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The Dissolution of Olivine in Aqueous Solutions of Inorganic Acids[1]

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The dissolution of olivine was studied in aqueous solutions of inorganic acids at temperatures of 35, 50, and 65°C in order to obtain basic information about the alteration and leaching processes in acid hot spring regions. The rates of dissolution have been determined by measuring the change in the concentrations of silica, magnesium, and the total iron leached in the solutions as a function of the time. Olivine dissolved in stirred aqueous solutions of 0.05—2N perchloric, hydrochloric, and sulphuric acids without any selective dissolution of components in the mineral. The rate at which olivine dissolved was found to be two-thirds of the reaction order with respect to the sample-powder (10—20 μ in diameter) weight (*i.e.*, first order with respect to the surface area) and to decrease in the order of $H_2SO_4 \gg HCl > HClO_4$. HSO_4^- enchanced the rate remarkably. The complexing affinity of the anions did not play an important part in the reaction with olivine powder.

Studies of the leaching of chemical elements from rocks and minerals from various points of view have been reported by many investigators.[2–5] Olivine is a common and important rock-forming mineral; it is particularly characteristic of basic and ultrabasic igneous rocks. The minerals of the olivine group are very susceptible to hydrothermal alteration, low-grade metamorphism, and weathering.[6] As a result, olivine has been observed to be more altered than magnetite, the glassy part, and pyroxene in natural altered rocks found in acid hot spring regions.[7]

Heterogeneous reactions between inorganic materials and aqueous solutions are important in discussing the alteration and weathering of rocks and minerals and the formation of ores and thermal waters. The kinetics of the dissolution of ferric oxide[8,9] and gibbsite[10] in aqueous solutions have been studied, while silicate minerals,[11–13] especially feldspars,[14,15] have also been investigated, mainly from the practical point of view. It is somewhat difficult to study the rate at which silicate minerals go into a solution, since their structures are complicated.

The olivine group has a fundamental structure in silicate minerals, which consist of independent $[SiO_4]^{4-}$ tetrahedra linked by divalent ions in a six-fold coordination. Leaching and hydrothermal alteration experiments of olivine have been carried out in order to clarify the origin of chemical species in natural waters,[16] the mechanism of weathering,[17] and alteration at high temperatures.[18]

The object of this paper is to obtain some basic information on the kinetic behavior of olivine in acid hot spring regions.

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Experimental

Materials. The olivine (Fo_{91}) sample used in the present study was separated from dunite[19] from Takashima, Karatsu, Saga Prefecture. The dunite was constituted of 94, 3, 3, and 0.1 vol% of olivine, spinels, clinopyroxene, and orthopyroxene respectively. The dunite was crushed in a steel Ellis mortar and powdered in an agate mortar. The fraction containing particles between 150 and 200 meshes was collected, washed with distilled water, and dried at 110°C. After this treatment, the olivine was separated by means of an iso-dynamic magnetic separator (S. G. Frantz Co., INC, Model L-1). This fraction will hereafter be called Sample A. This sample was further finely pulverized in an agate mortar again. This powder was sized by sedimentation in distilled water to 10—20 μ, and then dried at 110°C. This fraction will be called Sample B. The chemical composition of the olivine sample is given in Table 1. According to Dr. Kiyoshi Ishibashi, who examined this olivine sample microscopically, the spinel-group minerals (mainly chromite) and pyroxene comprized less than 3—4 vol%, while no hydrous minerals were observed as alteration products. The purity of the sample is sufficient for the present purposes.

TABLE 1. CHEMICAL COMPOSITION OF OLIVINE

Constituent	Content (%)
SiO_2	40.24
TiO_2	trace
Al_2O_3	0.24
Fe_2O_3	1.50
FeO	8.29
MnO	0.15
MgO	50.03
CaO	trace
Na_2O	trace
K_2O	trace
H_2O (−)	0.0
H_2O (+)	0.0
P_2O_5	trace
Total	100.45

Reagents. All the chemicals used were of analytical-reagent quality. Concentrated perchloric, hydrochloric, and sulphuric acid were diluted to the desired concentrations with redistilled water; the concentrations of the acid in the dilute solutions were determined by titration against a standard sodium carbonate solution. A sodium hydrogen sulphate solution (0.45 M) was prepared by adding a sodium hydroxide solution to a sulphuric acid standard solution in just half the volume required for neutralization.

