Surface Properties
Of Silicate Minerals

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NEW MEXICO INSTITUTE OF MINING & TECHNOLOGY

Stirling A. Colgate, *President*

STATE BUREAU OF MINES AND MINERAL RESOURCES

Alvin J. Thompson, *Director*

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Introduction

The basic structural unit of all silicate minerals is a tetrahedron with a silicon atom at the center and four oxygen atoms at the corners. The oxygen-silicon distance is about 1.6 A and the oxygen-oxygen distance about 2.6 A. The different types of oxygen-silicon frameworks in the various silicates are based entirely on the combinations of the tetrahedral oxygen-silicon groups through sharing of oxygen atoms.

In recent years, infrared spectroscopy has permitted estimation of the ratio of the ionic character of the oxygen-silicon bond to be 2.3 times that of the oxygen-carbon bond. The ratio of electronegativity of the two bonds has substantiated this finding, since it amounts to 51 per cent for the oxygen-silicon bond and only 22 per cent for the oxygen-carbon bond; this means a ratio of 51 to 22, or 2.3 to 1. On this basis, it seems safe to assume that the oxygen-silicon bond is the strongest one occurring in silicate minerals.

The compositions and structures of the most important naturally occurring silicate minerals have been

TABLE 1. PHYSICAL AND OPTICAL PROPERTIES OF SILICATES

Sample	Formula	Specific Gravity	Hardness Index	Crystalline Form & Color	Angle of the optic axis (2V)	Index of Refraction (Na) $(n, w, \beta; \alpha, \beta, \gamma)$	R_1	R_2	R_3	R_4
Olivine	$(Mg, Fe)_2SiO_4$	3.26-3.40	6.5-7.0	rhombic, olive green or grayish green	88°54'	1.662, 1.680, 1.699	0.500	0.333	2.000	4.000
Forsterite	Mg_2SiO_4	3.19-3.33	6.0-7.0	rhombic, white, greenish, yellowish	–	1.635, 1.651, 1.670	–	–	–	–
Fayalite	Fe_2SiO_4	3.91-4.34	6.5	rhombic yellowish black	–	1.835, 1.877, 1.886	–	–	–	–
Augite	$Ca(Mg, Fe)(SiO_3)_2$ $[(Al, Fe)_2O_3]_x$	3.20-3.60	5.0-6.0	monoclinic, dark green to black	60°	1.712, 1.717, 1.733	–	–	–	–
Enstatite	$MgO \cdot SiO_2$	3.10-3.43	5.0-6.0	rhombic, grayish, or yellowish, or greenish	31°	1.650, 1.653, 1.658	–	–	–	–
Spodumene	$Li_2O \cdot Al_2O_3 \cdot 4SiO_2$	2.64	5.5-6.0	monoclinic, white, gray, green, pink or purple	–	1.660, 1.666, 1.676	0.500	0.333	2.000	3.600
Hornblende	*	3.0-3.5	5.0-6.0	monoclinic, dark green to black	84°	1.629, 1.642, 1.653	–	–	–	–
Muscovite	$K_2O \cdot 3Al_2O_3 \cdot 6SiO_2 \cdot 2H_2O$	2.70-3.00	2.5-3.0	monoclinic colorless or pale yellow, or gray	40°(?)	1.561, 1.590, 1.594	–	–	–	–
Beryl	$3BeO \cdot Al_2O_3 \cdot 6SiO_2$	2.60-2.90	7.5-8.0	hexagonal Green, blue yellow, or reddish	–	1.581, 1.575, –	0.917	0.306	1.638	1.600
Albite	$Na_2O \cdot Al_2O_3 \cdot 6SiO_2$	2.61-2.64	6.0-6.5	triclinic, gray or colorless	70°	1.525, 1.529, 1.536	0.500	0.313	1.600	4.000
Microcline	$K_2O \cdot Al_2O_3 \cdot 6SiO_2$	2.54-2.57	6.0-6.5	triclinic white, yellowish, gray green or red	83°	1.522, 1.526, 1.530	0.500	0.313	1.600	4.000
Quartz	SiO_2	2.59-2.65	7.0	hexagonal, trigonal, colorless or colored	–	1.544, 1.553, –	–	0.250	2.000	–

