

## DISSOLUTION OF CLAY MINERALS IN DILUTE ORGANIC ACIDS AT ROOM TEMPERATURE

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### ABSTRACT

Two grams each of representative clay minerals were shaken at room temperature in distilled water, and in .01M aspartic, citric, salicylic, tartaric, and tannic acids (representative of components of humic acid). Aliquots of centrifuged solution, up to 102 days dissolution, were analyzed for Si, Al, Fe, Mg, Ca, Na, and K.

The total weight of clay minerals dissolved by strongly complexing organic acids exceeds that dissolved by distilled water by factors 5 to 75. Dissolved Si in strongly complexing acid solutions exceeded 2-35 times its concentration in distilled water; dissolved Al, 3-500 times. Aspartic, an amino-acid, dissolved Ca and Mg best.

Clay minerals dissolve incongruently in distilled water, Si preferentially to Al. In all acids used, Si incongruently exceeds Al dissolved from Arizona and Wyoming smectites, semi-plastic refractory clay, also for illites in salicylic acid, and Keokuk kaolinite in citric and tannic acid.

Congruent dissolution, or Al incongruently exceeding Si, 1.3-1.6:1, occurred with Bueker flint clay, Georgia kaolinite, and illites in citric, tartaric, and tannic acids.

Preferential solubilities of either Si or Al from clay minerals indicate genetic mechanisms for podsoles, laterites, kaolin (especially Moorverwitterung type), and bauxites. Geologic and pedologic examples are cited.

### INTRODUCTION

The weathering effects of humic and other organic acids have commonly been reported in the literature in descriptive or qualitative terms. This paper will document quantitative measurements on the dissolution of clay minerals in several dilute organic acids in the laboratory at room temperature. Possible interpretation and application of the laboratory data to natural systems will be made.

### EXPERIMENTAL

Two grams of finely dispersed,  $<2\mu\text{m}$ , e.s.d., clay minerals, namely: Keokuk and Georgia kaolinites, Bueker flint clay (kaolinite), semi-plastic kaolinite and illite refractory clay (Mexico, Mo.), Beavers Bend and Fithian illites, and Wyoming and Arizona montmorillonites were shaken at room temperature in distilled water, and .01M solutions of aspartic, citric, salicylic, tartaric, and tannic acids. These acids are representative of the various types present in humic acid and associated organic compounds in geologic and pedologic systems. The first one named is weakly complexing, whereas the last four are relatively strongly complexing or chelating. Aspartic is a di-carboxylic amino-acid. Citric acid is hydroxy, tricarboxylic aliphatic. Tartaric acid is di-hydroxy aliphatic. Salicylic acid, on the other hand is aromatic, and mono-hydroxy in structure. Tannic acid, insofar as it is digallic, is pentahydroxy, mono-carboxylic bonded to two six-carbon rings, but the "yellow organic acids" in organic coloring matter extracted from lake water was found

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by Shapiro (1964) to be a mixture of aliphatic and polyhydroxy carboxylic acids (Hem, 1965).

At intervals of 1, 5, 45, and 102 days the clay suspensions were centrifuged at 15,000 rpm for 2 hours, and 50 ml aliquots of clear solution withdrawn. By calculation all particles  $>.0185\mu$  would have been sedimented after the 2-hour centrifugation. The supernatant liquids showed no Tyndall cone. Si was determined colorimetrically, except that in the colored tannic acid solution it was run by atomic absorption. Na and K were determined by flame spectrometry, and the other elements by atomic absorption (Huang and Keller, 1970).

### ANALYTICAL RESULTS

The results of some 2000 analyses of solutions which were run during this study are summarized as follows. Individual analyses may be obtained from the writers upon request.

*Rate of Dissolution.* Most rapid dissolution occurs with the first 24 hours; it begins to slow down in the 5-day interval, and approaches, after 45 days, a constant value which is apparently near-achieved after 102 days, as typified by the curves representing Fithian illite, Figures 1 and 2. Although it is expected that the increase in amounts dissolved would follow a relatively smooth curve, lines were drawn straight between located points simply for convenience in identifying the elements. The patterns of solubility-rate in both water and organic acids is much the same, although the amounts dissolved in the acid solutions are notably greater. Figure 2 shows that the dissolution in tannic acid, which is known to be fairly common in nature although incompletely characterized chemically, behaves quite similarly to tartaric acid whose chemical constants are well established. Presumably the data from tartaric and other organic acids used may be extrapolated also with considerable confidence toward natural geologic and pedologic systems.

