

THE SOLUBILITY OF SILICA IN HYDROGEN BEIDELLITE¹

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ABSTRACT

Electrodialyzed suspensions of clay minerals are viewed generally as insoluble silicates in which the exchange complex is saturated with hydrogen. An investigation of the relative activities of different exchangeable ions on beidellite clay brought to light the fact that a freshly prepared hydrogen clay containing a trace of the non-adsorbed chloride ion, when filtered, yielded a solution containing the chloride ion in association with silica rather than with hydrogen.

The filtrate from the freshly prepared suspension was clear and had a pH value of 5.5. After standing 24 hours the filtrate became cloudy and the pH value dropped to 3.5 corresponding to the concentration of acid produced by the chlorides in association with hydrogen. Analysis of the clear filtrate revealed that the chlorides were associated with silica. The amount of soluble silica in the filtrate from the clay suspension was related directly to the amount of exchangeable hydrogen in the clay. No soluble silica was present in the filtrate from clay which had been neutralized with either potassium or calcium hydroxide.

INTRODUCTION

The high solubility of silica in alkaline media and the low solubility of silica in acid media are the basis for analytical methods of determining the silica content of rocks. The chemistry of these processes tends to influence the thinking when one considers the natural weathering that reduces rocks to soil. The arid climatic conditions which permit the accumulation of bases in soils to create an alkaline condition favorable for the solution of silicates also restrict the rate of weathering because of the absence of sufficient moisture to perpetuate the process. The humid regions of soil development which provide sufficient moisture to keep chemical processes active leach away the basic elements that are released by weathering so that the resulting chemical process is acid. Reasoning from the technique of the analytical chemist one would expect the acid weathering of the humid regions to retard the solution of silicates.

There is an abundance of evidence in the literature that suggests the presence of soluble silica as a by-product of the acid weathering of soils. Ash analyses of crop plants grown on acid soils show that silica is always

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present. Silica is found in the tissue of animals, both those feeding from the products of the land and those feeding on the fish of the sea. Natural springs, river water, and sea water contain measurable amounts of silica. The formation of claypans under the acid silt loam surface soils of the humid regions suggests the possibility that the soluble products of chemical weathering in the surface may have recombined in the subsoil to produce the clay silicates that are found there. The weathering of chert fragments in acid soils attests further to the fact that solution of silicates is not confined to alkaline weathering processes.

The objective of this paper is to show that acid conditions as they occur in soils favor the solution of silica.

SOLUBLE SILICA AT DIFFERENT LEVELS OF BASE SATURATION IN BEIDELLITE CLAY

Beidellite clay was extracted from the subsoil of the Putnam silt loam by dispersion and centrifugation of the resulting suspension. The fraction less than 0.2 microns in diameter was electrodyalized to obtain the hydrogen form of the clay. Titration of the clay with calcium hydroxide gave a base exchange capacity of 70 milliequivalents per 100 g of clay. Three stock suspensions of the clay were prepared, each containing 1 g of clay per 100 ml of suspension. One suspension was of the hydrogen clay, another of hydrogen clay neutralized to pH 7 with potassium, and a third of hydrogen clay neutralized with calcium. The hydrogen clay and the neutral clays were then mixed in different proportions in flasks to give two series of clays of increasing degrees of saturation with potassium and with calcium. The resulting suspensions were filtered under pressure through collodion membranes.

TABLE 1. — SOLUBLE SILICA AS PARTS PER MILLION IN FILTRATES FROM CLAYS CONTAINING DIFFERENT AMOUNTS OF EXCHANGEABLE HYDROGEN RECIPROCAL WITH POTASSIUM AND CALCIUM

Degree of saturation of clay with hydrogen	Concentration of silica in filtrate from	
	Potassium system	Calcium system
0	2.4	2.1
5	2.7	3.4
10	3.3	3.9
20	3.7	5.8
40	5.9	7.7
60	8.8	9.7
80	13.1	13.3
90	15.7	16.3
95	16.9	17.2
100	18.1	16.3

The concentrations of silica in the filtrates from the clay were determined colorimetrically as described by Snell and Snell (1949). In filtrates from both the potassium and the calcium systems only a trace of soluble silica was present. The concentration of silica increased with increased amounts of hydrogen on the clay, approaching a concentration of 20 parts per million of silica in the filtrates from the pure hydrogen systems. The results for the series of experiments are reported in Table 1.

