# The Dissolution of $CaMg(SiO_3)_2$ in Acid Solutions[1]

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The dissolution phenomena of synthesized diopside, $CaMg(SiO_3)_2$, and a glassy material of the same composition in an acid solution were studied. The results observed in the dissolution of the glass were as follows; the molar concentrations of Ca dissolved in the solution are equal to those of Mg throughout the dissolution of the glass. The rate at which the cations go into solutions are proportional to the surface area up to about a 60% dissolution. The dissolution behavior of silica is similar to that of cations. A residual layer rich in silica is formed, one which is no longer dissolved after the removal of the cations. The results observed in the dissolution of the crystalline diopside were as follows; there is an initial rapid dissolution of the components, followed by another process. The molar ratios of the Ca ions to the Mg ions, and of each cation to silica in the solutions, are larger than those in the solid during the course of the reaction; they are especially large in the initial dissolution stage. An essential feature of diopside dissolution is that the Ca ions are more readily removed from the crystal than are the Mg ions. This fact is also confirmed in the natural diopside crystal. While the rates of the dissolution of the cations are not affected by the concentrations of HCl and $HClO_4$, the concentration of $H_2SO_4$ does have an influence. Diopside cannot be dealt with as a single species participating in the heterogeneous reaction because its various components show selective dissolution. The mechanism of the dissolution of diopside will be discussed in connection with its structure.

Dissolution studies of minerals in various solutions have been made mainly from the practical point of view.[2,3] Only a few studies have been reported on the silicate structure and its reactivity in solution. Luce *et al.*,[4] however, who studied the dissolution of serpentine, forsterite, and enstatite, reported on the relationship between the silicate structure and the diffusion coefficients of silicon and magnesium.

In a previous paper,[5] the dissolution phenomena of olivine in various acid solutions were reported.

Pyroxenes can be divided, according to the crystal systems, into orthorhombic and monoclinic pyroxenes. The essential feature of all pyroxenes, however, is the linkage of $SiO_4$ tetrahedra by sharing two out of four corners, thus forming continuous chains with the composition of $(SiO_3)_n$,[6] in contrast to the olivine structure with fundamental isolated $SiO_4$ tetrahedra. Diopside, which has the monoclinic form, was studied crystallographically by Warren and Bragg,[7] and its unit cell was found to be $4[CaMg(SiO_3)_2]$.

In this experiment, the dissolution phenomenon of diopside in acid solutions was studied in comparison with that of a glassy material of the same composition in order to obtain some information concerning the reactivity and the solid structure.

## Experimental

*Materials.* In the present study, diopside was synthesized, because natural diopside always contains some iron. The synthetic method was as follows. Firstly, appropriate amounts of CaO, MgO, and $SiO_2$ corresponding to the composition of $CaMg(SiO_3)_2$ were thoroughly mixed with ethyl alcohol. Then the mixture was heated at 1450 °C and quenched in cold water to obtain a glassy material. The glass was crushed in an agate mortar and mixed well. The operations of mixing, melting, and rapid cooling were repeated three times. The glass was heated overnight at 1100 °C to obtain a completely crystallized phase. The powder X-ray diffraction pattern is in complete agreement with the NBS natural diopside data.[8] Electron microprobe analysis[9] showed homogeneous particles (about 5 $\mu$). The synthesized diopside and the glass were ground in an agate mortar and then fractionated by suspension in methyl alcohol. Two kinds of particle sizes of the glass were obtained: one was 20—40 $\mu$, and the other was 40—80 $\mu$. The particle size of the synthesized diopside was 20—40 $\mu$, but strict uniformity of size could not be obtained because of the brittle property of the particles.

In this study, a finely powdered sample of a natural diopside was used; it had been obtained from Gongen-yama, Ehime Prefecture. This diopside had the following chemical composition[10]: $SiO_2$, 51.86; $TiO_2$, 0.20; $Al_2O_3$, 1.02; $Fe_2O_3$, 0.99; FeO, 1.73; MnO, 0.02; MgO, 17.09; CaO, 25.24; $Na_2O$, 0.08; $K_2O$, 0.06; $H_2O(-)$, 0.25; $H_2O(+)$, 1.88%. The atomic percentages of Mg, Fe, and Ca were 46.6, 4.0, and 49.4 respectively.