*Dissolved Si, Al, Fe.* The framework cations of clay minerals, Si, Al, Mg, and Fe, are sparingly soluble in water, as is well known, but are found to be strikingly more soluble in complexing organic acids. In Figure 3 it is seen that the solubility of Si in water was least from Keokuk and Georgia kaolinites ( $.4-.5 \mu\text{g}/\text{ml}$  or ppm), but most soluble from the montmorillonites (4.5–8 ppm). The solubility of Si in aspartic acid was low also, only slightly greater than in water. In all the strongly complexing acids, however, Si solubility rose by a factor of 2 to 6 for the kaolinites, and by factors in the order of 5 to 10 for the 2:1 layer clays, going to 100 ppm.

Solubility of Al in complexing acids is increased most spectacularly however, going to as much as 500 times, or more, than that in water,

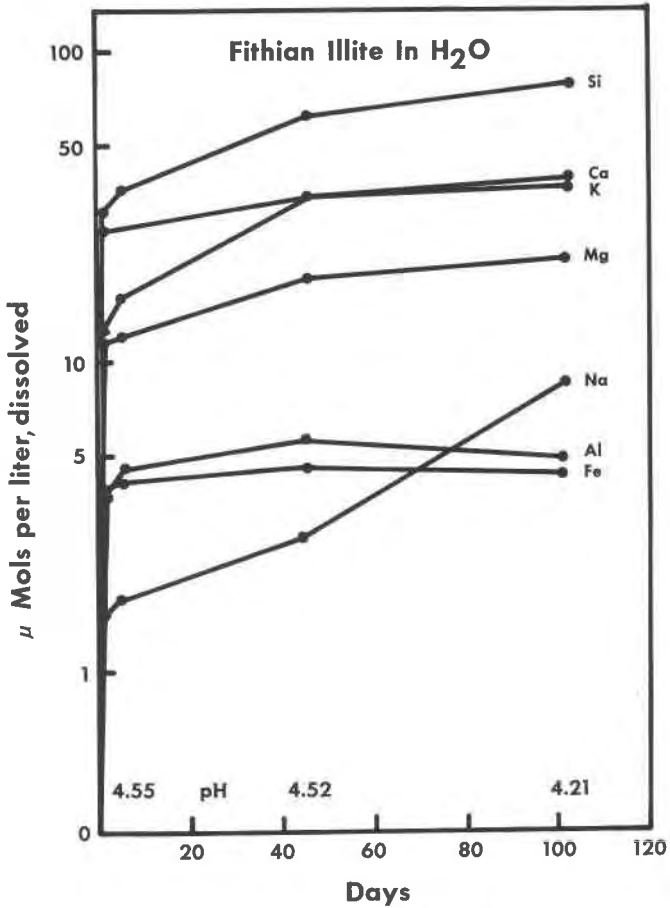


FIG. 1. Concentration of ions in  $\mu$  mols per liter dissolved from Fithian illite in  $H_2O$  open to the atmosphere at room temperature after days indicated.

Figure 4. Illites released most Al in acid solution, montmorillonites intermediate, and kaolinites least. The dissolution of 60 ppm Al from clay minerals in complexing acids is amazingly high compared to less than 1 ppm, the solubility typical in water.

The dissolution behavior of Fe parallels that of Al in ratios, absolute concentrations, and clay-mineral derivation, Figure 5. The logical explanation of the relatively high dissolution of Al and Fe in organic acids is that they are complexed (chelated) by those acids.

The dissolution behavior of Ca, Na, and K should be considered apart from that of the framework elements for several reasons. Ca, Na, and K may be released from clay minerals by ion-exchange reactions rather

than by destruction of framework. Furthermore, these ions are typically so highly soluble in pure water that chelation processes may not be detectible. One special effect is to be noted, however, Ca, and to a lesser extent Mg, are strongly and preferentially dissolved by aspartic acid with respect to Si. The fraction Ca/Si dissolved by aspartic acid is consistently 2 to 5 times higher (even more in extreme cases) than that dissolved by other organic acids or water from any of the clay minerals. Although the solubility of calcium aspartate in water is relatively low, the values of soluble Ca with regard to Si have been consistently obtained as reported herein. The reason this amino-acid reacts selectively with Ca is not known—can it relate to the relatively high demand of legumes (nitrogen or “amino” fixers) for Ca from soil?