* Hornblende $Ca_3(Mg, Fe, Al)_5$ $(OH)_2 [(Si, Al)_4O_{11}]_2$

$R_1 = \dfrac{number\ of\ cations}{total\ charge\ of\ cations}$ (excluding Si)

$R_2 = $ same as R_1 (including Si)

$R_3 = \dfrac{anions}{cations}$ (including Si)

$R_4 = $ same as R_3 (excluding Si)

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determined. Table 1 lists the accepted chemical compositions and some of the more important physical and optical properties of the silicates studied.

As the oxygen-silicon ratio increases from quartz to the olivines, a greater percentage of the oxygen bonding power is available for bonding to cations other than silicon. Hence, with an increasing oxygen-silicon ratio, there is increasing oxygen-to-metal bonding. Upon the fracturing of a silicate mineral crystal, the oxygen-metal bond, which is almost entirely ionic in character, should break more easily than the stronger oxygen-silicon bond, resulting in a great^{e}r number of unsatisfied negative forces on the surface. If, then, the mineral is immersed in a liquid containing hydrogen ions, these negative forces should tend to be neutralized by hydrogen ions from solution, resulting in a change of the pH of the solution. An increase in the degree of adsorption of hydrogen ions is to be expected as the oxygen-silicon ratio in the crystal structure increases.

This study attempted to correlate the oxygen-silicon ratio for various representative silicate minerals to the adsorption of hydrogen ions. Experiments to determine the effect of surface area on this adsorption and to investigate the effect of surface iron were also conducted. It is believed that such studies of the surface properties of silicate minerals will supply pertinent information about their behavior in froth flotation systems.

EXPERIMENTAL PROCEDURE

ION EXCHANGE

Carefully selected, hand-picked samples of the minerals investigated were dry-crushed in a ceramic ball mill and sieved to obtain a —100 + 200-mesh sample. The sized samples were then run through the electromagnetic separator to remove any iron-bearing particles.

A 10-gram sample of each mineral was placed in 100 milliliters of freshly deionized water previously adjusted to a pH of 3.50 with HC1. The beaker containing the sample and the water was placed under a bell jar from which the air was displaced at once by nitrogen gas from a tank. All experiments were carried out in a nitrogen atmosphere. The sample and solution were stirred gently but continuously during the entire experiment, the stirring speed being kept about the same for all runs. Changes in pH were followed with a Beckman Zeromatic pH meter and recorded on a Heathkit servo recorder (fig. 1). The results obtained indicate that the greater part of the reaction between
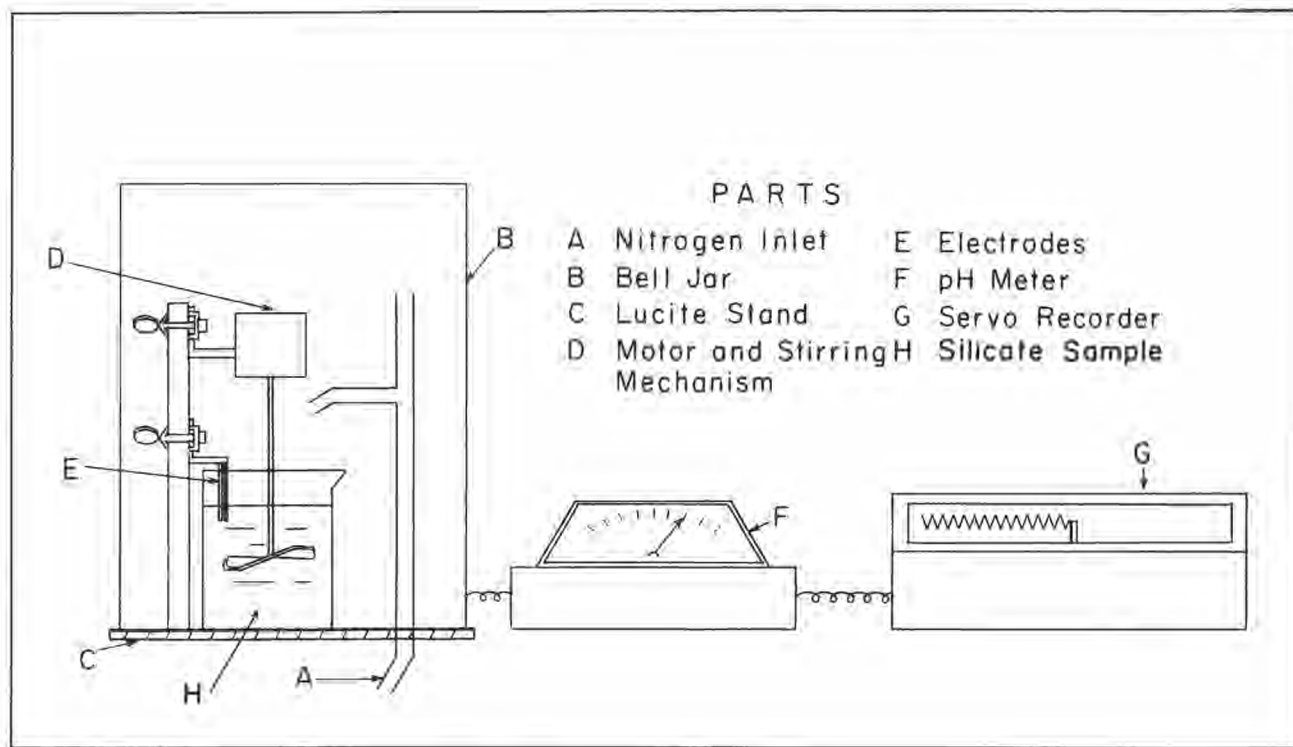