Equipment. The reaction vessel was a 300-m*l* glass flask with four necks; the center neck was connected with a water-sealed stirring rod, while the other three were fitted with a nitrogen-introducing tube, a condenser, and a stopper. The stoppered neck was utilized to add the sample powder to the aqueous solution and to take out the sample solution. The container was placed on a water bath thermostated at from 35—65°C to 0.1°C.

Measurements of Reaction Kinetics. The sample powder, 200 mg for Sample A and 100 mg for B, was disperesed in 200 m*l* of an aqueous acid solution in the reaction vessel, into which nitrogen gas had previously been introduced continuously. The mixture was then stirred at about 1000 rpm. The preliminary experiments revealed that the stirring speed, over the range of about 200 to 2000 rpm, did not affect the rate of dissolution of the sample powder. After various times, 2-m*l* aliquots of the sample solution were withdrawn for analysis in the following manner. When Sample A was used, the stirring was stopped for 30 sec before each desired time. The sample particles were allowed to settle on the bottom of the reaction vessel; then the supernatant was pippetted off at the prescribed time, and it was submitted to chemical analysis. On the other hand, when Sample B was used, a portion of the reaction solution containing sample particles was pippetted off immediately at each desired time with continuous stirring. The mixture was then filtered and washed with redistilled water through a membrane filter(having a porous size of 0.45 μ) with suction into a 25-m*l* volumetric flask.

Chemical Analysis of the Reaction Solution. The silica was determined photometrically by the silico-molybdate yellow method.[20] We found no colloidal silica under the present experimental conditions. The total iron was estimated photometrically with α,α'-dipyridyl after the reduction of all the iron to the ferrous state using sodium thioglycolate. The magnesium was determined by the Xylidyl blue-II[21] photometric method,[22] with some modifications.

Results and Discussion

The Amount of Each Element Dissolved from Olivine. Tarutani[16] reported, in his leaching studies in the pH range from 1.5 to 10 with or without organic acid (EDTA and citric acid), that olivine dissolved in the same ratio as that in the mineral into a solution of pH 1.5 and into solutions with the organic acids except at pH 10. However, his experiments lacked sufficient data, since his major attention was devoted to the effects of organic acids on the leaching process. On the contray, Hoppe,[17] who studied the question from the view of the weathering of rocks, assumed the presence of a residual layer rich in iron.

Figures 1, 2, and 3 show how amounts of silica,

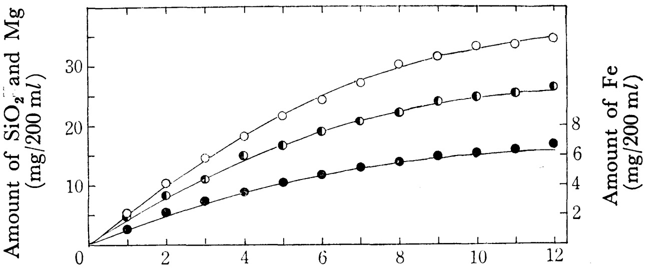

Fig. 1. Change in the amounts of silica, magnesium, and iron dissolved in a 0.1 N $HClO_4$ solution at 50°C with the time of reaction.
○: SiO_2 ◐: Mg ●: Fe

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[19] K. Ishibashi, *Mem. Fac. Sci., Kuyshu Univ.*, **20**, 85 (1970).

[20] T. Tarutani, *Nippon Kagaku Zasshi*, **77**, 743 (1956).

[21] Xylidyl blue-II is a commercial product with the chemical formura of 1-Azo-2-hydroxy-3-(2,4-dimethylcarboxyanilido)-naphthalene-1′-(2-hydroxybenzene).

[22] I. Iwasaki, M. Yoshida, S. Yoshida, H. Neriishi, and M. Sato, read at the 21st Annual Meeting of the Chemical Society of Japan, Osaka, Apr., 1968. (Preprints II, p. 896).