*Congruency, or Al:Si Ratios of Dissolved Ions.* In pure water clay minerals dissolve incongruently, as do most silicate minerals, yielding more Si than

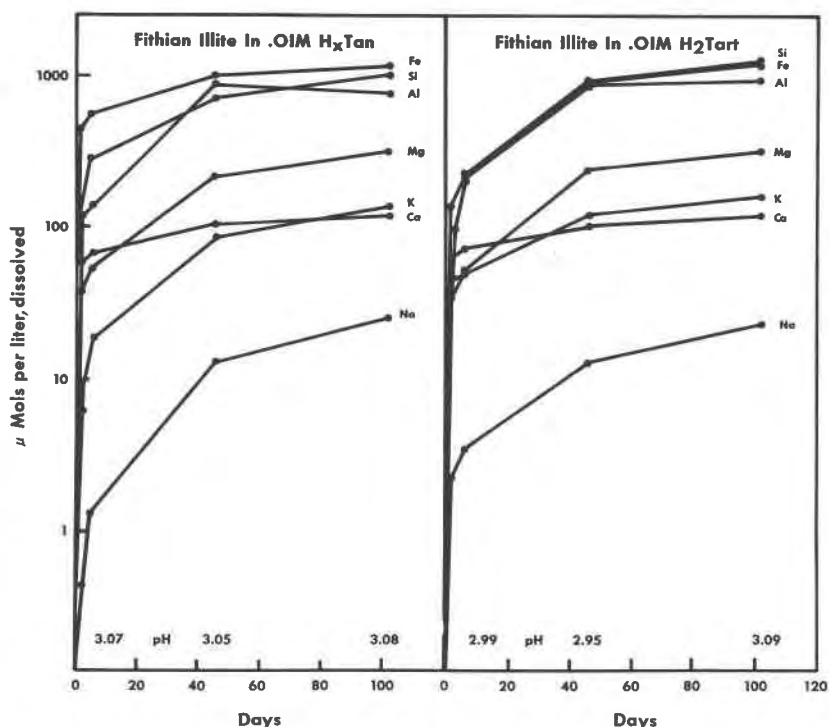


FIG. 2. Concentration of ions in  $\mu$  mols per liter dissolved from Fithian illite in .01M tannic and tartaric acids at room temperature after days indicated. Reaction in tartaric acid, whose chemical constants are well established, is similar to that in tannic acid, a less-well characterized compound that is common in natural pedologic and geologic systems.

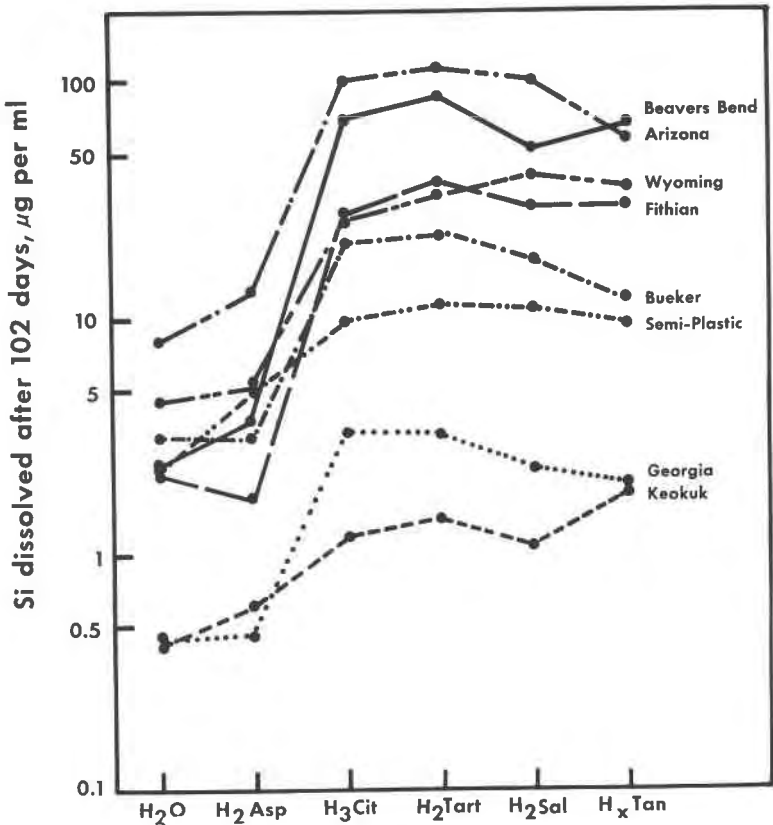


FIG. 3. Si dissolved after 102 days reaction at room temperature between clay minerals and reagents indicated. Note that solubility in the complexing organic acids is much greater than in water and aspartic acid.

Al in water solution. Accordingly, chemical weathering of silicates is so commonly regarded as processes of desilication by dissolution and residual concentration of Al, that significant dissolution and movement of Al in solution are considered to be anomalous even when evidence of them are observed. It is noteworthy, therefore, that complexing organic-acids may dissolve clay minerals, not only congruently with their formulas, but with Al/Si in excess of that in the parent minerals.