*Reagents, Equipment, and Measurements.* All the chemicals used were of an analytical-reagent grade. The apparatus used in the present study was the same as that described in the previous paper[5] except for the volume of the reaction vessel, which was 200 ml in the present study. The powdered sample (100—200 mg) was dispersed, with small amounts of water, in 100 ml of an acid solution, after which the mixture was stirred at 600 rpm. The rate of the dissolution of the sample was not affected by stirring in the range from 150 to 1200 rpm. Aliquots of the solution were

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[1] Read at the Symposium on Geochemistry of the Geochemical Society of Japan and the Chemical Society of Japan, Sendai, Sept., 1972.

[2] C. W. Corrence, *Clay Minerals Bull.*, **26**, 249 (1961).

[3] R. Wollast, *Geochim. Cosmochim. Acta*, **31**, 635 (1967).

[4] R. W. Luce, R. W. Bartlett, and G. A. Parks, *ibid.*, **36**, 35 (1972).

[5] I. Sanemasa, M. Yoshida, and T. Ozawa, This Bulletin, **45**, 1741 (1972).

[6] W. A. Deer, R. A. Howie, and J. Zussaman, "Rock-Forming Minerals," Vol. 2, Longmans, London (1965), p. 2.

[7] B. Warren and W. L. Bragg, *Z. Krist.*, **69**, 68 (1928).

[8] Nat. Bur. Stand. Monograph 25, sec. 5, 17 (1967).

[9] Measurements were made by Dr. S. Aramaki of The Earthquake Research Institute of The Univ. of Tokyo.

[10] Sample was given by and its analysis was done by Mr. H. Haramura of The University of Tokyo.

pipetted out at various reaction times and immediately filtered through a membrane-filter (0.45 $\mu$ in pore size), and the filtrates were submitted to chemical analysis. The silica was determined spectrophotometrically using the silicomolybdate yellow method. The calcium and magnesium were determined by atomic absorption measurements after the addition of a lanthanum buffer[11] to avoid interference due to the presence of silica.

## Results and Discussion

*Dissolution of $CaMg(SiO_3)_2$ Glass.* Figure 1 shows the relationship between the concentrations of Ca dissolved in HCl solutions and the reaction times under various conditions. The molar concentrations of Mg which are leached into the solutions were found to be nearly equal to those of Ca at any time under varying experimental conditions. Figure 2 shows the relationship between the concentrations of the dissolved silica and the reaction times under different conditions. From Figs. 1 and 2, it may be noted that the dissolution behavior of the cations and silica is virtually the same. The concentrations of silica, however, are much lower than those of the cations when their relative contents in the glass are taken into account. After the summation of Ca and Mg, the molar ratios to $SiO_2$ in the solution are almost constant; the ratio is approximately 6 throughout the reaction. Most of the cations in the sample were depleted by the reaction after reaching a constant value of about 4.25 mM. The broken lines in Fig. 1 show the results of experiments in which twice the amount of the sample was used as that represented by the solid lines. The constant value of 8.5 mM of the dotted lines in Fig. 1 is just twice as high as that of the solid lines, regardless of the sample size, the acid concentration, and the temperature. On the other hand, only 15% of the entire silica of the sample was dissolved when the concentration of dissolved silica approached a value of 1.4 mM, as represented by the solid lines in Fig. 2. No colloidal silica was found under the present experimental conditions. When taking 200 mg of a 40—80 $\mu$ size sample, the concentrations of silica in the 0.1 and 1 N HCl solutions are 2.3 and 2.6 mM respectively after reaching a constant value. These values are significantly lower than the value of 2.8 mM calculated from the 100 mg sample. This suggests that the dissolution of a silica-rich layer formed by the reaction depends on the acid concentration as well as on the specific surface area of the sample.

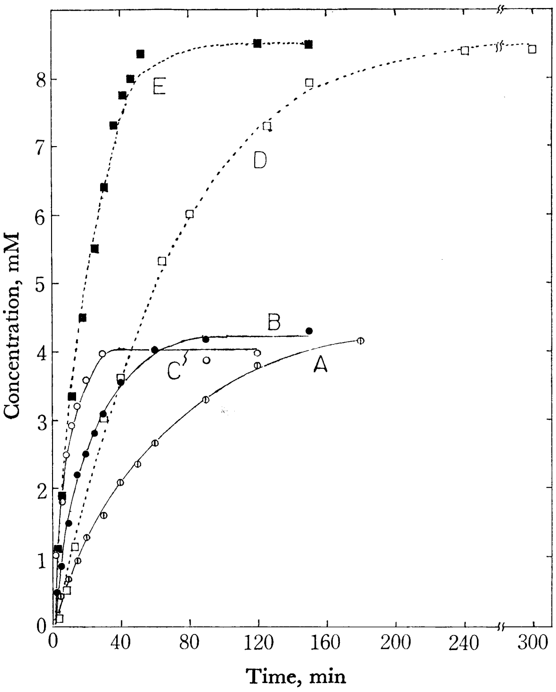

Fig. 1. Dissolution of calcium from the glass when taken 100 mg of 20—40 $\mu$ sample in 0.1 N HCl at 5 (A), 15 (B), and 25 °C(C) and when taken 200 mg of 40—80 $\mu$ sample in 0.1 N (D) and 1 N (E) HCl at 10 °C.