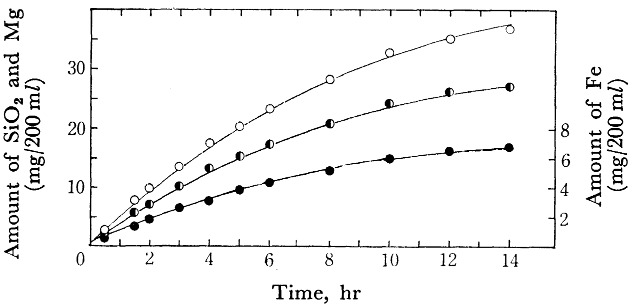

Fig. 2. Change in the amounts of silica, magnesium, and iron dissolved in a 0.1 N HCl solution at 50°C with the time of reaction.
○: SiO_2 ◐: Mg ●: Fe

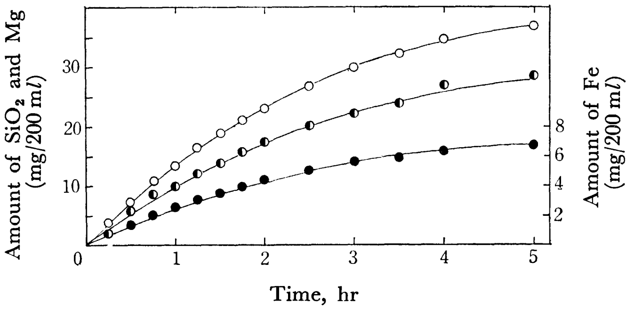

Fig. 3. Change in the amounts of silica, magnesium, and iron dissolved in a 0.1 N H_2SO_4 solution at 50°C with the time of reaction.
○: SiO_2 ◐: Mg ●: Fe

magnesium, and iron dissolved from olivine (Sample B) increase against the time of the reaction in 0.1 N perchloric, hydrochloric, and sulphuric acid solutions (200 m*l*) at 50°C.

The initial amount of each component presented in the olivine sample, W_0, can be calculated from Table 1, *i.e.*, 40.2 mg as SiO_2, 30.2 mg as Mg, and 7.49 mg as Fe for 100 mg of Sample B. Table 2 shows the amount of each component dissolved in a 0.1 N perchloric acid solution at different times, $(\Delta W)_{sol}$, and the ratios of each $(\Delta W)_{sol}$ to W_0. The amount of Fe is the sum of Fe^{2+} and Fe^{3+}. The $(\Delta W)_{sol}/W_0$ ratios for SiO_2, Mg, and Fe in solution are shown to be in fairly good agreement at any time of reaction. This suggests that olivine is dissolved in an acid inorganic solution without any selective dissolution of the components in the mineral, as was pointed out by Tarutani.[16] The selective dissolution of silica and magnesium, resulting in a residual layer rich in iron, was not observed under the present experimental conditions.

TABLE 2. AMOUNT OF EACH COMPONENT DISSOLVED
Reaction conditions: 0.1 N $HClO_4$, 200 m*l*, sample B, 100 mg, temp. 50°C

Time (hr)	Components					
	SiO_2		Mg		Fe	
	(a)	(b)	(a)	(b)	(a)	(b)
1	5.52	0.14	0.94	0.16	1.14	0.15
2	10.5	0.26	8.20	0.27	2.18	0.29
3	14.8	0.37	11.1	0.37	2.90	0.39
4	18.3	0.46	15.0	0.50	3.58	0.48
5	21.6	0.54	16.8	0.56	4.24	0.57
6	24.4	0.61	19.0	0.63	4.70	0.63
7	27.2	0.68	20.6	0.68	5.18	0.69
8	30.2	0.75	22.6	0.75	5.64	0.75
9	31.6	0.79	24.0	0.80	5.94	0.79
10	33.4	0.83	24.8	0.82	6.22	0.83
11	33.8	0.84	25.4	0.84	6.36	0.85
12	34.6	0.86	26.4	0.87	6.66	0.89