To quantify the stoichiometry of dissolution of clay minerals after 102 days the fraction was calculated of any given element, such as Al, Ca, K, dissolved in mols, in terms of the formula (computed from analysis) of the clay mineral; next the fraction was calculated of the Si dissolved, in mols, in terms of the clay mineral; then the fraction of the given dis-

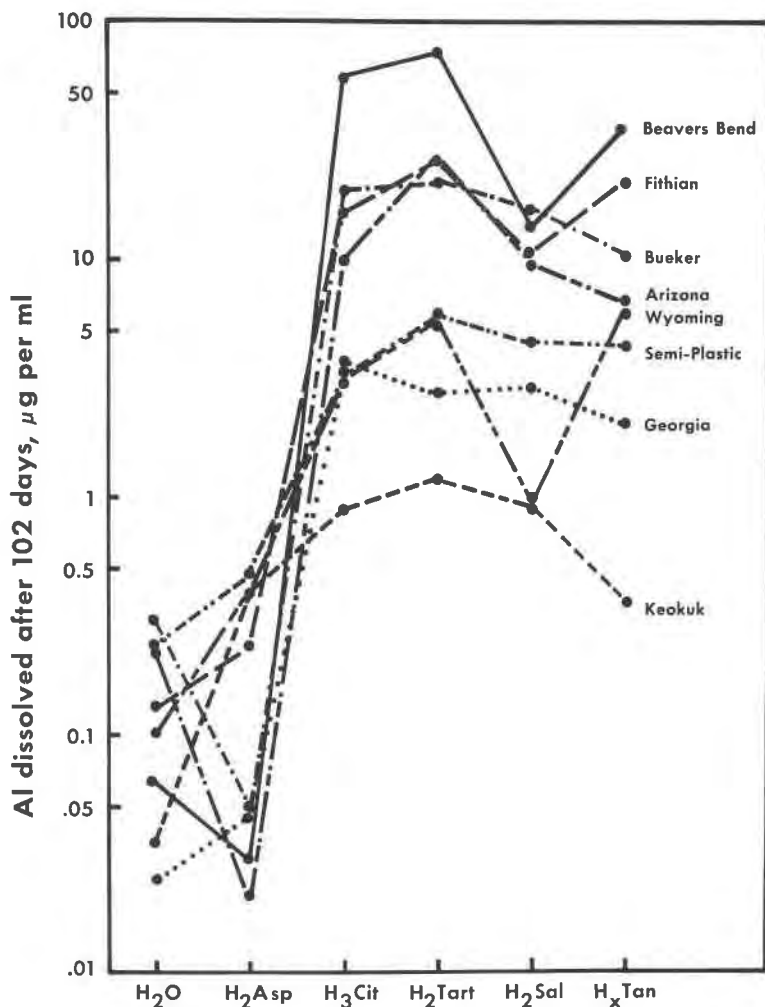


FIG. 4. Al dissolved after 102 days reaction at room temperature between clay minerals and reagents indicated. Note that solubility of Al, very scantily soluble in H<sub>2</sub>O and aspartic acid, may be 1000 times greater in a complexing acid.

solved element as a numerator was placed over the fraction of the Si dissolved. It follows that if the last ratio was 1.0, the given element and Si dissolved congruently; if the ratio was less than 1, Si dissolved in excess (incongruently); and if the ratio was greater than 1, the given element (such as Al, Ca) dissolved in excess of Si (incongruently), and Si would be relatively enriched in the undissolved solid.