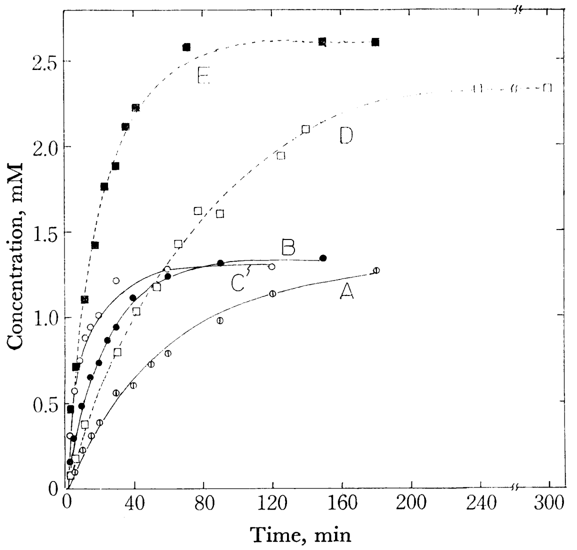

Fig. 2. Dissolution of silica from the glass. Each mark corresponds to that in Fig. 1.

Since the silica of the glass does not affect the dissolution process of the cation, regardless of the particle size and other experimental conditions, the cations in the glass may be considered to be independent parts of the solid. Consequently, the rate of the dissolution of the cation can be treated in the same way as in the case of olivine,[5] in which

$$-\mathrm{d}w/\mathrm{d}t = k_0 s C \qquad (1)$$

where $w$ and $s$ indicate the weight and the surface area of the "particle" which remains at the reaction time, $t$, respectively; where $k_0$ is the rate constant per unit area, and where $C$ is the concentration of the reactant. Equation (2) may be derived from Eq. (1) as has been described in a previous paper;[5]

$$1-(1-\alpha)^{1/3} = 1/3\, k W_0^{-1/3} t \qquad (2)$$

where $k$ is a constant and where $\alpha$ has the following definition;

$$\alpha = (W_0 - W)/W_0 = (\Delta W)_{t,\mathrm{sol}}/W_0$$

where $W_0$ is the weight of the sample taken at time zero and where $(\Delta W)_{t,\mathrm{sol}}$ is the weight loss of the cation in the sample at time $t$, as can be determined by

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[11] R. Nakagawa, M. Nanbu, and Y. Ohyagi, *Nippon Kagaku Kaishi*, **1**, 60 (1972).

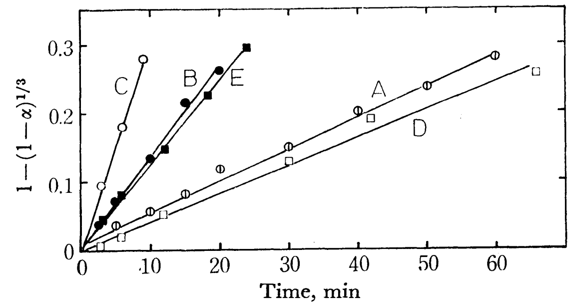

Fig. 3. Plots of dissolution rate of calcium from the glass according to Eq. (2). Each mark corresponds to that in Fig. 1.

the concentrations of the cations in the solution. The plot of $1-(1-\alpha)^{1/3}$ *vs.* *t* is shown in Fig. 3. As a matter of convenience, the plots are limited only to the case of the dissolution of Ca, but there is no distinction between Ca and Mg. Figure 3 gives straight lines up to about a 60% dissolution of the cations of the glass. This suggests that the rates of the dissolution of cations are directly proportional to the surface area of the solid sample. The relationship between the slopes of the straight lines in Fig. 3 and the reaction temperature is illustrated by the Arrhenius plot shown in Fig. 4. The apparent activation energy is found to be 16 kcal/mol.

