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The Dissolution of Titanium Minerals in Hydrochloric and Sulfuric Acids

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Kinetic dissolution experiments of powdered ilmenite and rutile were carried out in sulfuric and hydrochloric acids (0.03—1 M) at temperatures of 40, 65, and 90 °C in order to study the physico-chemical factors and the mechanism for the leaching of titanium and iron from these minerals and rocks under acidic conditions. The dissolution rate of ilmenite was strongly affected by the acidity and temperature of the acid solutions; the rate changes in the H_2SO_4 solutions were greater than those in the HCl solutions. The dissolution rate of rutile was much slower than that of ilmenite. Ilmenite was decomposed by the dissolution of titanium and iron in a nearly stoichiometric ratio under strongly acidic conditions such as 0.3—1 M. But under milder conditions, such as 0.03—0.1 M at 90 °C, the dissolution rate of titanium dropped rapidly in the initial step and the curved line for iron dissolution was nearly parabolic, suggesting the diffusion of iron through the residual layer of titanium.

Titanium is relatively abundant in the earth's crust: igneous rocks contain an average of approximately 0.44% of this element by weight.1) Titanium is usually found in igneous and metamorphic rocks as titanomagnetite (Fe_2TiO_4–Fe_3O_4), ilmenite ($FeTiO_3$), and rutile (TiO_2), and is also found in pyroxene, hornblend, and biotite. Generally titanium remains undissolved in its host rocks even through the process of weathering and hydrothermal alteration of igneous rocks,2) not only because it is present in the form of resistant minerals but also because it tends to form insoluble hydroxides in aqueous solutions. One of the authors3) reported the titanium content of hydrothermally-altered rocks from the Tateyama Jigokudani area; while most of the titanium had remained immobile in the rocks, a part of it had been leached out under the strongly acid conditions. According to Noguchi *et al.*,4) acid hot spring waters in Japan contain about 0.001*n*—0.1*n* mgTi/l and the titanium content of the waters tends to increase with increasing acidity. The titanium in the acid spring waters is likely to be derived from wall rocks by the attack of acid thermal solutions containing sulfuric and hydrochloric acids. The interaction between thermal solutions and rock-forming minerals may result in alterations of rocks, which would proceed through complicated processes: *i.e.*, hydration, ion exchange, dissolution, deposition, and recrystallization. All these processes should be affected by various physico-chemical factors, such as acidity, temperature, type of acid, *etc.* Some studies of the dissolution kinetics of rock-forming minerals have been reported,5—8) but few reports on titanium minerals have been presented, except for the mineralogical studies of the alteration of ilmenite and other minerals.9) In this study kinetic dissolution experiments on the decomposition of powdered ilmenite and rutile were carried out to examine the influence of the chemical character of active solutions and to analyze the mechanism of the decomposition of the minerals.

Experimental

Ilmenite and rutile were used in this study as titanium minerals. The dissolution experiments of powdered ilmenite (*cf.* Table 1) were carried out in H_2SO_4 and HCl solutions of 0.03—1 M at 40, 65, and 90 °C, and the experiments of rutile were also carried out in 1 M H_2SO_4 and HCl at 90 °C. The experiments were performed according to the procedure of Kamiya *et al.*10) The acid concentration of the leaching solutions was adjusted by the addition of sulfuric and hydrochloric acid into distilled water, and at the same time the pH value of the solutions was measured in the range from 40 to 90 °C with a pH meter for high temperatures. Slight differences were found in the pH values of the initial and final solutions. 1 g of ilmenite (120—200 mesh) and/or rutile (under 120 mesh) was suspended in 250 ml of leaching solution, temperature-regulated at 40, 65, or 90 °C, which was stirred continuously with a magnetic stirrer coated with polyethylene. The dissolution rate of titanium and iron was determined by periodically pipetting a 10 ml aliquot from the bottle, centrifuging for a few minutes to remove the titanium minerals, and chemically analyzing the supernatant solution. Titanium and iron were determined colorimetrically by DAM (diantipyrylmethane) and *o*-phenanthroline respectively.