(a): $(\Delta W)_{sol}$, mg. (b): $(\Delta W)_{sol}/W_0$

Dissolution Rate of Olivine. When the reaction at the solid surface is the rate-determining step, the reaction rate, dw/dt, is said to be given by the following equation:[23]

$$-dw/dt = k_0SC \tag{1}$$

where w and S indicate, respectively, the weight and the surface area of the particles remaining at the reaction time, t, where k_0 is the rate constant per unit of surface area, and where C is the concentration of the reactant. Spherical particles of W_0 grams, the average radius of which is r_0, are used as the initial material. The rate can be shown by Equation (2):

$$-dw/dt = 3k_0W_0^{1/3}W^{2/3}C/r_0d_s \tag{2}$$

where d_s is the specific gravity of the solid. As $3k_0W_0^{1/3}C/r_0d_s$ is constant, we can obtain Equation (3) by integrating Eq. (2):

$$W_0^{1/3} - W^{1/3} = 1/3\,kt \tag{3}$$

where k is constant. By substituting Eq. (3) for $W=W_0(1-\alpha)$, we obtain:

$$1-(1-\alpha)^{1/3} = 1/3\,kW_0^{-1/3}t \tag{4}$$

Since $1/3\,kW_0^{-1/3}$ is a constant, we can obtain a straight-line relationship by plotting $1-(1-\alpha)^{1/3}$ *vs.* t.

From the definition of α,
$\alpha=(W_0-W)/W_0=(\Delta W)_{t,sol}/W_0$, where $(\Delta W)_{t,sol}$ is the weight loss of the mineral into a solution at time t. Olivine, $(Mg, Fe)_2SiO_4$, dissolves into aqueous solutions of acids to form soluble aquo-magnesium and ferrous (ferric in part) cations and silicic acid.[24] Theoretical-

TABLE 3. THE AMOUNT OF EACH COMPONENT DISSOLVED AND THE WEIGHT LOSS OF OLIVINE

Run no.	Amount of each component dissolved (mg)				Weight loss of olivine (mg)
	SiO_2	MgO	FeO	Total	
I	15.59	18.90	3.87	38.36	39.05
II	45.45	60.53	12.35	121.33	125.05
III	22.25	28.30	5.84	56.39	58.05
IV	53.62	66.93	14.00	134.55	139.70

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[23] T. Kagiya, "Kinetic Studies in Chemical Reactions" (in Japanese), Kagakudojin, Tokyo (1970), p. 398.

[24] E. Weitz, H. Frank, and M. Schuchard, *Chem. Ztg.*, **74**, 256 (1950).

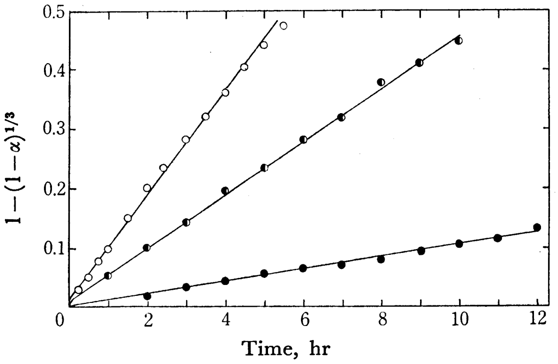

Fig. 4. Dissolution of olivine in a 0.1 N $HClO_4$ solution at 35, 50, and 65°C. Plots of $1-(1-\alpha)^{1/3}$ *vs.* time.
●: 35°C ◐: 50°C ○: 65°C

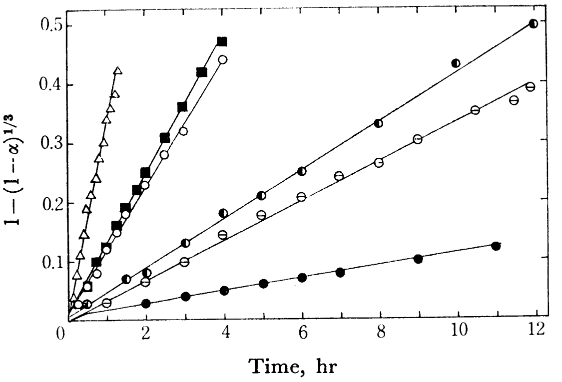

Fig. 5. Dissolution of olivine in 0.1 N HCl and H_2SO_4 solutions at 35, 50, and 65°C.
Plots of $1-(1-\alpha)^{1/3}$ *vs.* time.
●: 35°C ⊖: 35°C
◐: 50°C HCl ■: 50°C H_2SO_4
○: 65°C △: 65°C