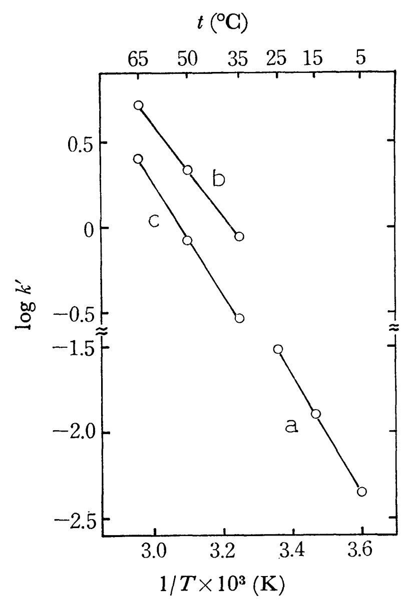

Fig. 4. Arrhenius plots for the dissolution of cation from the glass and diopside.
a: Ca from the glass, b: Ca from diopside, C: Mg from diopside.
In the case of the glass, $k'$ corresponds to $1/3\,kW_0^{-1/3}$ in Eq. (2), while in the case of diopside, $k'$ is estimated from the slopes in the plots of square concentration of each cation against time in Fig. 6 and is then expressed in $\text{mM}^2$/hr.

In order to give a more detailed explanation of the mechanism of the dissolution process of the cations of the glass, experiments were performed in which the cations were added at time zero. The results of these investigation are shown in Fig. 5. The concentrations of Ca and Mg added alternatively to a 0.1 N HCl solution at time zero were 3.5 and 1.99 mM respectively. From Fig. 5 it is evident that the added cation of Ca or Mg does not affect the dissolution of the Ca and Mg of the glass.

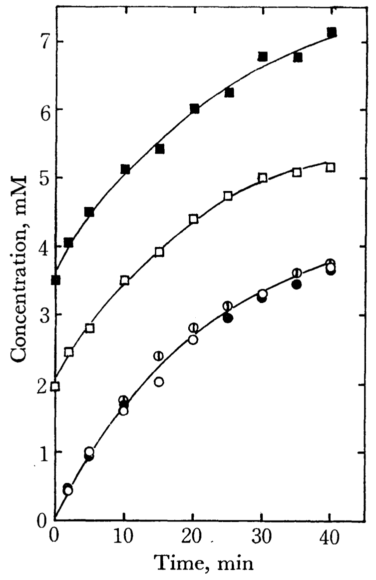

Fig. 5. Effect of added calcium, 3.50 mM (■) and magnesium, 1.99 mM (□) on the rate of dissolution of cation from the glass by using 0.1 N HCl at 15 °C.
○: none added, ⦶: Ca when Mg added, ●: Mg when Ca added.

Some of the results obtained in the present study are suitable to illustrate the mechanism of the dissolution of the glass in an acid solution. When cations on the surface of the glass pass into the solution by means of a reaction at the interface, hydrated protons diffuse into the solid and are adsorbed on negatively-charged oxygen ions. Then, cations of the glass, in which they are distributed at random and are undistinguishable from each other, are transported to the solution, thus leaving cavities. This is followed by a transportation to the bulk solution, involving diffusion through the residual layer of the silica. A part of the hydrated protons contained in the cavities can be used to break up the silica chain to be dissolved. The broken chains thus formed can be recombined by hydrogen bonds in various directions to form a three-dimensional framework such as silica gel. An X-ray examination of the sample after the reaction shows a broad peak corresponding to silica gel (22—23° as $2\theta$ in Cu$K_\alpha$). Therefore, the dissolution of the silica of the glass appears to be accompanied by that of the cations.

According to Bircumshaw,[12] a reaction between a solid and a solution generally comprises the following steps:

(a) the transportation of solute molecules to the interface,
(b) adsorption on the surface,
(c) reaction on the surface,
(d) the desorption of reaction products, and
(e) the recession of the products from the interface.

In addition to these steps, (f) the diffusion process

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[12] L. L. Bircumshaw and A. C. Riddiford, *Quart. Rev.*, **6**, 157 (1952).

through the residual layer formed by the reaction, must be considered in the present case. The rate of dissolution of the cations of the glass up to about 60% is considered to be controlled by step (c) in view of the following experimental results: the stirring speed has no influence on the rate, the activation energy is quite high (16 kcal/mol), the rate obeys Eq. (2) and not the so-called parabolic law, and additional cations have no influence on the rate. However, the rate of the dissolution of the cations over 60% is gradually lowered below the value anticipated from Eq. (2). This may be attributable to the influence of the diffusion process of the cations through the residual layer of silica, the thickness of which is increasing.