PARTS

A Nitrogen Inlet   E Electrodes
B Bell Jar   F pH Meter
C Lucite Stand   G Servo Recorder
D Motor and Stirring H Silicate Sample
   Mechanism

Figure 1

Experimental set-up

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the mineral and the acidified water occurs during the first few minutes and that an equilibrium pH is attained shortly thereafter.

The selected samples of silicate minerals tested and their classes are listed below:

MINERALS	CLASS	O:Si RATIO (calculated)
Forsterite	Olivine	4:1
Enstatite	Pyroxene	3:1
Augite	Pyroxene	3:1
Actinolite	Amphibole	11:4
Hornblende	Amphibole	11:4
Beryl	Cyclosilicate	——
Albite	Feldspar	2:1
Quartz	Quartz	2:1

Figure 2 is a plot of the change in pH with time for the eight minerals listed.

SURFACE AREA EFFECT

To test the effect of surface area, spherical glass beads, manufactured by the Minnesota Mining and Manufacturing Company, were used. With a composition comparable to feldspars, these beads are highly spherical, having .a mean radius of 0.01 centimeter and a density of 2.500 grams per cubic centimeter. The total surface area was changed by varying the total weight of the beads.

SURFACE IRON EFFECT

The effect of surface iron upon the reaction was studied using various samples of the same mineral containing different amounts of surface iron, as determined by leaching with 6N hydrochloric acid at room temperature.

