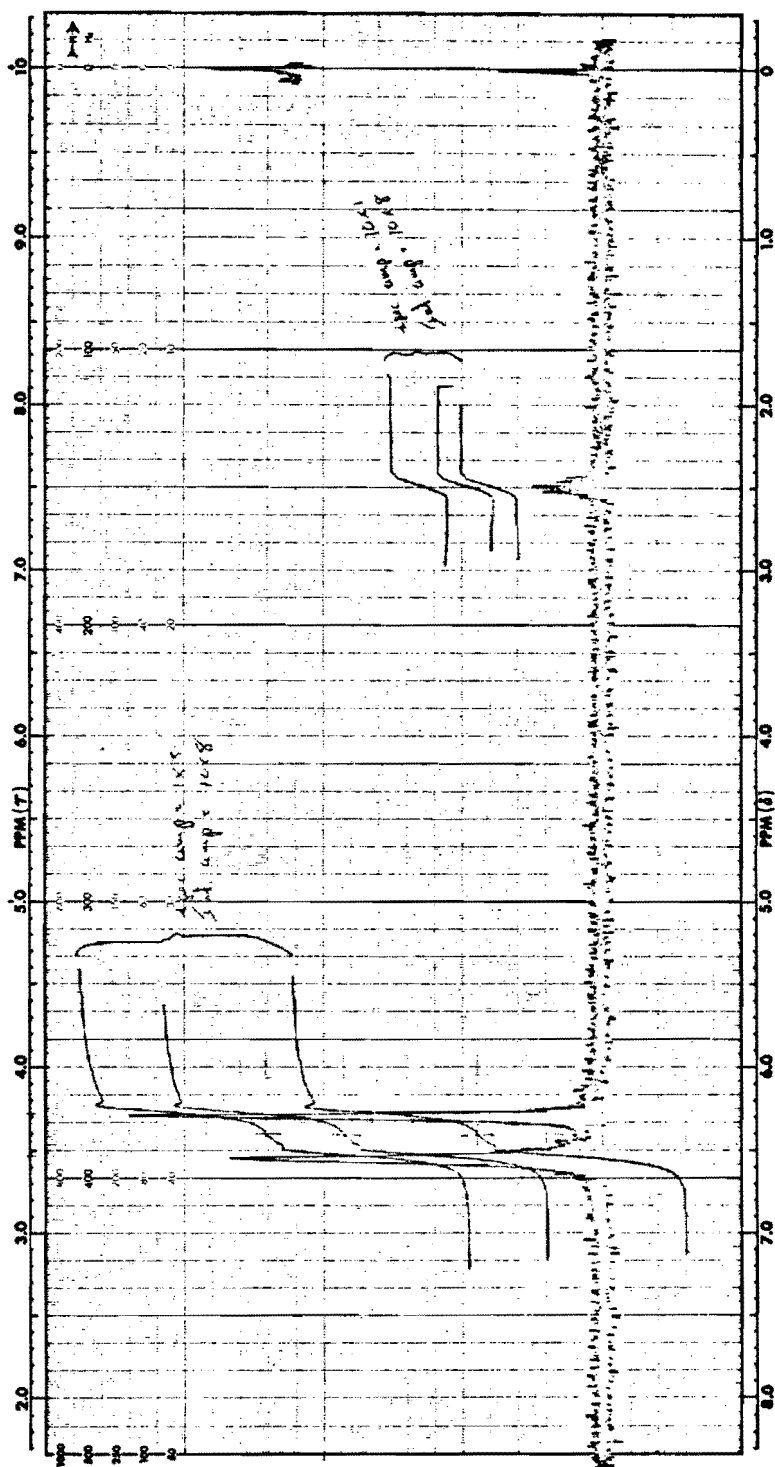
Figure A-3. NMR Spectrum of $[(H_2N)_2C=NH_2]_2[Si(Cat)_3] \cdot XH_2O$ in