

Dissolution of $\text{Na}_2\text{O} \cdot \text{CaO} \cdot n\text{SiO}_2$ glasses in Na_2CO_3 solution for long-term and short-term experiments

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Abstract

Dissolution of the glasses with compositions of $\text{Na}_2\text{O} \cdot \text{CaO} \cdot n\text{SiO}_2$ ($n = 2.5\text{--}6$) in 0.5 M Na_2CO_3 solution was studied experimentally. The experiments were carried out with autoclaves under the conditions of the autogeneous pressure, 150 °C, and durations from 16 hours to 60 days. Experimental results show that the dissolution rate is increased with the increase of silica-content of the glass, especially in long-term ones. By comparison, the dissolution rate is significantly slower in long-term experiments than in short-term ones. During dissolution, the surface reaction generally plays the main role in short-term experiments, whereas in long-term ones, the solid diffusion and the surface reaction may both act significantly. In this kind of alkaline solution, percentage of Ca would be rich on the glass surface, and Na/Si depletion occurred. As the solution was renewed in short-term systems, the dissolution rate of Na was faster than Si on the glass surface. While the precipitation occurred, Si were consumed by the precipitated phases continuously and therefore the depletion of Si became more obviously. In addition, the high-Si glasses own higher dissolution rates than low-Si ones in long-term experiments, because the minerals growing on the low-Si glasses are closed and they prevent the reaction solution and glass.

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1. Introduction

Many occurrences of volcanic glass are located in saline lakes which is often full of alkaline solution including Na_2CO_3 . In this kind of environment, silicic glass can transfer to other economic mineral ores fast. It is very interesting to know why the dissolution rate is so fast and what kind of mechanisms controlled the dissolution and precipitation processes. With the aid of previous research, the dissolution of the glasses of a simple $\text{Na}_2\text{O} \cdot \text{CaO} \cdot n\text{SiO}_2$ system in an alkaline Na_2CO_3 aque-

ous solution has been carried out in this study. Consequently, the dissolution behaviors of the simplified major elements of Na, Ca, and Si in glass can be clarified.

Different aspects on the dissolution of solid materials have extensively been studied [1–4]. They include the rate of dissolution [5,6], the congruent or incongruent dissolution [7–9], the mechanisms of dissolution [10–12], and so forth. Usually, the rate of dissolution may be obtained hardly by measuring the volume change or weight loss if a powdered sample is used [13,14]. The information of congruent or incongruent dissolution has generally been acquired by analyzing solution composition in a flow-system [15–17]. However, in a flow-system, the powdered sample will gradually decrease in amount through flowing from the system so as to decrease the solution concentration [18,19].

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In this study, a coarse-grained instead of a conventional powdered sample has been used in the experiments. So, the weight loss of the sample after treatment can be measured, and the compositional change may directly be gained by analyzing the residual solid. Additionally, two types of experiments have been utilized: short-term and long-term experiments. The former one is an experiment to be proceeded repeatedly in a suitable short duration and the reacting solution is renewed, so that no precipitation happened, whereas the latter occurs in closed systems and minerals precipitated. Actually, the short-term experimental technique is similar to that of the flow-system with an advantage of measuring the compositional change with the residual solid. Thus, dissolution behaviors under the non-precipitated and precipitated conditions can be compared. In general, we hope to solve the problems of glass dissolution rates, the congruent or incongruent dissolution, and the mechanism of dissolution.

2. Experimental procedures

2.1. Preparing materials

The synthetic glasses with compositions of $\text{Na}_2\text{O} \cdot \text{CaO} \cdot n\text{SiO}_2$ ($n = 2.5, 3, 3.5, 5,$ and 6) and $0.5 \text{ M Na}_2\text{CO}_3$ aqueous solution were used in the experiments. They are abbreviated to A, B, C, D, and E, respectively. The glasses were prepared from mixing of quartz powder (SiO_2 99.5%), marble powder (CaCO_3 99%) and Na_2CO_3 (99.8%) chemical to melt in graphite crucibles in a furnace of HT04/17 model which is made by Nabetherm in Germany. The glasses A and E were molten at 1500°C , the glass B at 1400°C , and the glasses C and D at 1300°C . After staying about 20 min at the melting temperature, the melt was taken out from the furnace and quenched quickly at the room temperature. The glasses were cut into $7.3 \pm 0.5 \text{ mm}$ for each edge of a cube, and then we took about $5.0000 \pm 0.0100 \text{ g}$ of glass cubes and 20 ml Na_2CO_3 solution for each experiment. The experiments were carried out with teflon-lined autoclaves under the conditions of the autogeneous pressure, 150°C and durations from 16 hours to 60 days.