DISCUSSION

ION EXCHANGE

As Figure 2 illustrates, an increase both in the change of pH and in the hydrogen ion adsorption takes place as the oxygen-silicon ratio in the crystal structure increases, the olivines experiencing the greatest change
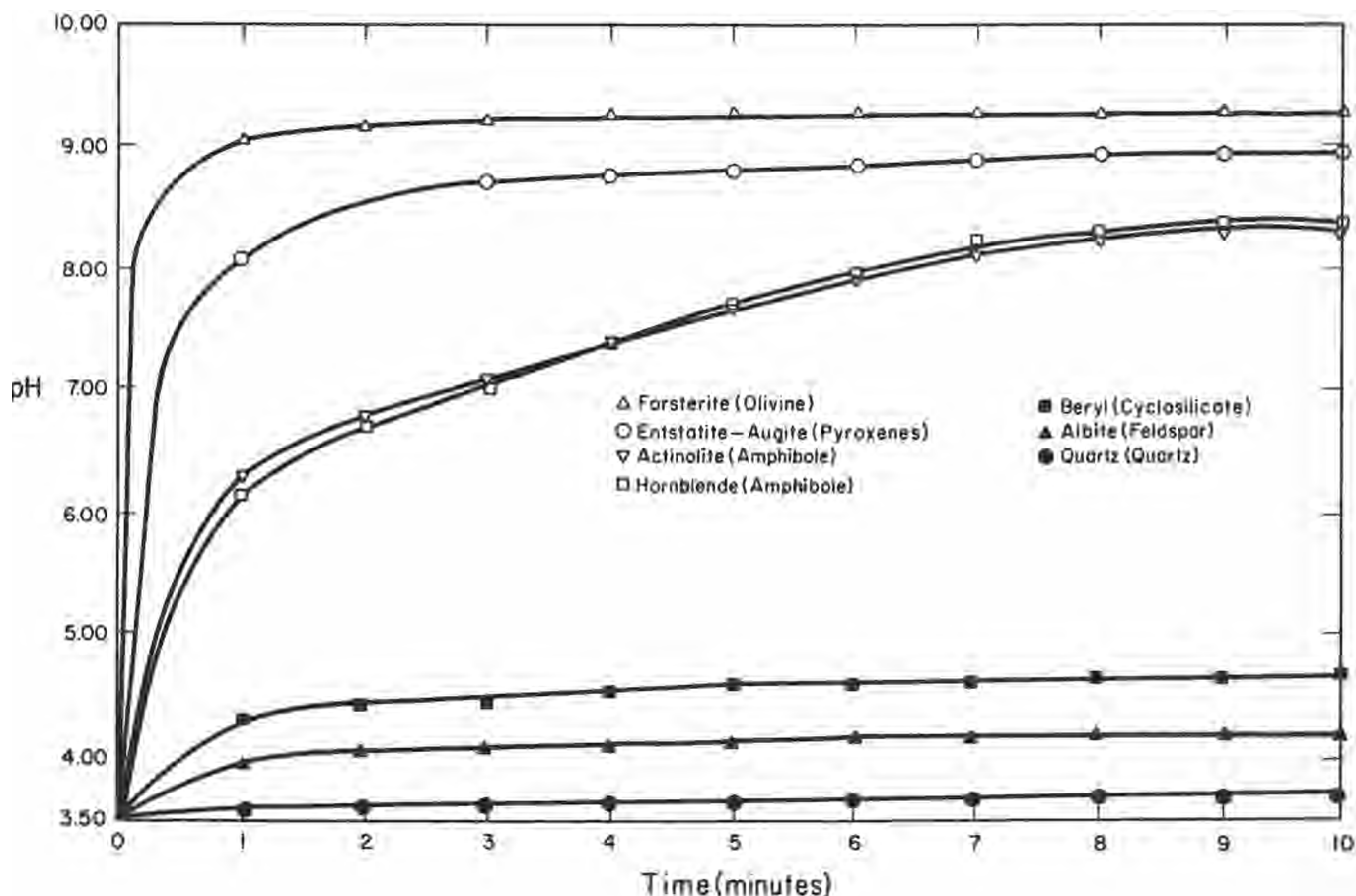

Figure 2

CHANGE OF PH AS A FUNCTION OF TIME

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in pH while quartz shows almost no change. Moreover, the greatest change in pH occurs during the first three minutes of the reaction. The results suggest that the proposed hypothesis concerning oxygen-sharing may be correct.

This attraction of hydrogen ions in some form or other to the surface of the mineral, however, does not fully explain what goes on during the reaction. There may also be an ion exchange (hydrolysis) between exposed metal ions of the lattice and hydrogen ions of

and C_2 are expected to be different for each mineral.

The results indicate that there seems to be a point beyond which increasing the surface area of the solid sample produces no further increase of pH, provided all other factors are kept constant.