Deuterated DMSO (7 % solution).
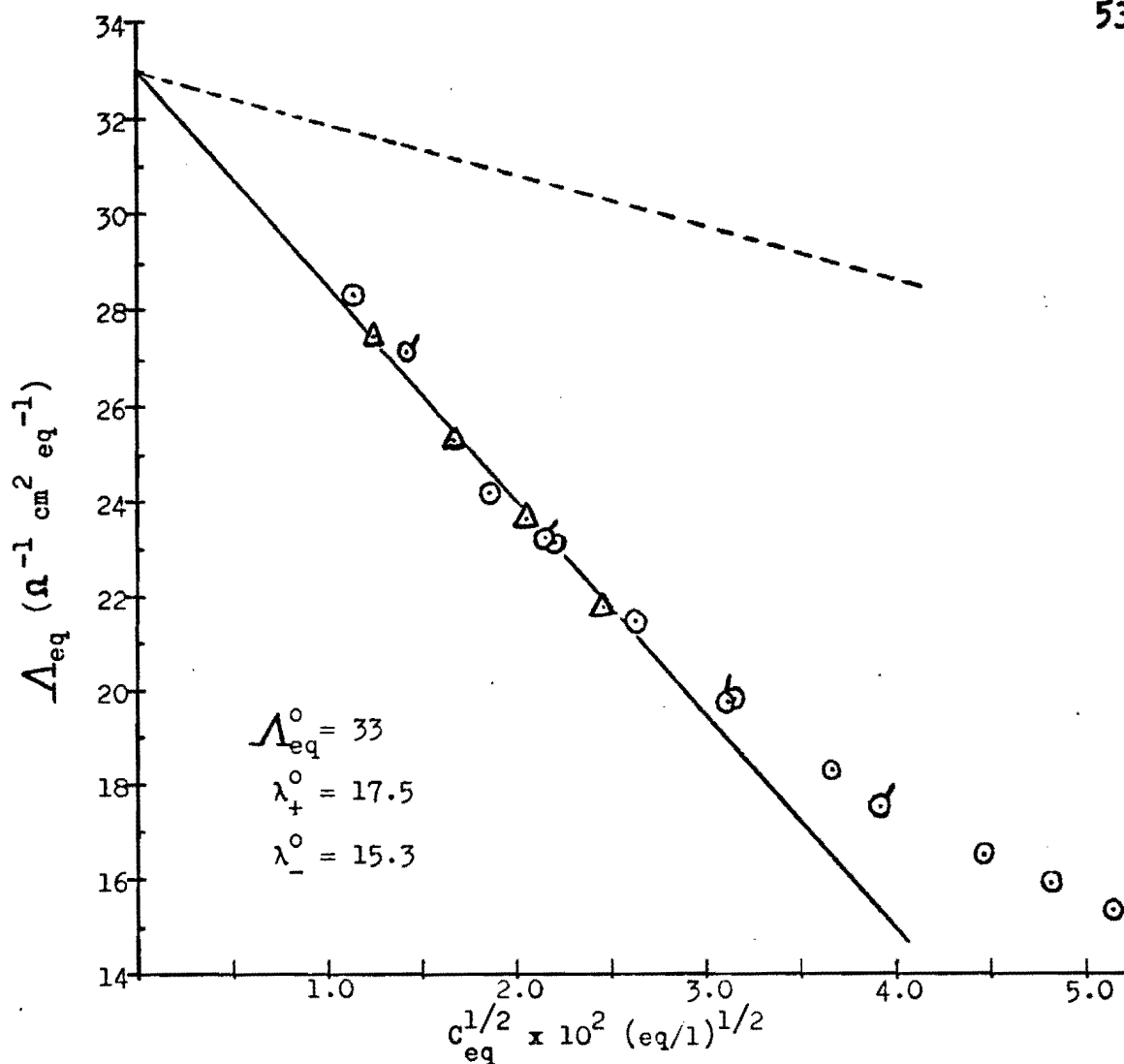
a. Observed limiting slope(—————) = -450