2.2. Experimental design

Two types of the experiments have been designed: one is short-term and the other is long-term as stated previously. In the short-term experiment, each sample was carried out every 16 h then renewed with fresh solution each time. This procedure was repeated for about 13 times. The long-term one was simply a conventional batch experiment proceeded for 16 hours to 60 days. An experiment was proceeding to the scheduled duration, and then each sample was washed with deionized water,

and treated with supersonic vibration about 30 min. The treated glass was dried at 110°C about 24 h, and then was weighted for obtaining the percentage of weight loss. In addition, the dimensions of the glass cube were measured for comparing the dissolution rates of glasses. The calculation method will be described in Section 3.1.

2.3. Analytical methods

The chemical compositions of untreated glasses were analyzed by using X-ray fluorescence (XRF) of RIX-2000 model which is made by the RIGAKU in Japan. For the short-term experiments, compositions of some glass surfaces were tested with an energy dispersive spectrometer (EDS), while the compositions of the inner part of the glasses were analyzed with an electron microprobe (EMP) for the long-term experiments. The surface morphology of the glasses was observed with an optical microscope and a scanning electron microscope (SEM). Both of the machines of SEM and EMP are produced by the JEOL in Japan, and the former is JSM-T100, and the latter is JXA-8900R. In addition, the products of secondary minerals and amorphous materials were also examined with a SEM, X-ray powder diffractometer (XRD) and EMP. The XRD machine of Science Mxp3 model is made by MAC in Japan, and the experimental voltage is 35 kV and current is 15 mA. Most of the samples are run with the scanning speed of $5^\circ/\text{min}$.

Furthermore, an EDS of Hitachi H-2400 type setting with a narrow beam of $0.5 \mu\text{m}$ was used for detecting the composition of etched pits and hills on the glass surface. Although there will be some surface relief effects, the data also can be compared with a semi-quantification. Before examining, we used some given glass standards to reconstruct the values. In addition, we picked large pits and hills ($>1 \mu\text{m}$) to get five data of different positions and then calculated the average values with contrast. In the long-term experiments, some glasses were cut into half and the inner part of glasses were analyzed by EMP, which was generally set with a broad beam in a diameter of $8 \mu\text{m}$ and a short exposure time for preventing the loss of sodium.

3. Results

The chemical compositions of untreated glasses were analyzed by XRF showing in Table 1. It is shown that the sodium loss is apparent, and may be due to heating during glass preparation; and minor impurities of other elements are probably inherited from the raw materials, for example, MgO from the marble powder. Moreover, EMP analyses for five spots in each glass show a deviation of less than 1.7% for Na_2O , 2.9% for CaO, and 1% for SiO_2 . It implies a less homogeneity of CaO in the

Table 1
Chemical compositions of the untreated glasses (by XRF)

Oxide wt%	Glass				
	A (1:1:2.5)*	B (1:1:3)*	C (1:1:3.5)*	D (1:1:5)*	E (1:1:6)*
SiO ₂	56.57	58.73	63.62	70.15	74.73
TiO ₂	–	–	0.02	0.03	0.05
Al ₂ O ₃	0.03	0.04	0.01	–	0.02
Fe ₂ O ₃	–	–	–	–	0.12
MgO	0.44	0.36	0.45	0.28	0.40
CaO	21.30	19.01	16.73	13.26	11.74
Na ₂ O	21.01	20.52	18.70	14.58	12.12
P ₂ O ₅	0.04	–	–	0.03	0.04
Total	99.39	98.66	99.53	98.33	99.22
<i>The real molar ratios</i>					
Na ₂ O/CaO	0.89	0.97	1.01	0.99	0.93
SiO ₂ /CaO	2.48	2.88	3.55	4.94	5.94

–: not detectable.

* Ideal molar ratios of Na₂O:CaO:SiO₂.

untreated glasses, possibly due to minor phase separation during quenching [20].