SURFACE IRON EFFECT

The total change of pH and the rate of change of pH with time (dpH/dt) for the reaction seem to be greatly

TABLE 2. RESULTS OF ION EXCHANGE TESTS

MINERAL	IONS EXCHANGED				H+ IONS GOING INTO SOLID SURFACE PER LITER SOL.	−IONS GOING INTO SOLUTION PER LITER SOL.
Spodumene	Li	Ca	Mg	Na	10.0×10^{20}	12.5×10^{20}
Spodumene	Li	Ca	—	Na	5.24×10^{20}	5.53×10^{20}
Spodumene	Li	Ca	—	Na	1.9×10^{20}	1.75×10^{20}
Spodumene	—	Ca	—	Na	6.02×10^{20}	5.98×10^{20}
Spodumene	Li	—	—	Na	2.71×10^{20}	2.50×10^{20}
Spodumene	Li	Ca	—	Na	3.80×10^{20}	3.95×10^{20}
Spodumene	Li	—	—	Na	5.00×10^{20}	5.00×10^{20}
Glass beads* (feldspar)	Li	—	—	Na	2.35×10^{19}	2.36×10^{19}
Augite	—	K	—	Na	1.90×10^{20}	1.98×10^{20}
Augite	—	K	—	Na	1.90×10^{20}	2.00×10^{20}
Augite	—	K	—	Na	1.90×10^{20}	1.88×10^{20}

* 3-M, Superbrite

measured by a determination of pH

measured by a determination of ppm of ions in the liquid before and after the reaction.

water. For this reason, the crystal surface may gain additional hydrogen ions, and the liquid phase may acquire further alkalinity.

The results obtained from the tests to determine the number of ions exchanged during the reaction (summarized in table 2) show that the exchange of hydrogen for metal ions of the mineral surface is approximately equal; the principal ions exchanged in each instance are also summarized in the table. From these data, it appears that the reaction can be explained on the basis of ion exchange rather than simple adsorption.

SURFACE AREA EFFECT

Figure 3 is a plot of the change of pH versus the total surface area of the spherical beads. The same initial pH was used for each point. This plot is an exponential growth curve and follows the equation

$$\triangle pH = C_1\left(1 - e^{-C_2 \sum_{1}^{n} S_A}\right),$$

where SA is the total surface area of a bead and C_1 and C_2 are constants. C_1 can be defined as the maximum change in pH possible for the sample tested. Both C_1

affected by the amount of iron present on the surface of the solid. The results of the tests (fig. 4) seem to indicate that the more iron present, the faster the reaction and the greater the total change in pH, suggesting that in the flotation of silicate minerals, the amount of surface iron may directly affect their floatability.

CONCLUSIONS

The reaction between the silicate mineral particles and the acidified water involves mainly an exchange of metal ions for hydrogen ions on the surface of the solid, leading to an increase in pH of the aqueous phase. Physical adsorption appears to play a minor role.

The degree of reaction depends directly on the oxygen-silicon ratio of the silicate structure, being greatest for the olivines.

The reaction seems to depend on the total surface area of the solid; that is, on the number of exchange sites available.