b. Theoretical limiting slope(————) = -102

c. The limiting slope of the plot shown above of Λ^{o}_{eq} vs $c^{1/2}_{eq}$ for $[(H_2N)_2C=NH_2]_2[Si(Cat)_3]\cdot XH_2O$ in DMSO does not approach that predicted by Onsager's theory. It appears that the guanidinium salt forms ion pairs in DMSO.

d. The plot is constructed from data taken from a yet to be published article by Kelley, Barnum, and Eigner titled "Conductivity in Dimethylsulfoxide of Some Electrolytes with Multiply Charged Ions."

Figure A-4. Equivalent Conductance of Guanidinium Tris(catecholato)siliconate in DMSO.

APPENDIX B

X-RAY POWDER DIFFRACTION PATTERNS OF SILICATE MINERALS AND SILICATE MINERAL REACTION RESIDUES

Powder diffraction patterns were measured with a General Electric XRD-5 x-ray spectrometer using a copper target and a nickel filter. I/I_o=relative intensity on a scale running from 0 to 100; d Å= distance, in angstrom units, between crystal planes.
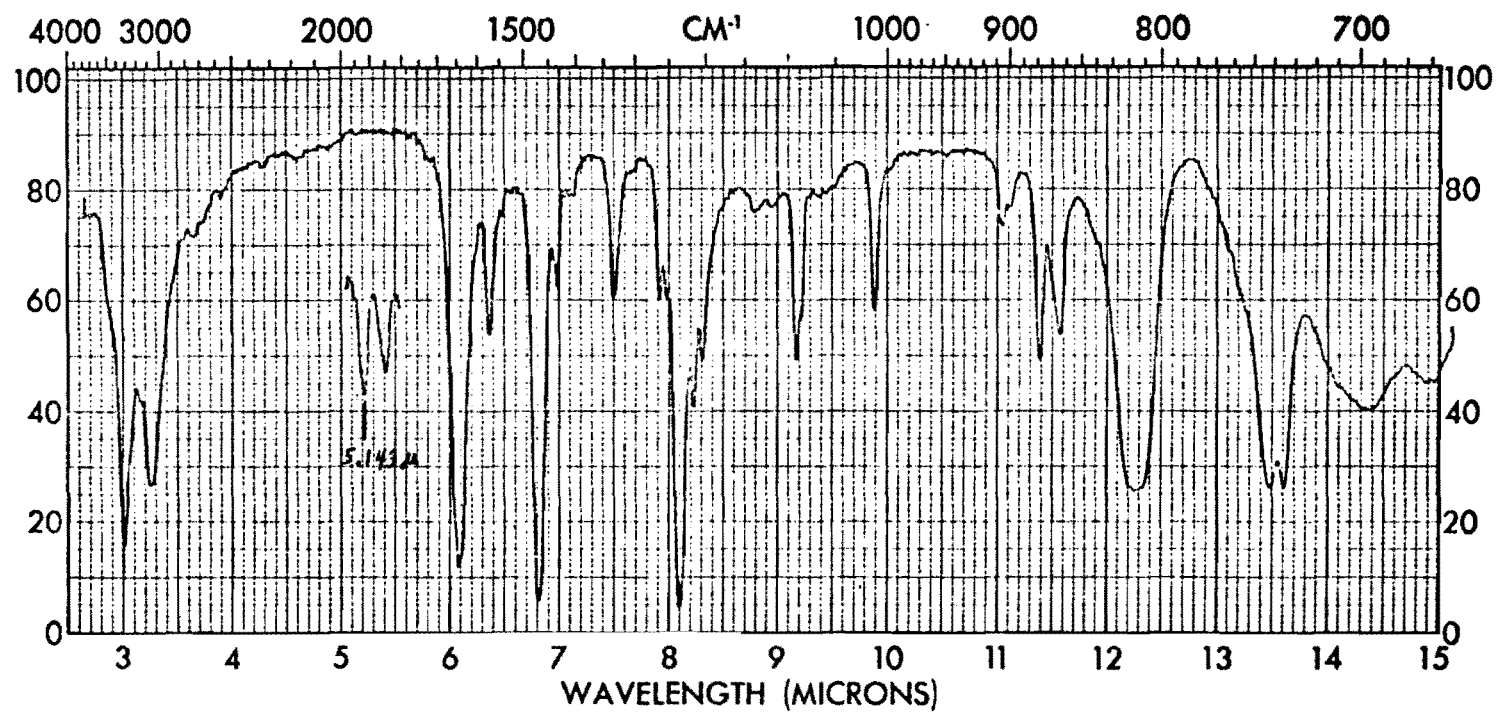
TABLE B-1

X-RAY POWDER DIFFRACTION PATTERNS OF ALBITE

ASTM 9-466		Starting Mineral		Reaction Residue	
Source: Amelia, Virginia.		Source: Bancroft, Ontario, Canada.		Source: Residue from the reaction of albite with catechol @ pH 10.	
I/I_0: Diffractometer		I/I_0: Diffractometer		I/I_0: Visual estimate	
d $\overset{\circ}{A}$	I/I_0	d $\overset{\circ}{A}$	I/I_0	d $\overset{\circ}{A}$	I/I_0
		9.93	4		
6.39	20	6.37	8	6.38	8
5.94	1			5.90	2
5.59	1			5.59	2
				4.436	6
4.030	15	4.037	65	4.037	40
3.857	7	3.872	5	3.870	5
3.780	25	3.759	15		
3.684	20	3.705	14	3.693	15
3.663	15	3.648	15		
3.509	10	3.538	3		
3.484	1	3.477	8	3.461	5
3.375	7	3.336	5	3.338	10
3.196	100	3.189	100	3.197	100
3.151	9	2.991	7	2.998	7
2.964	9				
2.933	15	2.933	9	2.919	12
2.866	7				
2.843	1	2.846	8	2.829	6
2.787	1				
2.639	5	2.646	4	2.634	6
2.563	7				
2.538	1	2.537	5	2.533	10
2.511	1				
2.496	5	2.479	5		
2.460	5			2.469	8
2.443	3				
2.431	1				
2.405	1			2.410	2
2.388	3			2.378	5
2.320	3			2.292	2
2.278	1			2.272	2
2.189	3			2.195	2
2.125	7	2.132	4	2.126	7
2.119	5				
2.076	1			2.090	10

TABLE B-1 (CONTINUED)

ASTM 9-466		Starting Mineral		Reaction Residue	
d Å	I/I_o	d Å	I/I_o	d Å	I/I_o
2.035	1				
2.000	1				
1.980	3				
1.927	1			1.907	7
1.889	7				
				1.846	8
		1.824	4	1.818	11
		1.796	4		
		1.776	14	1.770	9
		1.743	8		