ly, the sum of the components in a solution should be equal to the weight loss of the solid. The results obtained, given in Table 3, confirmed the material balance among them. Thus, $(\Delta W)_{t,\mathrm{sol}}$ is equal to the sum of the amounts of each component dissolved in the solution at time t. The amounts of the other components in olivine are negligibly small compared with those of the three components. The plots of $1-(1-\alpha)^{1/3}$ against time t, in 0.1 N perchloric, hydrochloric, and sulphuric acid solutions at 35, 50, and 65°C, are shown in Figs. 4 and 5, which give straight lines up to about 85% dissolution. These results suggest that olivine powder (10—20 μ) reacts with well-stirred aqueous perchloric, hydrochloric, and sulphuric acid solutions according to a two-thirds reaction order with respect to the powder weight; that is, the reaction is first-order with respect to the surface area. It may be seen from Figs. 4 and 5 that the rate at which olivine goes into $HClO_4$ solutions is almost the same as that at which it goes into HCl solutions, but it is apparently enhanced in H_2SO_4 solutions under the same reaction conditions.

The Estimation of the Activation Energy. The relation between the slopes of the straight lines in Figs. 4 and 5 and the reaction temperatures is illustrated in Fig. 6 according to the Arrhenius plot. The apparent activation energy, 14 Kcal/mol, obtained for the reaction with $HClO_4$ is similar to that for the reaction with HCl. For the reaction with H_2SO_4, it is somewhat higher, *i.e.*, 16 Kcal/mol. That is, the enhanced rate of the reaction with a sulphuric acid solution corresponds to the increase in the pre-exponential term in the Arrhenius equation.

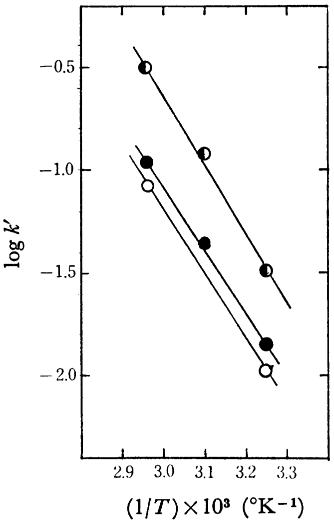

Fig. 6. Arrhenius plots for the dissolution of olivine in $HClO_4$, HCl, and H_2SO_4 solutions. k' corresponds to 1/3 $k\,W_0^{-1/3}$ in Eq. (4).
○: $HClO_4$, ●: HCl, ◐: H_2SO_4

In the subsequent experiments, Sample A was used; its particle size was larger than that of Sample B. The rate of the reaction was measured by estimating only the total iron dissolved in the solution at various times. The rate of dissolution was interpreted by comparing it with the slopes of straight lines for the range where a plot of the amount of total iron against the time is linear.

Effect of the HSO_4^- Ion. The dissolution curves at 50°C for $HClO_4$ with a concentration of 0.05—2 N, HCl with one of 0.05—1 N, and H_2SO_4 with one of 0.05—1 N are illustrated in Figs. 7, 8, and 9 respectively. The straight lines break early in the reaction at an about 5% dissolution. These breaks are also observed in the cases of silica and magnesium. No explanation for these bends can be offered at the

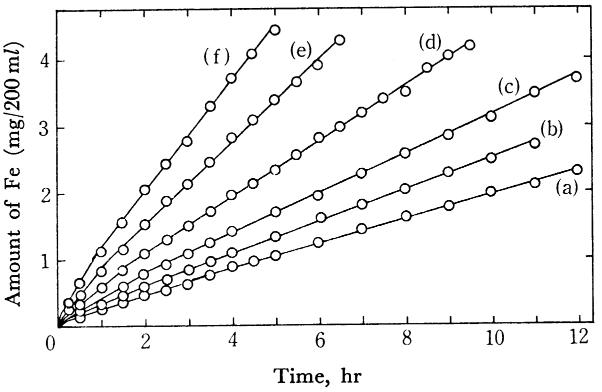

Fig. 7. Change in the amount of iron dissolved in $HClO_4$ solutions with various acid normalities at 50°C.
(a): 0.05, (b): 0.1, (c): 0.2, (d): 0.5, (e): 1, (f): 2