Results and Discussion

The amounts of titanium and iron leached from the powdered ilmenite at different times are shown in Figs. 1 to 6 and Figs. 9 and 10 respectively. These figures show that the leached amounts of titanium and iron are strongly affected by the acidity and temperature of the leaching solutions, and that these amounts in H_2SO_4 solutions are larger than those in HCl solutions at the same molality and temperature. As seen in Fig. 7, the amount of titanium leached from powdered rutile was very small compared with the ilmenite; the amount in the H_2SO_4 solutions was also larger than that in the HCl solutions. It can be seen from these figures that the titanium and iron ions are transported to the solution when hydrated protons diffuse into the solid, as indicated by Sanemasa and Katsura,8) and that the dissolution rate of the ions from the minerals in the H_2SO_4 solutions is faster than that in the HCl solutions. Packter *et al.*11) observed that the dissolution rate of gibbsite in the H_2SO_4 solutions was markedly faster than the rates in the HCl and $HClO_4$ solutions. They attributed the rate-promoting effect of sulfuric acid to the dipole interaction between the HSO_4^- ion or $H^+\cdots\cdots SO_4^{2-}$ ion pairs and the active sites on the solid surface. The study of olivine dissolution7) also showed an effect from sulfuric acid similar to the case of gibbsite.

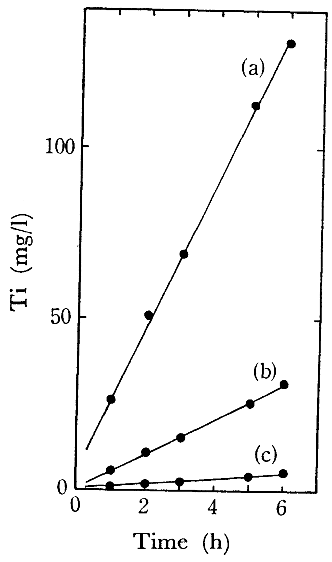


Fig. 1.

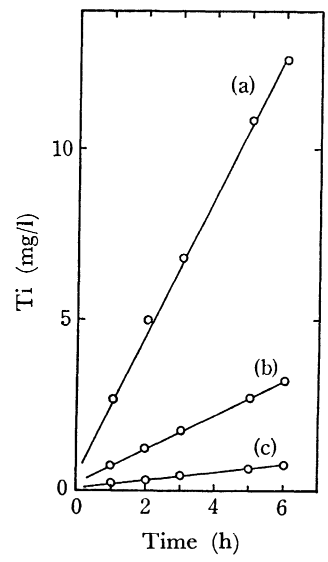


Fig. 2.

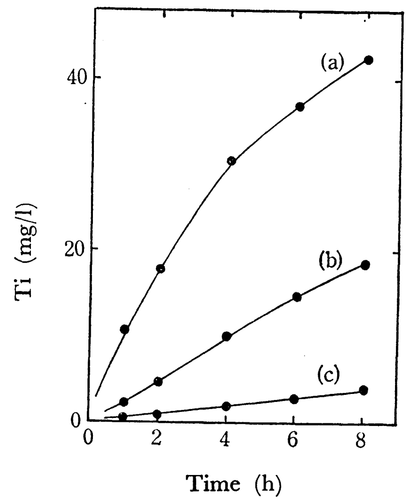


Fig. 3.

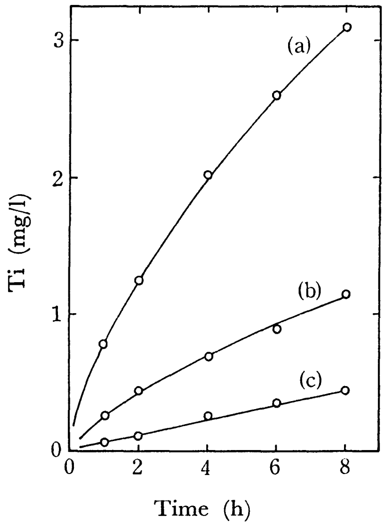


Fig. 4.