The reaction also seems to be greatly influenced by the amount of iron present on the solid, more iron increasing the degree of reaction.
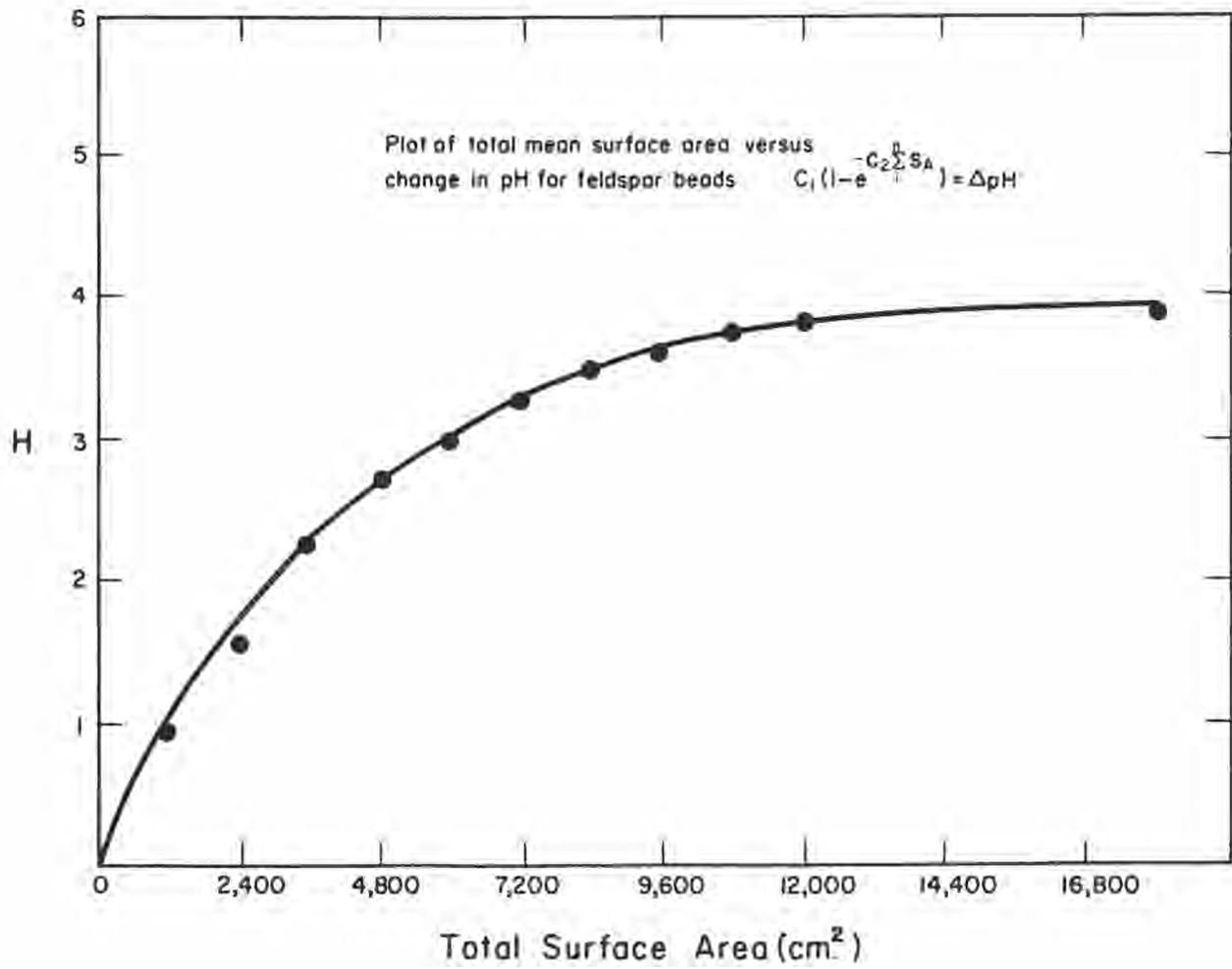
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Figure 3