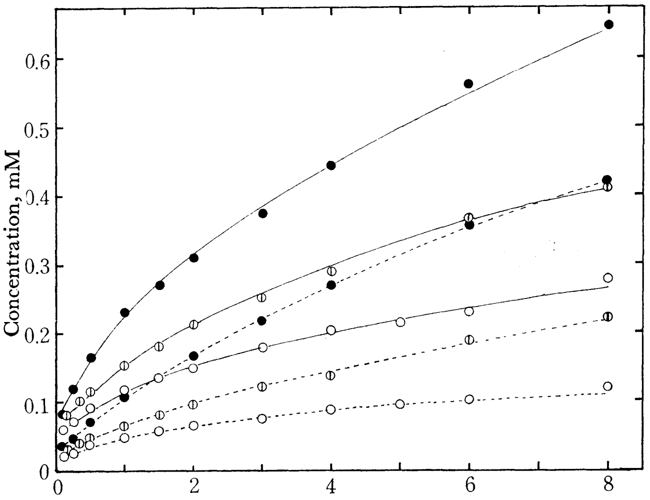

Fig. 6. Dissolution of calcium (solid) and magnesium (broken) from diopside in 0.1 N HCl at 65 (●), 50 (⦶) and 35 °C (○).

*The Dissolution of Diopside.* Figure 6 shows the concentrations of Ca and Mg which are leached from 200 mg of the synthetic diopside with 0.1 N HCl solutions at 35, 50, and 65 °C. The molar ratios of Ca/Mg in the solutions are greater than unity, and are especially high in the earlier part of the reaction, in which the ratios are in the range from about 2 to 3. In order to ascertain the effect of the temperature on the rate of the dissolution of cations, the square concentrations of Ca and Mg in the solution are plotted against the time for the sake of convenience. Straight lines are thus obtained for Ca, while in the case of Mg linear plots can be drawn after 2 or 3 hr. The relationship between the slope of the straight line for each cation and the reaction temperature is illustrated in Fig. 4. According to the Arrhenius plot, the apparent activation energies for Ca and Mg can be estimated from Fig. 4 to be 12 and 15 kcal/mol respectively. This suggests that the rate of the dissolution of Mg is affected by the temperature change more intensively than that of Ca.

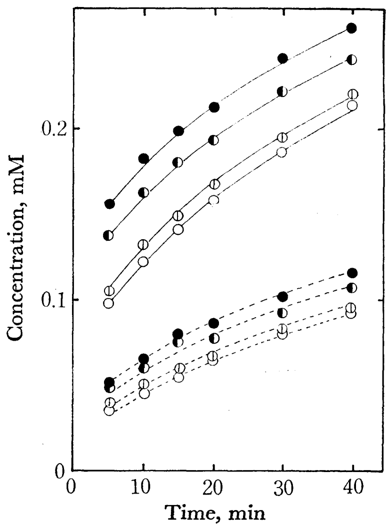

Fig. 7. Effect of HCl concentration on the dissolution of calcium (solid) and magnesium (broken) from diopside at 65 °C. ●, 1; ◐, 0.5; ⦶, 0.2; ○, 0.1 N.

In order to investigate the effect of the acid concentration on the dissolution of diopside, experiments were carried out at 65 °C by using HCl solutions of concentrations ranging from 0.1 to 1 M. From the results, it can be seen that the concentration of HCl solutions in this range has no influence on the rate of the dissolution of either Ca or Mg during the course of the reaction (8 hr), but is reflected only by the initially-dissolved amount of the cations. This effect was investigated in more detail by varying the concentrations of HCl solutions, with emphasis on the earlier part of the reaction (Fig. 7). It can be seen from Fig. 7 that variations in the acid concentration affect the initially-dissolved amount of Ca more intensively than that of Mg. There is an initial rapid increase in the concentration of each cation, an increase which cannot be followed by lowering both the reaction temperature and the acid concentration. The results in the $HClO_4$ solutions ranging from 0.1 to 2 N are almost the same as those obtained