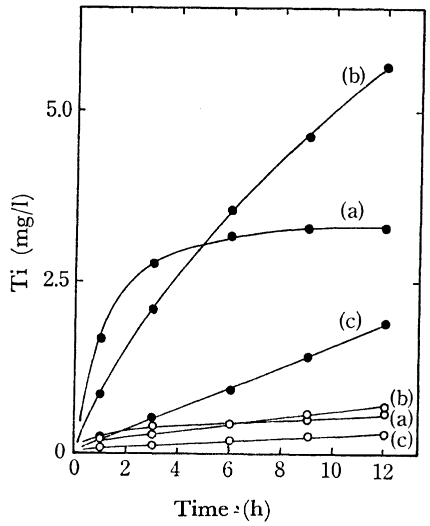


Fig. 5.

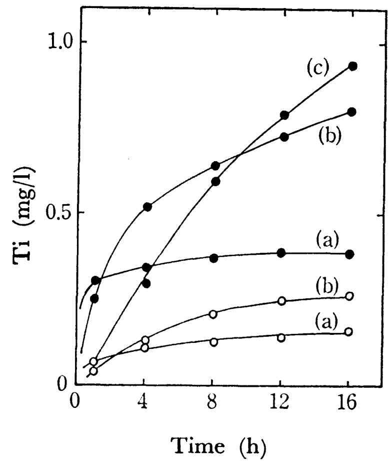


Fig. 6.

Figs. 1—6. Change in concentration of titanium dissolved in H_2SO_4 and HCl solutions from ilmenite at 40, 65 and 90 °C with the time of reaction.
(a): 90 °C, (b): 65 °C, (c) 40 °C, —●—: H_2SO_4, —○—: HCl.
Figs. 1 and 2: 1 M, Figs. 3 and 4: 0.3 M, Fig. 5: 0.1 M, Fig. 6: 0.03 M.

Table 1. Chemical composition of ilmenite

Constituent	Content (wt%)
TiO_2	52.96
FeO	46.06
MnO	1.58
$H_2O(-)$	0.00
$H_2O(+)$	0.18
Total	100.78

On the other hand, Kamiya *et al.*[10] reported that the dissolution of powdered quartz was catalyzed by sulfate and chloride ions and that the catalytic activity of the divalent sulfate ion was higher than that of the monovalent chloride ion. As described previously, the dissolution rates of titanium and iron from ilmenite were affected more highly by sulfate ions (and HSO_4^-) than by chloride ions, but the effect of sulfate ions on iron was not so large as on titanium. This may be due to the differences of valences and ionic radii between titanium and iron. Furthermore, the dissolution experiments of microcline[12] showed that Al^{3+} dissolution from the mineral was accelerated in the presence of sulfuric acid. These experiments, however, do not enable us to determine whether the interaction between titanium and sulfate (HSO_4^-) ion resulted from an electrostatic force or from an electronic force such as the bonding in coordination compounds. In any event, it is evident that sulfate and hydrogensulfate ions play an important role in the dissolution of ilmenite and rutile.

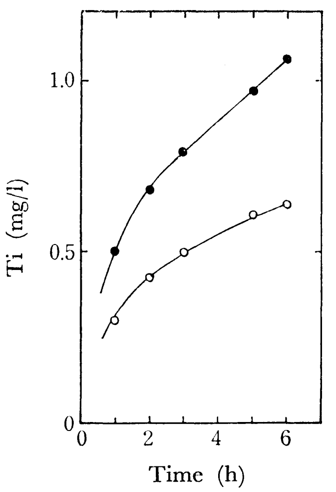


Fig. 7. Change in concentration of titanium dissolved in 1 M H_2SO_4 and HCl solutions from rutile at 90 °C with the time of reaction.
—●—: H_2SO_4, —○—: HCl.