TABLE B-2

X-RAY POWDER DIFFRACTION PATTERNS OF ANDRADITE

ASTM 10-288		Starting Mineral		Reaction Residue	
Source: Synthetic.		Source: Eagle Mts., Riverside Co., California.		Source: Residue from the reaction of andradite with catechol @ pH 10.	
I/I_0: Diffractometer		I/I_0: Diffractometer		I/I_0: Visual estimate	
d Å	I/I_0	d Å	I/I_0	d Å	I/I_0
4.263	13	4.25	24	4.27	5-20
		3.34	16	3.328	5
3.015	60	3.01	62	3.000	60
2.696	100	2.69	100	2.687	80
2.571	13			2.559	5
2.462	45	2.45	65	2.450	60
2.365	17	2.36	17	2.354	10
2.202	17	2.19	17	2.189	10
1.9564	25	1.95	21	1.947	17
1.9068	11	1.90	10	1.901	13
1.7406	9			1.734	6
1.6728	25	1.67	25	1.665	50
1.6412	3				
1.6112	60	1.61	74	1.605	100
1.5073	13	1.50	12	1.503	20
1.4213	3				
1.3483	13	1.35	11	1.344	25
1.3157	20	1.31	12	1.311	25
1.2856	13	1.28	11	1.282	20
1.2309	3				
1.2182	5				
1.1195	25	1.12	11		
1.1008	15	1.10	12		

TABLE B-3

X-RAY POWDER DIFFRACTION PATTERNS OF MUSCOVITE

ASTM 6-0263		Starting Mineral		Reaction Residue	
Source: Not listed.		Source: Spruce Pine, Mitchell Co., North Carolina.		Source: Residue from the reaction of muscovite with catechol @ pH 10.	
I/I_o: Geiger counter		I/I_o: Diffractometer		I/I_o: Visual estimate	
d Å	I/I_o	d Å	I/I_o	d Å	I/I_o
		11.04	4		
9.95	95	10.04	100	9.99	10
4.97	31	5.007	38	4.968	7
4.47	21	4.480	4	4.453	70
4.30	4			4.283	5
4.11	4			4.103	5
3.95	6				
3.882	14	3.889	3	3.857	8
3.731	17	3.744	3	3.723	8
		3.682	4		
3.489	22	3.490	5	3.482	9
3.342	23				
3.320	100	3.330	88	3.319	15
3.199	28			3.188	10
3.122	2	3.092	6		
2.987	34	2.986	7	2.980	10
		2.952	7		
2.859	24			2.857	8
2.789	21	2.790	6	2.781	6
2.596	16				
2.566	54	2.565	5	2.579	100
2.505	7				
2.491	14	2.493	11		
2.465	8				
2.450	7			2.453	9
2.398	10	2.396	2		
2.384	27			2.378	15
2.254	9				
2.236	4			2.241	9
2.208	7	2.207	2	2.202	7
2.189	4			2.175	2
2.149	15				
2.132	21	2.135	2	2.128	14
2.070	4				
2.053	6			2.054	5

TABLE B-3 (CONTINUED)

ASTM 6-0263		Starting Mineral		Reaction Residue	
d Å	I/I$_0$	d Å	I/I$_0$	d Å	I/I$_0$
1.993	49	1.996	37	1.984	10
1.972	9				
1.951	6			1.960	3
1.941	3			1.940	2
1.894	2				
1.871	3				
1.822	3				
1.746	3				
1.731	8	1.731	2	1.721	2
1.710	5				
1.704	5				
1.699	4			1.696	5
1.662	11	1.658	2	1.656	5
1.646	23	1.645	4		
1.631	6			1.638	10
1.620	6				
1.603	6			1.595	5
1.573	3			1.575	5
1.559	7				
1.541	3				
1.524	11			1.515	2
1.504	30			1.495	60
1.453	4				
1.424	1				
1.414	1				
1.388	1				
1.375	2				
1.352	11	1.351	5	1.347	5
1.335	9			1.334	2
1.321	3				
1.299	8				
1.292	6			1.294	15
1.274	5			1.270	5
1.267	4				
1.253	5			1.257	10
1.246	8	1.245	3		