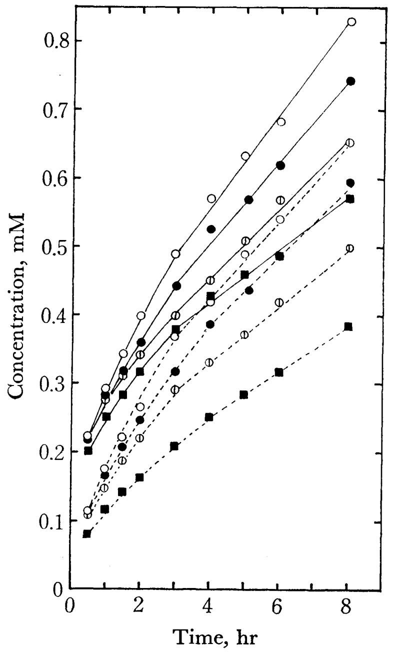

Fig. 8. Effect of $H_2SO_4$ concentration on the dissolution of calcium (solid) and magnesium (broken) from diopside at 65 °C.
○, 2; ●, 1; ⦶, 0.5; ■, 0.1 N.

in HCl. On the other hand, the results in $H_2SO_4$ solutions (see Fig. 8) are different from those in HCl and $HClO_4$ solutions. From Fig. 8, it is evident that the rates of the dissolution of cations increase with an increase in the concentrations of acid, and that the concentrations of cations increase linearly with the time in the later steps of the reaction. There is also a difference in the reactivities of the cations; that is, the amount of Ca initially dissolved is about three times larger than that of Mg. Responsible for the specific action of $H_2SO_4$ appear to be the $HSO_4^-$ species in the solution, as has also been observed in the dissolution of olivine[5] and gibbsite.[13]

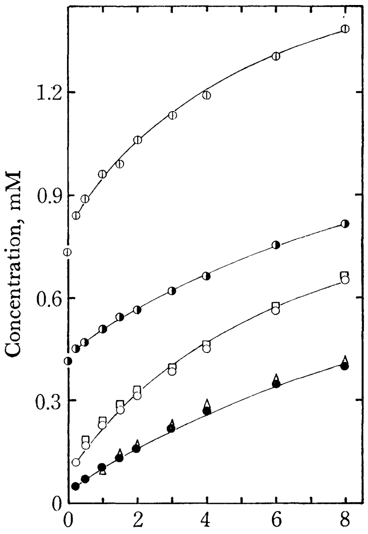

Fig. 9. Effect of added calcium, 0.73 mM (⦶) and magnesium, 0.411 mM (◑) on the rate of dissolution of cation from diopside in 0.1 N HCl solutions at 65 °C.
○, Ca when none added; □, Ca when 0.411 mM of Mg added; ●, Mg when none added; △, Mg when 0.73 mM of Ca added.

In order to obtain information about the leaching of cations from diopside, experiments were carried out in which known amounts of Ca or Mg ions were added at the start of the reaction by using 0.1 N HCl solutions at 65 °C. From the results of these investigations (shown in Fig. 9), it can be seen that, on the addition of 0.73 mM of Ca or 0.41 mM of Mg, the concentration of each cation observed at any time is equivalent to the sum of the concentrations of the added and the dissolved cations. In the presence of a twofold concentration of each cation, this sum is lowered to about 10% in each case. However, this value is not precise because of an uncertainty in the determination of such a high concentration of added cation.

As the next step, the dissolution of silica from diopside was investigated. Figure 10 shows the results of a series of experiments which were carried out at 65 °C by using HCl and $H_2SO_4$ solutions of varying concentrations. Colloidal silica was not detectable under these experimental conditions. It can be seen from Fig. 10 that the rate of the dissolution of silica increases with an increase in the acid concentration.

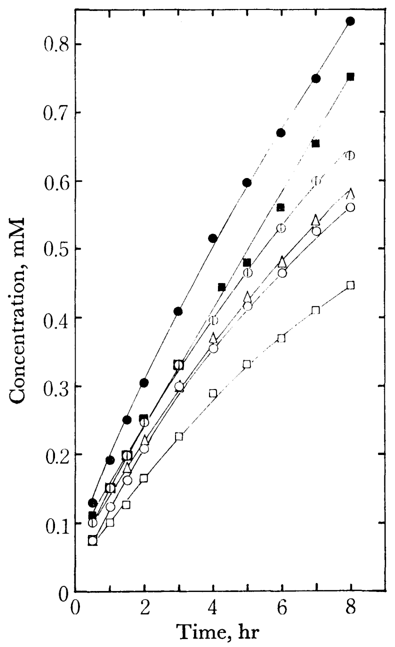

Fig. 10. Dissolution of silica from diopside at 65 °C.
HCl: ●, 1; ⦶, 0.5; ○, 0.1 N. $H_2SO_4$: ■, 1; △, 0.5; □, 0.1 N.