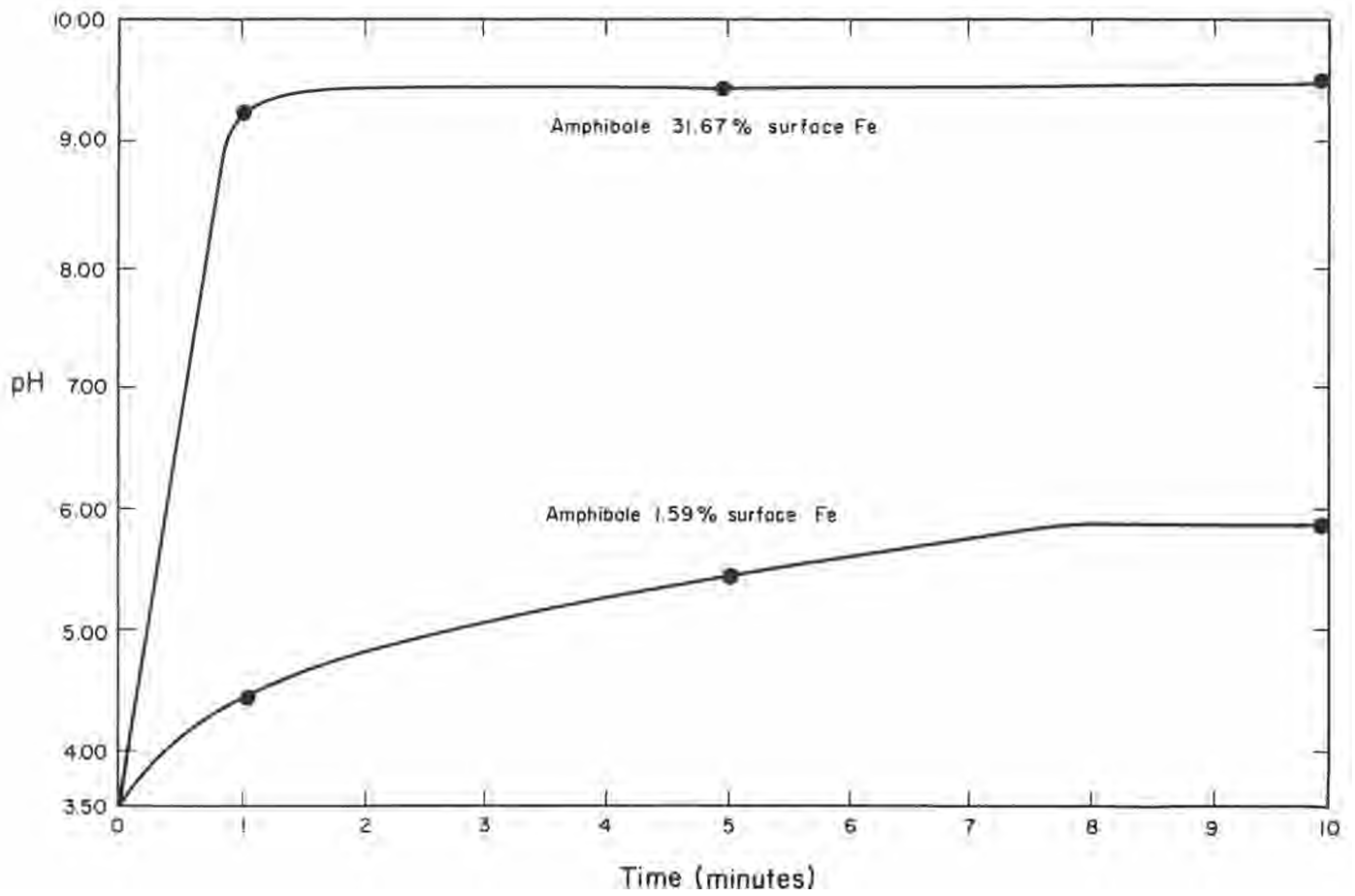PLOT OF TOTAL MEAN SURFACE AREA VERSUS CHANGE IN PH FOR FELDSPAR BEADS

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Figure 4

THE EFFECT OF SURFACE IRON UPON THE REACTION

References

Ahrens, L. H. (1954) *Quantitative spectrochemical analysis of silicates,* New York: Pergamon Press.

Berman, H. (1937) *Constitution and classification of the natural silicates,* Am. Mineralogist, v. 22, n. 5, p. 342-408.

Bragg, W. L. (1930) *The structure of silicates,* Zeitschr. Kryst., v. 74, p. 237-305.

Clarke, F. W. (1914) *The constitution of the natural silicates,* U.S. Geol. Surv., Bull. 588.

Eitel, Wilhelm (1951) *Silica melt equilibria,* New Brunswick, N.J.: Rutgers Univ. Press.

– – – – (1954) *The physical chemistry of the silicates,* Chicago: Univ. Chicago Press.

Gruner, J. W. (1931) *Structures of some silicates,* Am. Mineralogist, v. 16, n. 10, p. 437.

Leet, L. D., and Judson, Sheldon (1954) *Physical geology,* New York: Prentice Hall.