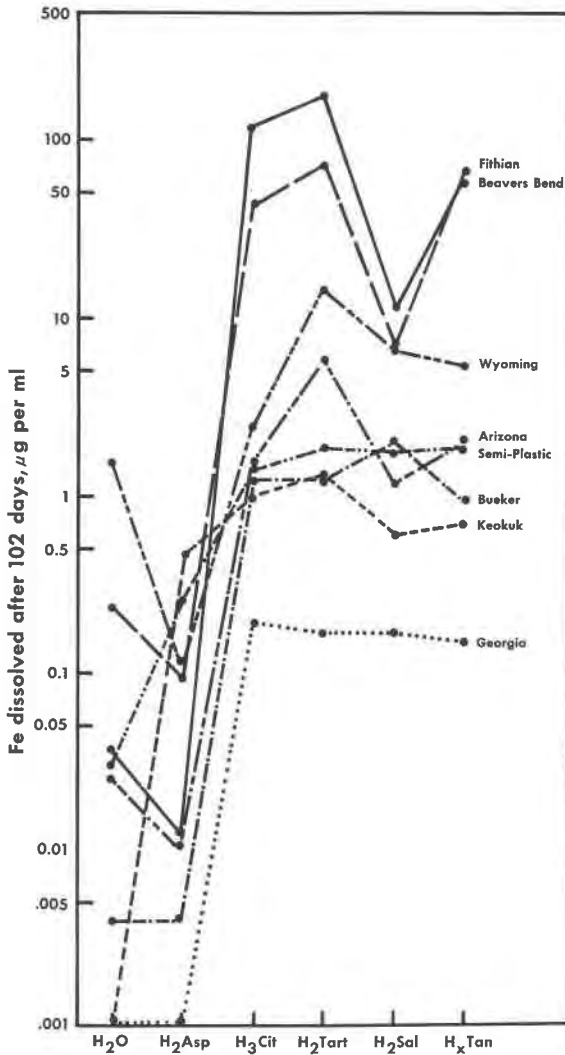


FIG. 5. Fe dissolved after 102 days reaction at room temperature between clay minerals and reagents indicated. Fe resembles Al in behavior, but shows even greater difference between solubilities in water and strongly complexing acids.

These calculations are plotted for Al/Si in Figure 6, where it is seen that Fithian and Beavers Bend illites lose notably more Al than Si in solution in citric, tartaric, and tannic acids—by factors of incongruence, 1.3 to 1.7. From Georgia kaolinite Al is dissolved by factors 1.4 to 1.5 in excess over Si, incongruently, in citric, salicylic, and tannic acids, and

congruently in tartaric acid. Bueker flint-clay kaolinite dissolves essentially congruently in all the acids used, but Keokuk kaolinite loses Si in solution more easily than Al. Likewise, the montmorillonites and semi-plastic refractory clay lose more Si than Al to solution even in complexing acids. The determinant(s) whether Si or Al is dissolved preferentially appear to be complex, or alternatively we lack perception to see them in generalization. It may be noted that illite has a higher Al:Si ratio than does montmorillonite and yields more Al in solution but, on the other hand, the kaolinites, in which Al:Si is closest to 1:1, respond indi-

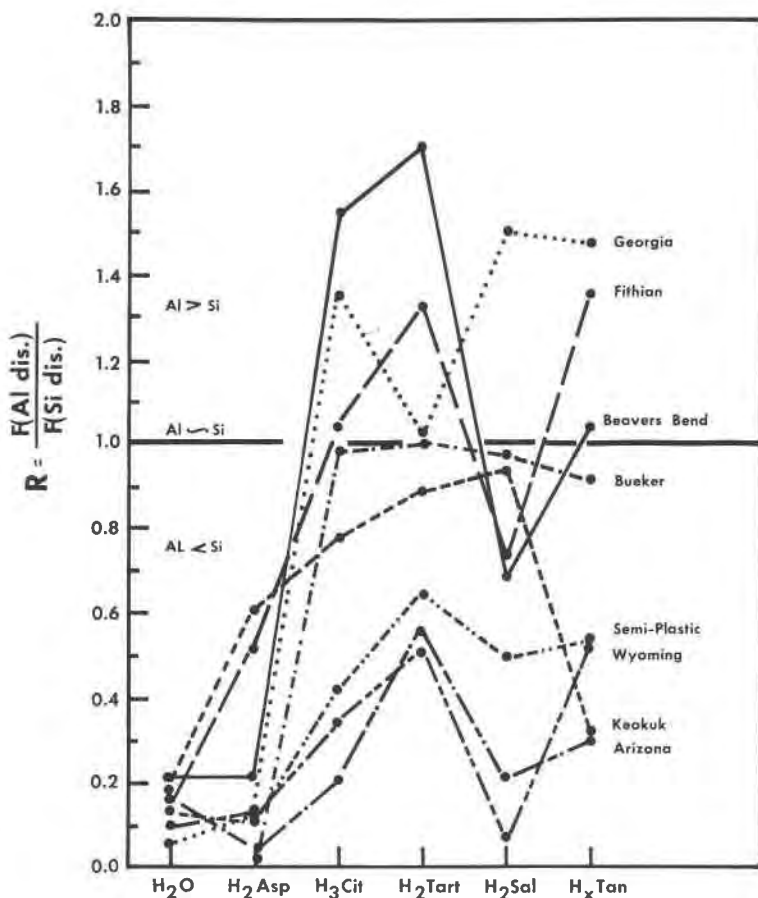


FIG. 6. The fraction of Al in the mineral that was dissolved, divided by the fraction of Si dissolved. If the quotient, *i.e.*, ratio, is 1, Al and Si dissolved congruently. If the ratio is greater than 1, Al dissolved incongruently in excess of Si; if less than 1, Si dissolved incongruently in excess of Al.