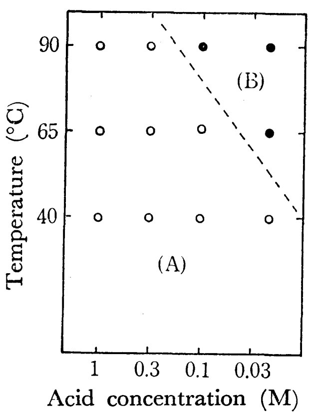


Fig. 8. Temperature and acid concentrations used in this experiment.

Figures 11 and 12 show the values of the molar ratio for the amount of titanium and iron dissolved at different times. The values were always smaller than 1, but these tended to become larger or smaller with time according to the conditions. Therefore, we have divided the conditions into the two groups shown in Fig. 8. Under the conditions of group A, the dissolution rate of iron from ilmenite was larger than that of titanium during the initial step of the dissolution, and over a very long time period the ratio of titanium to iron approached the stoichiometric ratio, *i.e.* Ti/Fe=1. On the other hand, under the conditions of group B, the values of the ratio tended to become smaller with time, and the amount of titanium leached in the course of the leaching experiments at high temperatures became less than that at low temperatures.

If we assume that the change in the surface of powdered ilmenite brings about the depression of the dissolution rate with time, we get the following approximate equations[10] for the A group:

$$m = K_1St + m_0 \qquad S = S_0(1-K_2t)$$
$$m - m_0 = K_1S_0 - K_1K_2S_0t^2$$

Fig. 9.

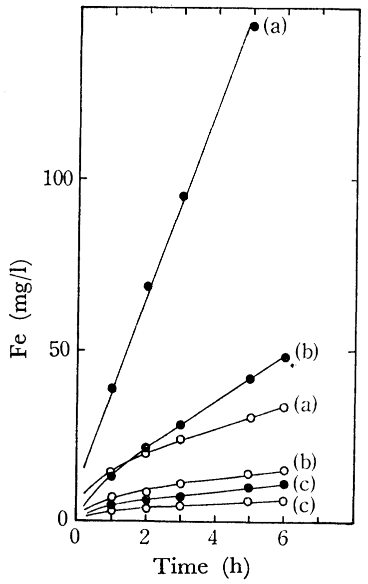
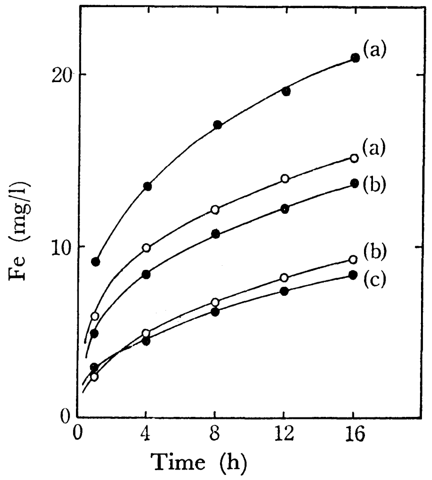


Fig. 10.



Figs. 9 and 10. Change in concentration of iron dissolved in H_2SO_4 and HCl solutions from ilmenite at 40, 65 and 90 °C with the time of reaction.
(a): 90 °C, (b): 65 °C, (c): 40 °C,
—●—: H_2SO_4, —○—: HCl.
Fig. 9: 1 M, Fig. 10: 0.03 M.

where m and m_0 are the amounts of dissolved titanium at time t and at the beginning, S and S_0 are the surface areas of powdered ilmenite at time t and at the beginning, and K_1 and K_2 are the constants for dissolution of titanium and for decrease in surface area, respectively. As the surface area of powdered ilmenite was not measured in our experiments, K_1S_0 represents the apparent dissolution rate of titanium at time zero. Figure 13 shows the values for K_1S_0 at different acid concentrations; the values tend to become smaller with decreasing temperature under the A conditions. On the other hand, under the B conditions (*e.g.*, 0.03 M at 90 °C) the amount of titanium leached at intervals of one hour was reduced rapidly in the initial step of the dissolution, as shown in Fig. 14. Therefore, under the B conditions it must be considered that some other factor besides the decrease of surface area brought about the depression of the dissolution rate. It might be thought to be the formation of insoluble

Fig. 11.