The results support the conclusion that acid weathering of soils favors the solution of silica from the beidellite type of clay. They also suggest that the movement of soluble silica from a zone of acid soil into a zone of more neutral soil would result in a precipitation or recombination of the silica into a less soluble form.

SOLUBLE SILICA AT DIFFERENT LEVELS OF CONCENTRATION OF RAW CLAY IN DISTILLED WATER

Raw clay from the subsoil of the Putnam silt loam was weighed into a series of flasks containing distilled water to give a range of concentrations of from 1 to 64 parts of clay per 100 ml of distilled water. The exchangeable bases, principally calcium, in the raw clay make up approximately 30 percent of the total exchange capacity, the remainder being hydrogen. After equilibrating for a period of 24 days, the suspensions were filtered and the filtrate was analyzed for silica. The results are reported in Table 2.

TABLE 2. — SOLUBLE SILICA IN FILTRATES FROM SUSPENSIONS OF RAW CLAY IN DISTILLED WATER

Grams of clay per 100 ml of water	Parts per million of silica in filtrate
1	3.2
2	6.4
4	11.5
8	14.5
16	16.2
32	18.2
64	24.4

The soluble silica in the filtrates from the clay increased in proportion to the amount of clay in the dilute suspensions, but approached a constant value in the concentrated suspensions. These results suggest that in concentrated systems there is a limit to the amount of silica that can exist in solution. However, there are at least two possible explanations of the behavior of the dilute systems. Either there was a limited amount of silica associated with the clay that would go into solution, or the overall acidity of the dilute systems was so low that it limited the quantity of silica that could be maintained in solution. The results of the previous study, in which

the amount of soluble silica was found to be associated with the amount of exchangeable hydrogen on the clay, suggest that the amount of soluble silica recorded for the dilute systems may have been limited by the amounts of exchangeable hydrogen in the systems. In any event, the naturally occurring acid clays released silica into solution, and one may conclude that the acid weathering of surface soils releases silica in solution that may later recombine with other elements to form the clays of the subsoil or may polymerize to form colloidal gels that upon drying cement the particles of the deeper horizons of soil together to form hardpans.

SUMMARY

The solubility of silica associated with beidellite clay was determined for different degrees of saturation of the clay with hydrogen. Very little soluble silica was found in filtrates from the neutral clays whether they were potassium or calcium systems. However, the solubility of silica from the clay increased with increasing amounts of hydrogen on the clay. The raw clay, which is acid as it occurs naturally, yielded appreciable quantities of soluble silica confirming the general observation that silica is soluble under acid conditions of rock weathering.

LITERATURE CITED

Snell, F. D., and Snell, C. T. (1949) *Colorimetric methods of analysis*: D. Van Nostrand Company, Inc., New York, 3rd ed., v. 2, 950 p.

DISCUSSION

M. L. Jackson. — I wonder if the removal of aluminum from the alumino-silicate structure is not partly responsible for the greater extent of release of the silica in the more acid degree of saturation? The solubility of silica which increases with acidity is of considerable interest in connection with the leaching of silica from Latosols.

C. M. Woodruff. — The pretreatment of the clay by electro dialysis did remove most of the soluble aluminum and other multivalent cations as well, leaving no bases to react with silicic acid. The results suggest the possibility that the hardpans and clay pans of soils which develop under acid conditions of weathering may be attributed to the increased solubility of silica in the surface layers following the loss of multivalent cations by acid leaching.

A. T. Perkins. — What would be the effect of adding soluble phosphate to the soil on solubility of silica? Would the phosphate precipitate the Al^{3+} and increase silica solubility?

C. M. Woodruff. — The samples were analyzed for soluble aluminum. The results showed that it amounted to less than one-half part per million. In the absence of significant amounts of aluminum in the samples that were analyzed, the effects of phosphates in precipitating aluminum would have no bearing on the results obtained.