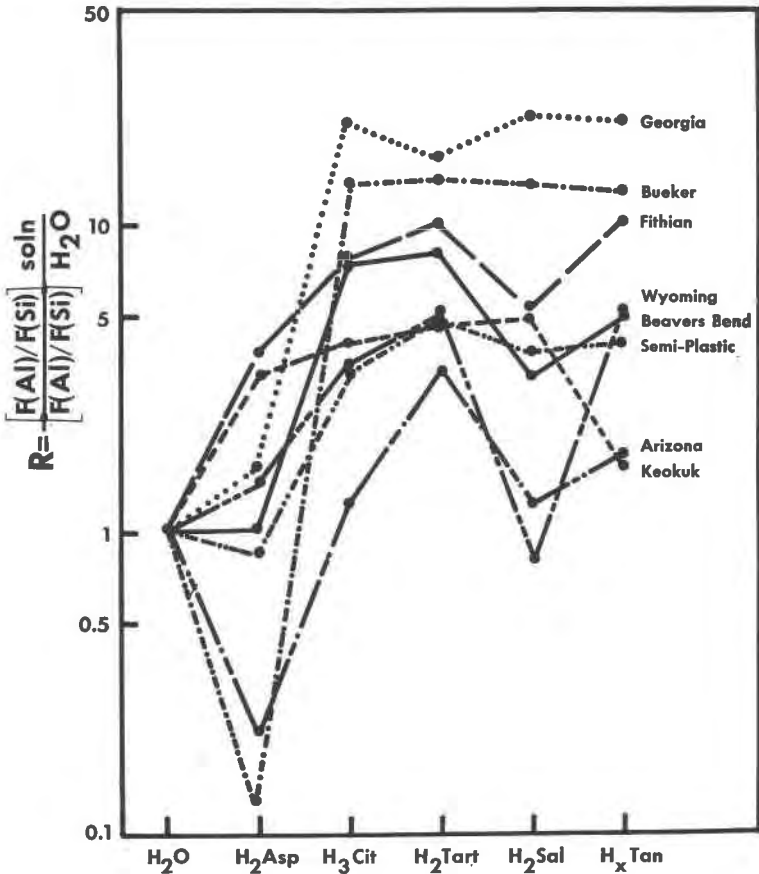


FIG. 7. The ratio of: fractional Al over fractional Si dissolved in a given clay-acid solution, to the same pair in clay-water solution. Illustrates the stronger dissolution effect by strongly complexing acids for Al than by water.

vidually  $Al > Si$  or  $Si > Al$ . Excellence of crystallinity, or crystal ordering, is not an overriding control because both Keokuk kaolinite and Beavers Bend illite are well ordered but respond dissimilarly with respect to Al:Si dissolution in organic acids.

Although the role of the clay mineral in the relative dissolution of Al versus Si is not clear, the power of the complexing acids to effect preferential dissolution of Al can be shown also by comparing their action to that of water. If the fraction of Al divided by the fraction of Si dissolved from any clay mineral in a given solvent is set above, similar fractions dissolved in water, the ensuing ratio, "R," describes the relative dissolv-

ing effect of the acid to water in terms of Al/Si, Figure 7. A ratio, "R," less than 1 means water was the more potent solvent, whereas greater than 1 shows the extent to which organic acids were more effective than water extracting Al/Si from the several clay minerals. The ratio goes as high as 20.

In contrast to the behavior of Al/Si, the ratio K/Si shows notably less difference between the several acids and water, Figure 8. Presumably K dissolves freely and independently of complexing activities. Na behaves similarly to K, though not illustrated here. Ca, as mentioned before, is strongly dissolved relative to Si by aspartic acid from all clays except Fithian illite, Figure 9.

CALCULATED DIMENSIONS OF DISSOLUTION (RADIALLY INWARD)  
BY ORGANIC ACIDS ON CLAY FLAKES

The depth of dissolution, *i.e.* inward from the periphery of clay mineral flakes, by organic acids after 102 days reaction was calculated, Table 1, assuming arbitrarily the following dimensions for uniform-size individual clay particles: kaolinites and flint clay, platelet.  $.8 \mu$  in radius (r)