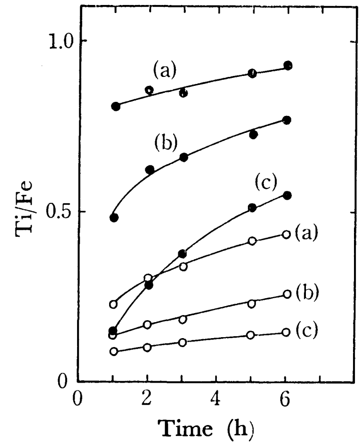
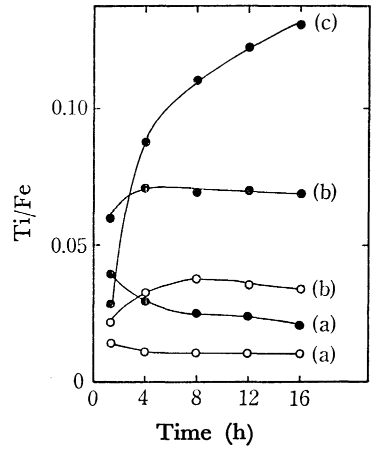


Fig. 12.



Figs. 11 and 12. Change in the Ti/Fe ratio dissolved in H_2SO_4 and HCl solutions from ilmenite at 40, 65 and 90 °C with the time of reaction.
(a): 90 °C, (b): 65 °C, (c): 40 °C
—●—: H_2SO_4, —○—: HCl.
Fig. 11: 1 M, Fig. 12: 0.03 M.

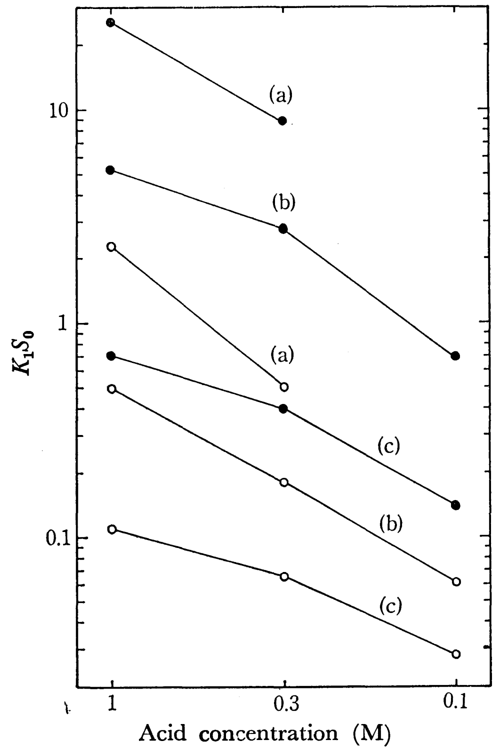


Fig. 13. Apparent dissolution rate of titanium from ilmenite at different acidities.
(a): 90 °C, (b): 65 °C, (c): 40 °C
—●—: H_2SO_4, —○—: HCl.