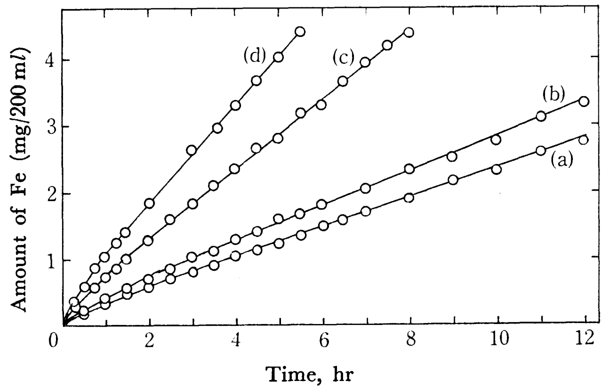

Fig. 8. Change in the amount of iron dissolved in HCl solutions of various acid normalities at 50°C.
(a): 0.05, (b): 0.1, (c): 0.5, (d):1

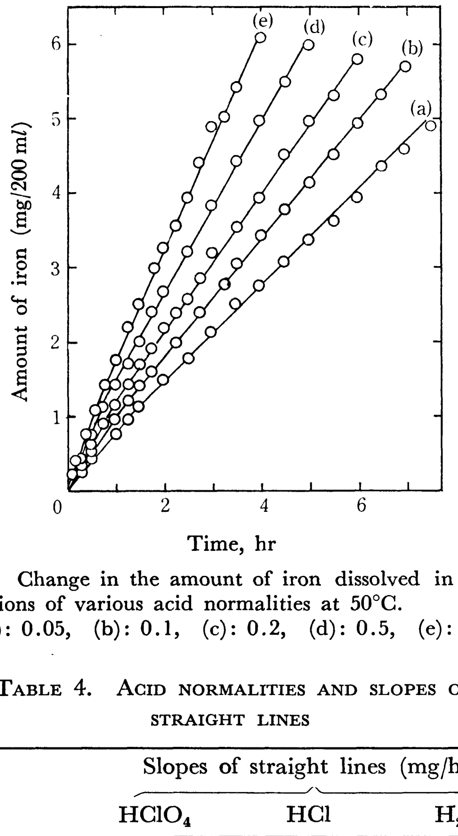

Fig. 9. Change in the amount of iron dissolved in H_2SO_4 solutions of various acid normalities at 50°C.
(a): 0.05, (b): 0.1, (c): 0.2, (d): 0.5, (e): 1

TABLE 4. ACID NORMALITIES AND SLOPES OF STRAIGHT LINES

N	Slopes of straight lines (mg/hr)		
	$HClO_4$	HCl	H_2SO_4
0.05	0.18	0.22	0.50
0.1	0.24	0.26	0.78
0.2	0.29		0.93
0.5	0.41	0.53	1.2
1	0.61	0.75	1.5
2	0.80		

present time. The slopes of these lines, ranging from about 5 to 35% dissolution at various acid normalities, are listed in Table 4. Table 4 shows that the values for HCl are somewhat greater than those for $HClO_4$, while those for H_2SO_4 are markedly greater than those $HClO_4$ and HCl with the same hydrogen-ion concentration.

In order to confirm the remarkable enhancement in the sulphuric acid solution, experiments were made in

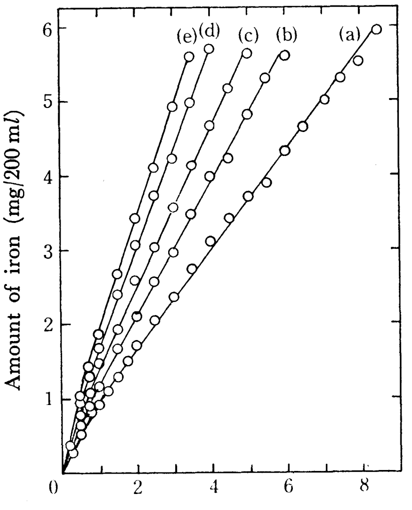

Fig. 10. Effect of the HSO_4^- ion on the dissolution of olivine at 50°C.
(a): 1 M $HClO_4$
(b): 1 M $HClO_4$+0.98×10^{-3} M $NaHSO_4$
(c): 1 M $HClO_4$+0.49×10^{-2} M $NaHSO_4$
(d): 1 M $HClO_4$+0.49×10^{-1} M $NaHSO_4$
(e): 1 M $HClO_4$+0.2 M $NaHSO_4$

solutions containing 1 M $HClO_4$ and $NaHSO_4$ in various concentrations. At such a high hydrogen-ion concentration, the dissociation of the HSO_4^- ion is negligible. The results obtained are shown in Fig. 10. It is apparent from Fig. 10 that the presence of the HSO_4^- ion in only one-thousandth the concentration of $HClO_4$ promotes the dissolution rate considerably.