TABLE B-4

X-RAY POWDER DIFFRACTION PATTERNS OF PYROPHYLLITE

ASTM 2-0613		Starting Mineral		Reaction Residue	
Source: Tres Cerritos, Mariposa Co., California ($-H_2O$ @ $> 100°$).		Source: Tres Cerritos, Mariposa Co., California.		Source: Residue from the reaction of pyrophyllite with catechol @ pH 10.	
I/I_o:Visual estimate		I/I_o: Diffractometer		I/I_o: Visual estimate	
d Å	I/I_o	d Å	I/I_o	d Å	I/I_o
		10.04	4		
9.14	40	9.11	100	9.32	10
		5.063	2		
4.57	50	4.583	50	4.590	5
				4.453	15
		4.237*	6	4.259*	25
4.15*	20				
3.87	5				
		3.697	2	3.717	7
		3.379	4		
3.34*	20-40	3.336*	42	3.338*	100
3.04	100	3.074	88	3.072	15
				2.562	15
2.52	20			2.533	15
		2.453*	13	2.458*	13
2.40	40	2.409	2	2.412	30
2.20*	20	2.203*	5	2.280*	15
				2.235*	10
				2.159	5
2.14*	10-20			2.128*	10
2.07	10			2.083	5
2.04	10			2.054	5
1.88	5			1.938*	10
1.83*	40	1.836*	10		
		1.812*	3	1.813*	30
		1.668*	2	1.669*	10
1.64	20-40				
1.62	10-20				
1.57	3				
		1.538*	3	1.540*	25
1.52	10	1.529	2		
1.49	20-40			1.489	30

* These lines indicate the presence of α-quartz.

TABLE B-4 (CONTINUED)

ASTM 2-0613		Starting Mineral		Reaction Residue	
d Å	I/I_o	d Å	I/I_o	d Å	I/I_o
1.46	5			1.468	5
1.43	5			1.453	5
1.42	5				
1.38	40	1.381	3	1.382	20
		1.370	3	1.372	30
1.36	40				
1.34	5				
1.33	5				
1.31	10-20				
1.28	10			1.285	10
1.26	10-20			1.265	5
1.25	5			1.254	7
1.24	10				
1.21	5				

TABLE B-5

X-RAY POWDER DIFFRACTION PATTERNS OF TALC

ASTM 13-558		Starting Mineral		Reaction Residue	
Source: manchuria.		Source: Unknown.		Source: Residue from the reaction of talc with catechol @ pH 10.	
I/I_0: Diffractometer		I/I_0: Diffractometer		I/I_0: Visual estimate	
d Å	I/I_0	d Å	I/I_0	d Å	I/I_0
		10.37	6	15.44	50
9.34	100	9.39	100	9.44	90
		5.20	1		
4.66	90	4.68	32		
4.55	30			4.571	80
				4.187	10
3.51	4				
3.43	1	3.453	6		
3.116	100	3.118	99	3.093	70
2.892	1				
2.629	12			2.614	15
2.595	30			2.582	30
2.476	65	2.477	1	2.461	100
2.335	16	2.338	3		
2.212	20				
2.196	10			2.199	20
2.122	8				
2.103	20			2.092	10
1.930	6				
1.870	40	1.871	11	1.863	5
1.725	--			1.719	10
1.682	20			1.701	8
1.557	20	1.559	6		
1.527	40			1.518	80
1.509	10			1.501	8
1.460	8				
1.406	16				
1.394	20	1.396	1		
1.336	16	1.336	5		
1.318	10			1.313	15
1.297	10			1.291	10
1.269	10			1.264	8
1.169	6	1.169	1		

TABLE B-6

X-RAY POWDER DIFFRACTION PATTERN OF WOLLASTONITE

ASTM 10-487		Starting Mineral	
Source: Chiapas, Mexico.		Source: Calico, San Bernadino Co., California.	
I/I_0: Visual estimate		I/I_0: Diffractometer	
d Å	I/I_0	d Å	I/I_0
7.7	40	7.65	32
		5.43	4
4.05	10	4.247*	9
3.83	80	3.838	90
3.52	80	3.517	57
3.40	5		
3.31*	80	3.320*	100
3.16	5	3.241	6
3.09	30	3.087	19
2.97**	100	2.976	10
2.80	10		
2.72	10	2.720	10
2.55**	30	2.558	21
2.47	60	2.479	10
2.33	40	2.339	9
2.29	40	2.302	21
2.18	60	2.182	4
		2.167	5
2.08**	5		
2.01	20		
1.98	20	1.982	3
1.91	20	1.918	10
1.88	20		
1.86	10		
1.83	60		
1.80	5	1.811*	6
1.79	5		
1.75	40	1.757	14
1.72**	60	1.719	3
1.602**	40		
1.531*	10	1.537*	19
1.515	5		
1.478**	20		

* These lines indicate the presence of α-quartz.