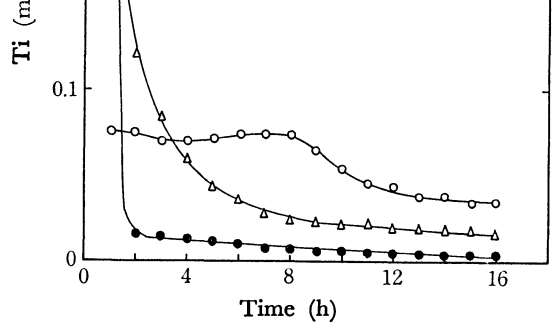


Fig. 14. Change in amount of titanium dissolved in 0.03 M H_2SO_4 from ilmenite at intervals of one hour.
—●—: 90 °C, —△—: 65 °C, —○—: 40 °C.

materials on the surface. And in fact, under the A conditions the curved line for iron dissolution was nearly linear, while the line was nearly parabolic under the B conditions. As shown in Figs. 15 and 16, an approximately linear relationship exists between the square of the leached amount of iron and time, *i.e.*, $m^2=kt+k'$, where m=leached amount of iron, t=time, and k=constant; this relationship is presumed to show that the iron ion diffuses through the residual layers into the solution. However, we could not discover any change of the structure of ilmenite by X-ray diffraction analysis after the 36 h leaching experiment at 90 °C in 0.1 M H_2SO_4. The amount of residual materials, therefore, is likely to be slight and the layer, if present, to be amorphous.

It may be concluded that ilmenite is decomposed by the dissolution of titanium and iron in a nearly stoichiometric ratio in the H_2SO_4 and HCl solutions ranging from 0.3 to 1 M, but in the solutions ranging from 0.03 to 0.1 M (pH 1—1.5) at 65—90 °C the dissolution rate of titanium decreases rapidly in the initial step. Consequently, the iron ion may diffuse into the acid solution through the insoluble residual layer of titanium. The insoluble materials of titanium seem to be changed into resistant oxide minerals such as rutile over a long period, although we could not identify the minerals in this experiment in the limited time of 16 h. As described previously, the solubility of rutile in 1 M H_2SO_4 and HCl solutions was very much smaller than that of ilmenite, and rutile, therefore, does not seem to dissolve very much in acid

Fig. 15.

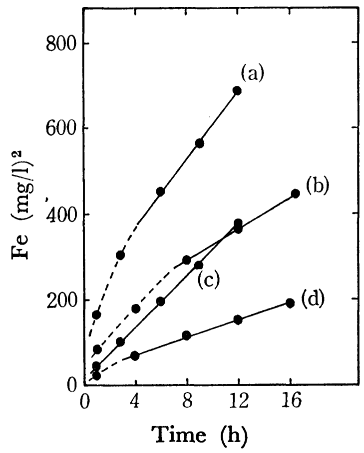
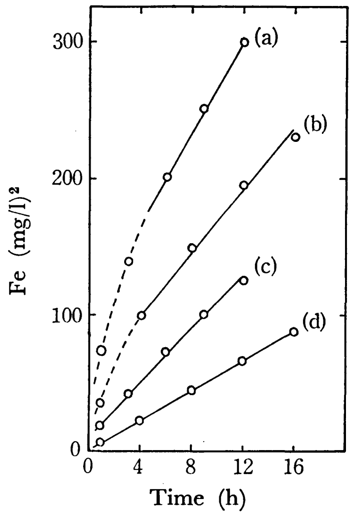


Fig. 16.



Figs. 15 and 16. Change in square of dissolved amount of iron from ilmenite at 65 and 90 °C.
—●—: H_2SO_4, —○—: HCl.
(a): 0.1 M at 90 °C, (b): 0.03 M at 90 °C
(c): 0.1 M at 65 °C, (d): 0.03 M at 65 °C.

solutions having concentrations below 0.1 M or pH 1. This supports the view that rutile is a fairly common alteration product of other titanium minerals, chiefly ilmenite, titanomagnetite, sphene, and perovskite, as well as of its polymorphs anatase.$^{13)}$ It is reasonable to expect, moreover, that titanium minerals such as ilmenite and titanomagnetite in igneous rocks are changed into a titanium oxide mineral during the hydrothermal alteration at high temperature for pH 1.5 or above. The high content of titanium in hydrothermally-altered rocks from acid hot spring areas$^{3)}$ seems to be due to the insolubility of the oxide minerals described above.

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