According to the studies of the dissolution of hydrous ferric oxide by Furuichi *et al.*[25] and of α-ferric oxide by Pryor *et al.*[9] and Azuma,[8] each in aqueous acid solutions, the rate of dissolution is in accord with the order of decrease in the complexing affinity of the anions for the ferric ion, *i.e.*, $HCl>H_2SO_4>HClO_4$. On the other hand, Packter *et al.*[10] observed that the rate of the dissolution of gibbsite in the H_2SO_4 solution was markedly enhanced as compared to those in the HCl and $HClO_4$ solutions. They attributed the promoting effect of sulphuric acid to dipole interaction between the HSO_4^- ion or $H^+\cdots SO_4^{2-}$ ion-paris and active sites on the solid surface. Our study of olivine showed the effect of sulphuric acid to be similar to the case of gibbsite.

Effect of Cl^- and ClO_4^- ions. The rate of dissolution was measured in 0.2 M $HClO_4$ solutions with varying NaCl concentrations, and was also measured in 0.1 M $HClO_4$ solutions containing an adequate amount of $NaClO_4$. The results are shown in Fig. 11 and 12. The rate of the dissolution of olivine was found to be greater in the solutions containing the ClO_4^- ion as well as Cl^- ion than in the solutions without them. The effects of the Cl^- and ClO_4^- ions were, however, very small compared with that of the HSO_4^- ion. The roles of each anion, HSO_4^-, Cl^-, and ClO_4^-, in the reaction of dissolution may be

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[25] R. Furuichi, N. Sato, G. Okamoto, and T. Takeuchi, *Kogyo Kagaku Zasshi*, **72**, 1455 (1969).

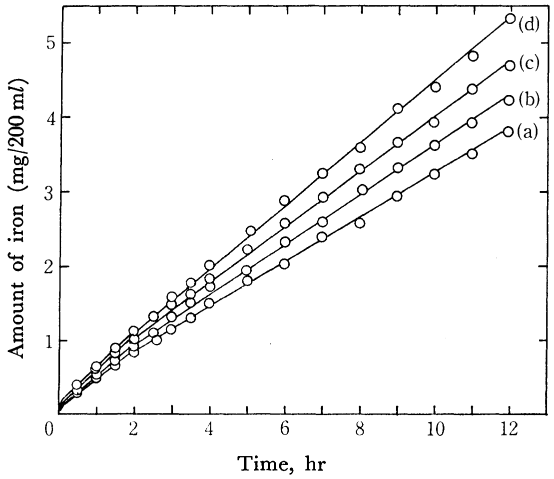

Fig. 11. Effect of the Cl$^-$ ion on the dissolution of olivine at 50°C.
(a): 0.2 M $HClO_4$, (b): 0.2 M $HClO_4$+0.2 M NaCl
(c): 0.2 M $HClO_4$+0.5 M NaCl
(d): 0.2 M $HClO_4$+1.0 M NaCl

understood in terms of the structure of olivine, which consists of individual silicon-oxygen tetrahedra linked by magnesium and iron atoms, each of which has six nearest oxygen neighbours.

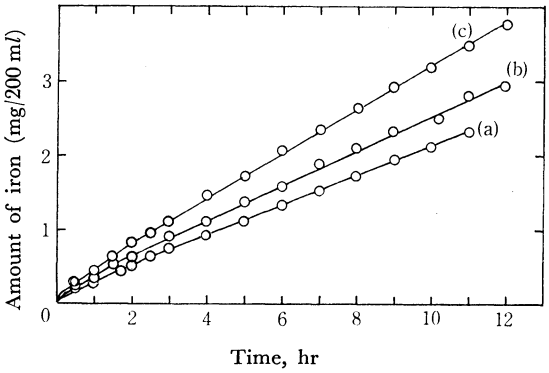

Fig. 12. Effect of the ClO_4^- ion on the dissolution of olivine at 50°C.
(a): 0.1 M $HClO_4$, (b): 0.1 M $HClO_4$+0.09 M $NaClO_4$
(c): 0.1 M $HClO_4$+0.36 M $NaClO_4$

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