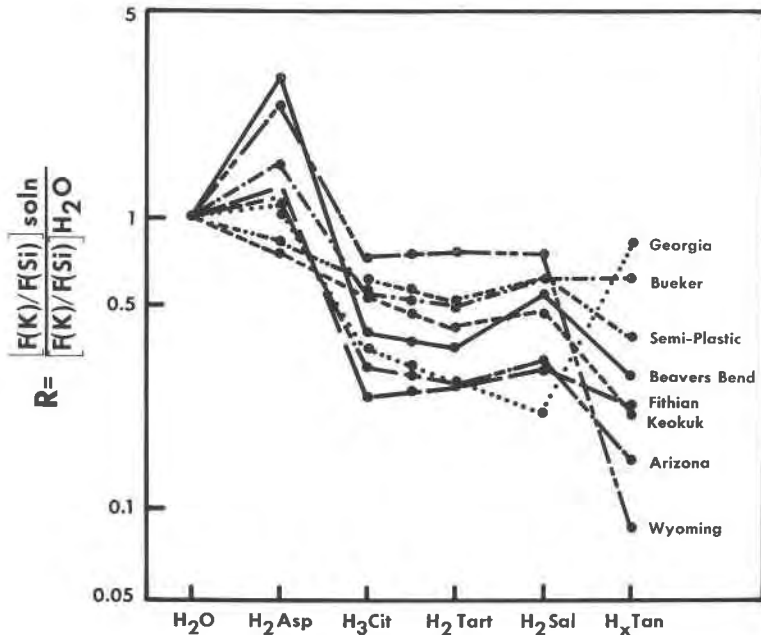


FIG. 8. Ratio of K/Si fractions dissolved in acids and water. The closer bunching of solubility ratios for K than for the framework cations is presumed to be due to dissolution of K without complexing.

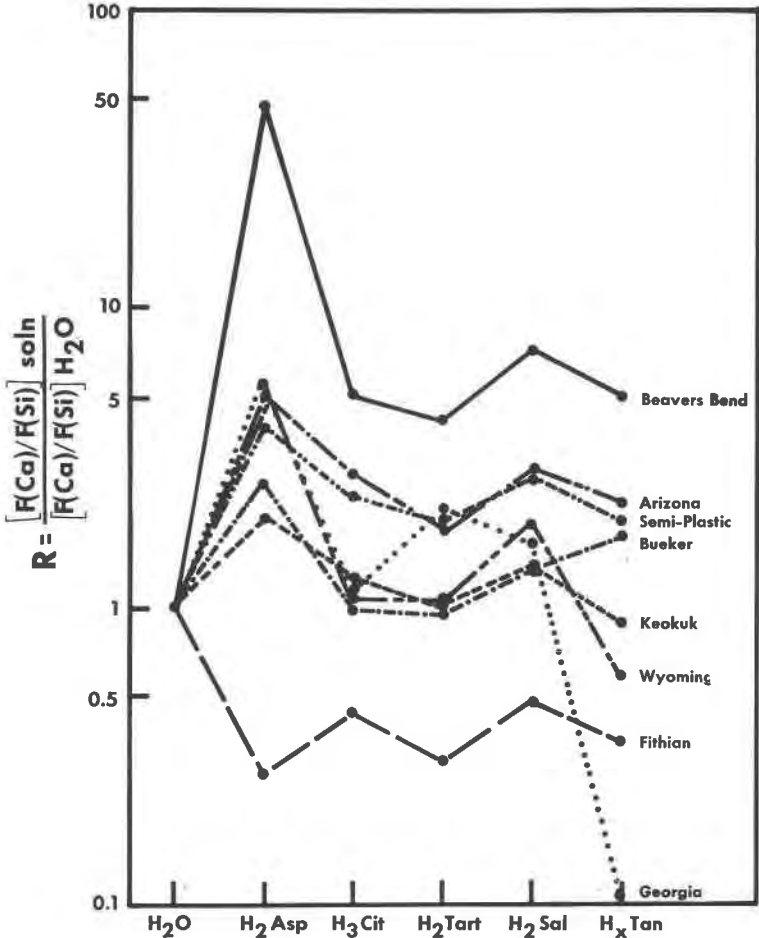


FIG. 9. Ratio of Ca/Si fractions dissolved in acids and water. Note that Ca is dissolved relatively more strongly by aspartic acid than by other reagents, except in the case of Fithian illite.

and 1000A thick; illites  $.3\mu \times 1000A$ ; montmorillonite,  $.1\mu \times 1000A$  (Huang and Keller, 1970). The depth of dissolution assumes complete removal of Si or Al to that depth. Because the clay particles are not uniform in size as postulated, and dimensions are arbitrarily assumed, and dissolution zones will be gradational rather than abruptly bounded, the calculated depths indicate comparative attack rather than absolute values.

Beavers Bend illite in tartaric acid shows greatest depth of dissolution, followed by Bueker flint clay (kaolinite). Fithian illite, Arizona

TABLE 1. CALCULATED DEPTH IN Å OF REMOVAL RADIALLY, OF Si AND Al FROM EDGES OF CLAY MINERAL PLATES OF ASSUMED RADIUS AS INDICATED, AND THICKNESS 1000 Å.