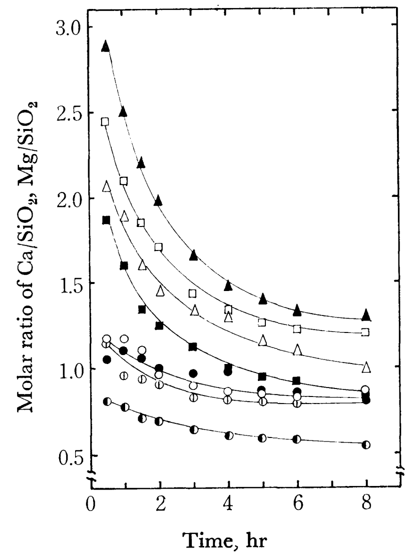

Fig. 11. Molar ratio of $Ca/SiO_2$ and $Mg/SiO_2$ in solution dissolved from diopside at 65 °C.
$Ca/SiO_2$: ■, 1 N HCl; □, 0.1 N HCl; △, 1 N $H_2SO_4$; ▲, 0.1 N $H_2SO_4$.
$Mg/SiO_2$: ◐, 1 N HCl; ⦶, 0.1 N HCl; ●, 1 N $H_2SO_4$; ○, 0.1 N $H_2SO_4$.

The dependence on the time of the molar ratios of Ca or Mg to $SiO_2$ in the solutions under the same experimental conditions is shown in Fig. 11. From the figure it can be seen that the dissolution is selective not only with respect to Ca and Mg, but also between cations and silica, since the ratio of each cation to silica in the solid is 0.5. At higher concentrations of HCl, however, the molar ratio of $Mg/SiO_2$ in solution approaches that in the solid because the dissolution of silica is enhanced by an increase in the acid concentration, while that of the cation is not.

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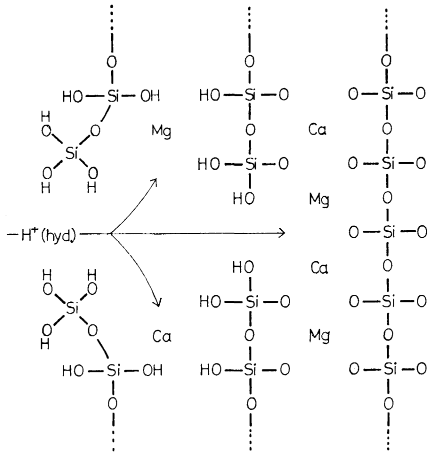
[13] A. Packter and H. S. Dhillon, *J. Chem. Soc., Ser. A*, **1969**, 2588.

*Discussion on the Dissolution of Diopside.* The dissolution of diopside can be divided into two processes: one is the initial rapid dissolution, which cannot be followed even if the reaction temperature and the acid concentration are both lowered, while the other is the successive dissolution after the initial dissolution. Cations to be dissolved in the solution must be liberated from the negatively-charged oxgen ions surrounding them. On the solid surface, the distances of Ca–O and Mg–O will be slightly different from those in the "perfect" diopside lattice, as was pointed out by Pryor *et al.*[14] in their dissolution study of ferric oxide. In the diopside crystal, moreover, there are good cleavages parallel to the direction of the silica-chain arrangement. Consequently, the dissolution takes place most readily at the surface, where the energy required for dislodging the cations is smaller than in the interior. At the same time, silica is dissolved, but its amount is considerably smaller than that of the cation (see Fig. 11). This selective dissolution of silica might be due to its chain structure, which consists of $SiO_4$ tetrahedra. Consequently, after the removal of the cations, the silica-chain, parts of which are broken, remains, forming a residual layer containing Si–OH groups which probably shows almost the same directional arrangement as the crystal. Judging from the selective dissolution between Ca and Mg, a part of the Mg may be contained in this residual layer. The problem is, however, to find out from which direction of the silica-chain, *i.e.*, parallel or at right angles, .the reactants (hydrated protons) enter into the solid and in which direction the soluble products go out. If the existence of cleavages in the diopside parallel to the direction of the chain is assumed, the reaction may proceed predominantly at right angles to the chains, and a dissolution process of the kind shown in Scheme 1 may be suggested. In the diopside, silica-chains are combined to one another by an equal number of Ca and Mg ions. After the rapid removal of cations and the severance of the silica-chain, which may be caused by the adsorption of hydrated protons on the negatively-charged oxygen ions of the solid surface, the hydrated protons enter the solid through the open parts of the chain; a part of them permeate parallel to the chains, and the remainder, at right angles. As cations are removed from the chains, these are set free just as if opening a "fastener" and undergo successive hydrolysis to be dissolved. The hydrated protons participating in the reaction may mainly be consumed in the hydrolysis reaction, because the rates of the dissolution of cations are not affected by the concentration of acid, while that of silica is dependent on the acidity. Consequently, the dissolutions of the cations and the silica appear to be independent of each other. In this respect, there is a substantial difference between diopside and its glass (see Figs. 1, 2, and 11). This difference may be attributed to residual silica layers in diopside which are not in a suitable arrangement to be recombined in the three-dimensional networks as they are in the glass.