** These lines indicate that the ASTM sample contained magnetite.

TABLE B-7

X-RAY POWDER DIFFRACTION PATTERN OF THE CALCITE RESIDUE RECOVERED AFTER THE REACTION OF WOLLASTONITE WITH CATECHOL AT pH 10.0

ASTM 5-0586 (Calcite)		Reaction Residue	
I/I_0: Diffractometer		I/I_0: Visual estimate	
d $\overset{o}{A}$	I/I_0	d $\overset{o}{A}$	I/I_0
		4.259*	15
3.86	12	3.857	15
		3.333*	90
3.035	100	3.027	100
2.845	3		
2.495	14	2.485	20
		2.443*	7
2.285	18	2.272*	30
		2.224*	3
		2.113*	7
2.095	18	2.081	25
1.927	5	1.965	3
1.913	17	1.904	25
1.875	17	1.863	27
		1.806*	17
		1.659*	5
1.626	4	1.616	10
1.604	8		
1.587	2	1.594*	20
1.525	5	1.534*	10
1.518	4	1.518	8
1.510	3		
1.473	2	1.471	3
1.440	5	1.433	17
1.422	3	1.415	10
		1.375*	8
1.356	1	1.368	15

* These lines indicate that α-quartz is also present.

TABLE B-8

X-RAY POWDER DIFFRACTION PATTERN OF THE QUARTZ RESIDUE RECOVERED AFTER THE REACTION OF WOLLASTONITE WITH CATECHOL AT pH 4.0

ASTM 5-0490 (α-Quartz)		Reaction Residue	
I/I_0: Diffractometer		I/I_0: Visual estimate	
d Å	I/I_0	d Å	I/I_0
		5.310	2
4.26	35	4.300	60
		3.705*	5
3.343	100	3.328	100
		3.000*	7
		2.801*	2
		2.728*	2
		2.536*	9
2.458	12	2.456	15
2.282	12	2.285	15
2.237	6	2.239	10
2.128	9	2.126*	14
		2.014	5
1.980	6	1.981	10
1.817	17	1.817	60
1.801	< 1		
1.672	7	1.673	15
1.659	3	1.657	7
1.608	1	1.627	5
1.541	15	1.542	50
1.453	3	1.453	10
1.418	1		
1.382	7	1.382	20
1.375	11		
1.372	9	1.372	50
1.288	3	1.287	10
1.256	4	1.256	10
1.228	2	1.228	7
1.1997	5	1.199	10

* These lines indicate that a trace of wollastonite is still present.

APPENDIX C

X-RAY POWDER DIFFRACTION PATTERN AND INFRARED AND NMR SPECTRA OF AN UNIDENTIFIED CALCIUM SALT, COMPOUND A

A Perkin-Elmer 137 B INFRACORD spectrophotometer was used to obtain infrared spectra. The nmr spectrum was obtained by using a Varian A-60 nmr spectrometer.

The powder diffraction pattern was measured with a General Electric XRD-5 x-ray spectrometer using a copper target and a nickel filter. I/I_0 = relative intensity on a scale running from 0 to 100; d $Å$ = distance, in angstrom units, between crystal planes.

TABLE C-1

X-RAY POWDER DIFFRACTION PATTERN OF COMPOUND A

Radiation: CuKα   I/I₀: Diffractometer

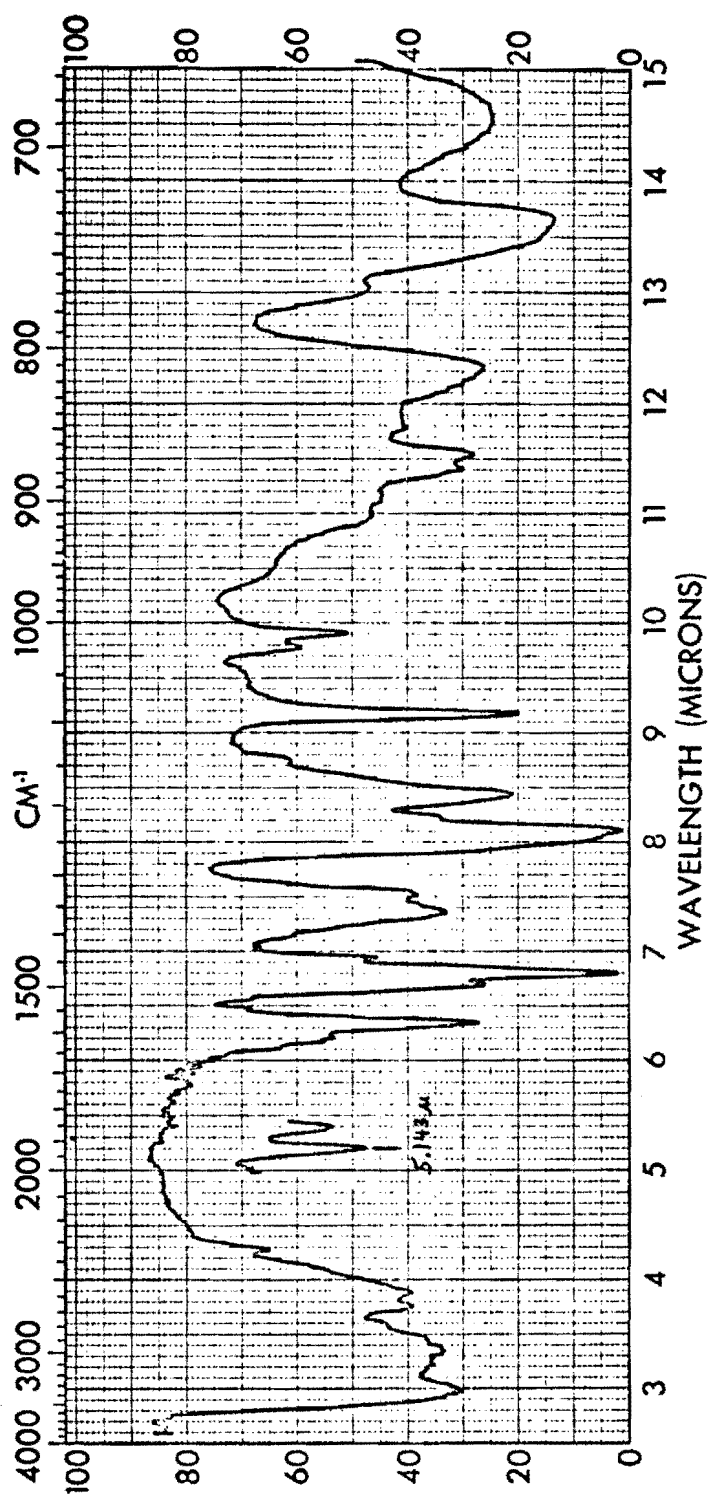| d Å	I/I₀
11.70	8
10.64	100
9.55	25
8.83	13
8.58	7
8.07	12
6.39	4
6.21	6
5.71	2
4.99	6
4.831	16
4.350	10
4.149	6
4.037*	3
3.847*	8
3.782*	9
3.517*	5
3.324*	8
3.092*	4
2.991*	5
2.732*	3
2.558*	2
2.486*	5
2.308*	2
1.760*	1