	H <sub>2</sub> O	H <sub>2</sub> Asp	H <sub>3</sub> Cit	H <sub>2</sub> Tart	H <sub>2</sub> Sal	H <sub>x</sub> Tan
(1) Bueker flint clay ( $r=0.8\mu$ )						
Si	8.96	8.88	45.2	48.2	39.0	28.1
Al	.64	.08	44.2	48.5	37.9	25.8
(2) Semi-plastic refractory clay ( $r=0.8\mu$ )						
Si	5.92	10.6	20.4	22.2	21.7	20.2
Al	.80	1.20	8.56	14.4	10.8	10.9
(3) Georgia kaolinite ( $r=0.8\mu$ )						
Si	1.12	1.36	6.48	6.16	4.64	3.36
Al	.08	.16	8.80	7.12	6.96	4.96
(4) Keokuk kaolinite ( $r=0.8\mu$ )						
Si	1.12	1.28	2.40	2.80	2.16	3.12
Al	.24	.80	1.92	2.48	2.0	.96
(5) Beavers Bend illite ( $r=0.3\mu$ )						
Si	1.98	3.45	45.3	45.2	32.4	40.2
Al	.42	.75	70.2	94.5	21.9	52.0
(6) Fithian illite ( $r=0.3\mu$ )						
Si	1.77	1.68	18.3	23.9	18.6	19.5
Al	.24	.81	18.9	31.8	13.2	26.4
(7) Arizona montmorillonite ( $r=0.1\mu$ )						
Si	2.33	4.12	21.8	23.6	20.8	13.0
Al	.40	.15	4.58	13.5	4.48	4.0
Si	1.33	1.94	6.09	7.05	8.07	7.95
Al	.13	.27	2.07	3.58	.62	4.07

montmorillonite, and semi-plastic refractory clay (kaolinite and illite) show considerable attack. Wyoming montmorillonite, Georgia kaolinite, and the outstandingly well-ordered Keokuk kaolinite, were dissolved in decreasing order. The greatest attack was some 15 to 30 times the least attack.

Less difference occurs in attack of different clay minerals by water than by organic acids.

#### GEOLOGIC AND PEDOLOGIC APPLICATIONS

In at least two ways the action of organic acids on clay minerals (and other silicates) is significant in geologic and pedologic systems: (1)

that the solubilities of framework cations, Si, Al, and Fe, are greatly increased over those in pure water, and (2) that Al may be more soluble than silica, in terms of congruency with the parent-mineral formula, in certain acid-mineral combinations.

Lovering's report (1959) of notably high concentrations of dissolved Si and Al in association with organic substances, and the accumulation of certain elements and removal of others, due to chelation or complexing, is confirmed by our experiments. Not only may rates of weathering, residual accumulation, and preferential dissolution be accelerated, but the transport by solution of generally sparingly soluble elements be facilitated. For example, the deposition of secondary, well-crystallized kaolinite, or other clay minerals, within solid rocks can be accounted for much easier geochemically if increased concentrations of Al can be moved in ground-water solutions.

Well-crystallized gibbsite in bauxite deposits, and even large portions of the bauxite itself, may develop by reason of soluble Al. Much of the bauxite in Arkansas underlies or is closely associated with lignite which, in itself, is a source of organic acids and a product of organic materials and organic-acid derivatives.

The deposition of both Al and Si minerals from solution has generally been considered to be independent of Eh. The Eh of the system can no longer be disregarded, however, if any organic compound vulnerable to oxidation or attack by bacteria is the solution complexed.

If and where Al is dissolved in excess of congruence with Si, a new view, in addition to the old one about desilication in general must be entertained. Podzols, in which the residue is rich in silica are characteristically found in an environment where humus is abundant, and therefore Al has been removed by organic complexing. That is, the "end-product" in weathering here is silica, not alumina and iron oxide, as in lateritic "end-product" weathering. "Silicate wreckage" (Keller, 1957, page 52) and parent material for siliceous, but not sandy, shales may be logically derived by organic reaction. The order of susceptibility to weathering of silicate minerals in water, which is the same as the old Rosenbusch order, may not prevail in reactions with organic acids. Aspartic acid is especially active in dissolving Ca and Mg. Other combinations of strongly complexing acids and minerals in which Al or Fe is dissolved preferentially may not follow the Rosenbusch sequence. For example, it is well known that from diabases the first mineral to be weathered is pyroxene in some environments, but it is plagioclase first in others. Indeed, a large number of statistical permutations may be set up between a half-dozen common Al-silicate rock-forming minerals and a half-dozen organic acids, in addition to water, to yield a myriad of different weathering and deposi-

tional situations. The action of organic acids and compounds on clay minerals, and other silicates, expands tremendously the geochemical interrelationship within the environments of weathering, transport, deposition, and diagenesis.

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