Scheme 1.

It is problematical whether or not the rates of dissolution of cations are controlled by their diffusion process through the channels in the residual silica layers, as is shown in Scheme 1. It is, however, somewhat difficult in our present study to clarify the rate-determining step for two reasons. One reason is the uncertainty of the sample size. A part of the synthesized diopside probably consists of agglomerates of particles of a smaller size; therefore, the particle size is not uniform. The other is that the amounts of cations dissolved into the solution are only 8% or less of the solid under the selected experimental conditions. Regardless of these disadvantages, though, the results summarized below can be used in examining the problem of diffusion:

(1) The concentrations of the cations increase almost linearly with $t^{1/2}$ except for the initial rapid stages in HCl and $HClO_4$ (Fig. 6).
(2) While in $H_2SO_4$ they increase almost linearly with $t$ in the later stages of the reaction (Fig. 8).
(3) The apparent activation energies of Ca and Mg are different from each other (Fig. 4).
(4) The addition of cations has no influence on the rates of dissolution (Fig. 9).
(5) Although the molar ratio of $Mg/SiO_2$ in the 1 N HCl solution approaches that in the solid as the reaction proceeds (Fig. 11), the dissolution mode of Mg is not changed.

Of these results, (1) seems to indicate that the rate of the dissolution of cations is controlled by the diffusion of the reactants and/or the reaction products. On the other hand, (2), (4), and (5) do not seem to show that the rate of dissolution of cation is controlled by the diffusion of the reaction products. Furthermore, (2) and (3) seem to give little evidence that the rate of dissolution of cations is controlled by the diffusion of the reactants. Consequently, the present experimental results do not necessarily support the assumption that the rate of the dissolution of cations is controlled by the diffusion process only. A better picture or a more detailed mechanism of acid-reactivity of diopside in connection with the silica-chain structure could be obtained by employing a single crystal.

In the dissolution of cations, there is an important and substantial difference between diopside and its

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[14] M. J. Pryor and U. R. Evans, *J. Chem. Soc.*, 3330 (1947).

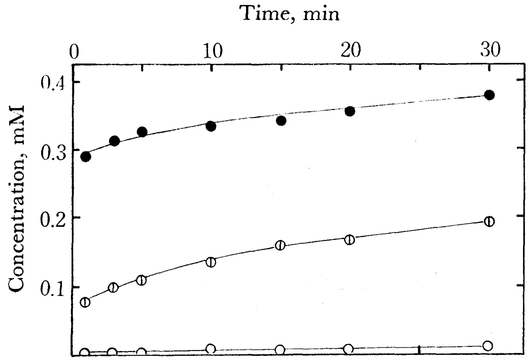

Fig. 12. Dissolution of calcium (●), magnesium (⦶), and iron (○) from natural diopside in 0.1 N HCl at 65 °C.

glass. That is, in the glass the dissolution behavior of Ca and that of Mg are undistinguishable from each other, while in diopside Ca is more readily dissolved than Mg, especially in the preliminary stage of the reaction. This phenomenon appears to be essential for diopside; it was also observed in the dissolution of natural diopside (see Fig. 12). It can be seen from Fig. 12 that the concentration of Ca which is initially dissolved is more than three times larger than that of Mg, and that the initial rapid dissolution of the cations is promoted because of the large specific surface area of the pulverized sample, with its abundant cleavages. The reason why Ca in diopside passes more readily into a solution than does Mg might be attributable, when this case is compared with that of glass, to the difference in the states of the cations. That is to say, in the glass a fused structure is "frozen in" in which Ca and Mg are randomly distributed and in which the cations are kept as far apart as possible by vigorous thermal movement and by mutual repulsion. On the other hand, in diopside Ca is surrounded by eight, and Mg by six oxygen atoms. However, we cannot offer a more detailed explanation of the situation.

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