* These lines indicate the presence of wollastonite.

Figure C-1. IR Spectrum of Compound A.
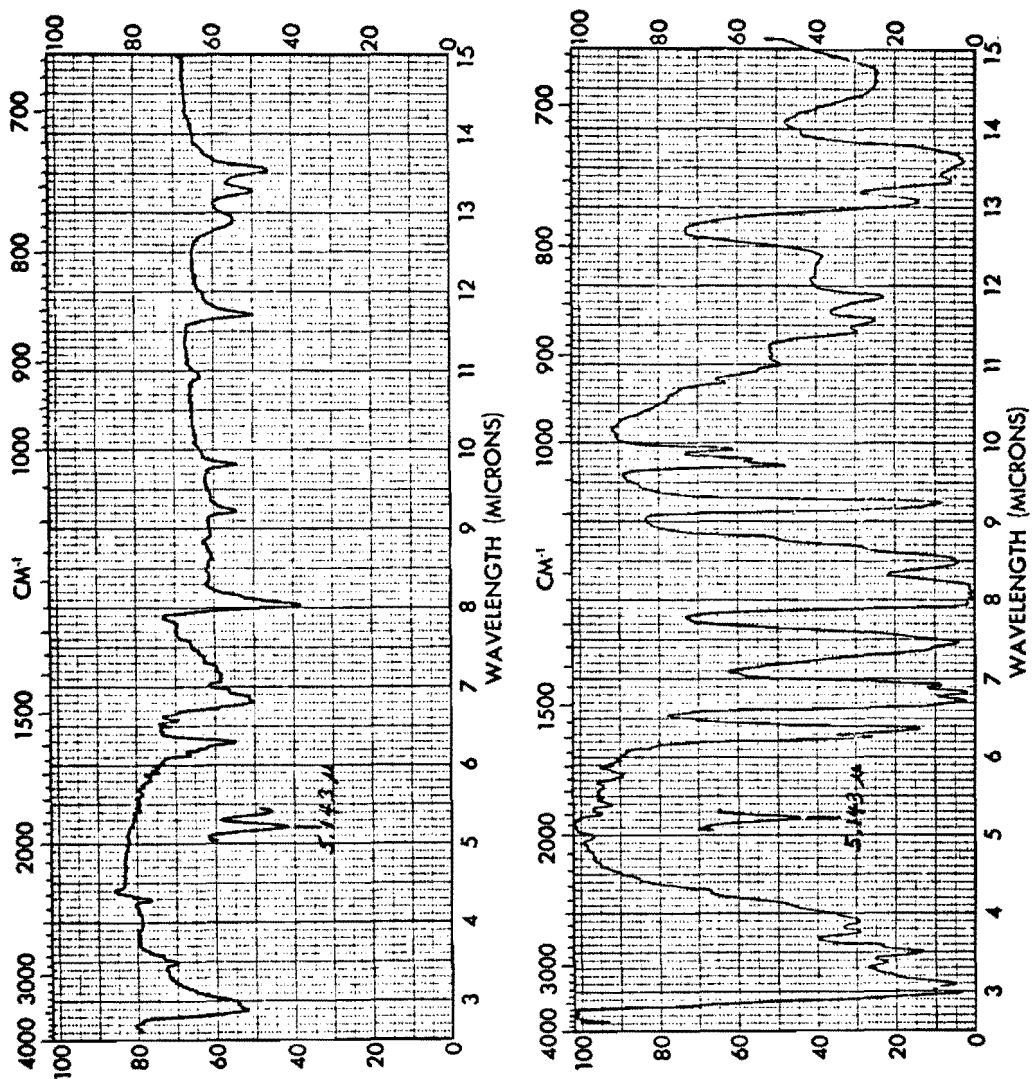
Figure C-2. IR Spectra of:

Top - Ca(HCat)$_2 \cdot$XH$_2$O
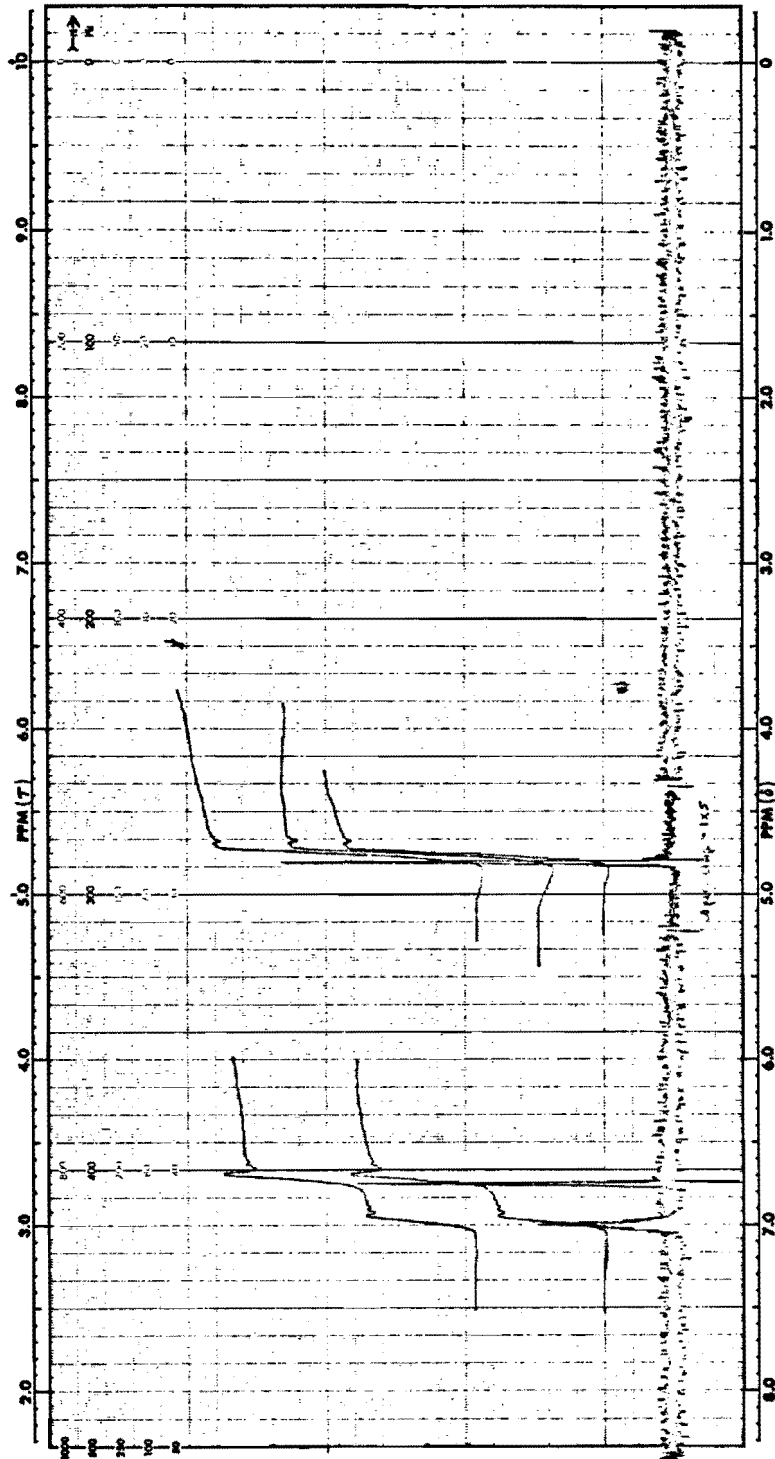
Bottom - Compound A Contaminated with Catechol

Figure C-3. NMR Spectrum of Compound A in D_2O (Saturated Solution).