3.1. Calculation method

The experimental results are separated into two portions: the short-term dissolution results and the long-term ones. Firstly, the basic formulas used are:

Accumulated dissolution percent

$$= [(W_i - W_f)/W_i] \times 100\% \dots [21],$$

Surface – normal rate of dissolution (v_n)

$$= (h_i - h_f)/2\Delta t \dots [6],$$

where,

W_i	the initial weight of glass cubes before an experiment (gw)
W_f	the final weight of glass cubes after an experiment (gw)
h_i	the average dimension of glass cubes before an experiment (mm)
h_f	the average dimension of glass cubes after an experiment (mm)
Δt	the experimental duration (h)
v_n	the surface-normal rate of dissolution (mm/s)

The results of accumulated dissolution percents can be compared easily with the differences between the short-term and long-term ones. However, it should be considered that the weight loss cannot reflect the real molecule loss. Therefore, the surface-normal rate of dissolution (v_n) should be normalized to the molar volume (V_0) of each glass in order to compare the dissolution rate of different glasses. The normalized dissolution rate k (mol/cm² h) is [6,22]:

Table 2

Molar weight, specific gravity, and molar volume of the untreated glasses

	Glass no.				
	A	B	C	D	E
Molar weight (gw/mol)	224.20	221.58	218.11	208.75	204.38
Specific gravity (gw/cm ³)	2.67	2.65	2.61	2.53	2.48
Molar volume (cm ³ /mol)	85.09	83.62	83.57	82.51	82.41

$$v_n = kV_0,$$

$$k = v_n/V_0.$$

The molar volumes, specific gravities and molar weights of the glasses are measured by Archimedes method and listed in Table 2.

3.2. Dissolution results

The accumulated dissolution percent versus accumulated duration of different glasses are shown in Figs. 1 and 2 for the short-term and the long-term experiments, respectively. It is obvious that the short-term results display a similarity of the accumulated dissolution percent for the same accumulated duration except the silica-rich glass E (Fig. 1) and a good linear increasing correlation between the dissolution percent and duration for each glass. It indicates similar dissolution rates ($\Delta W/\Delta t$) for them. However, the high-Si glass shows a slightly higher dissolution rate. Fig. 3 shows relationships between the normalized dissolution rate and the average volume of each glass cube for the short-term experiments. Apparently, the normalized dissolution rates increase with decreasing the average volume of each glass cube as expected, and increase to a certain degree with increasing silica-content of the glasses, but the differences between them are not so obvious.

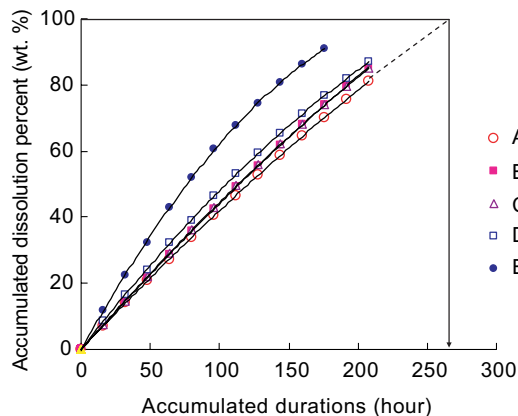


Fig. 1. Accumulated dissolution percent versus accumulated duration in the short-term experiments.

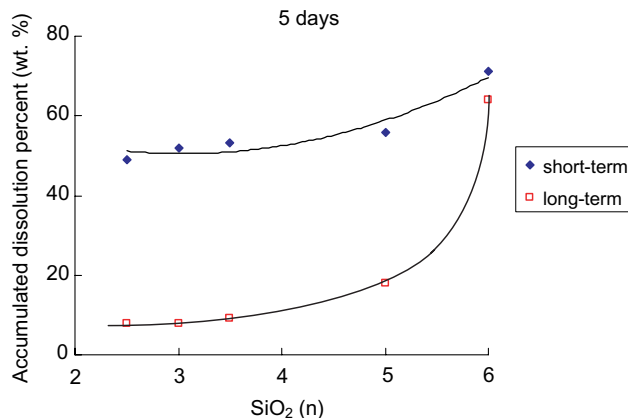


Fig. 4. Accumulated dissolution percent versus silica-content of the glasses for the short-term and long-term experiments in 5 days.

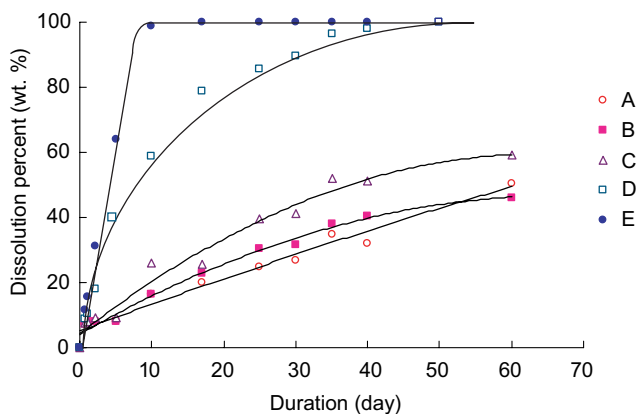


Fig. 2. Dissolution percent versus duration in the long-term experiments.

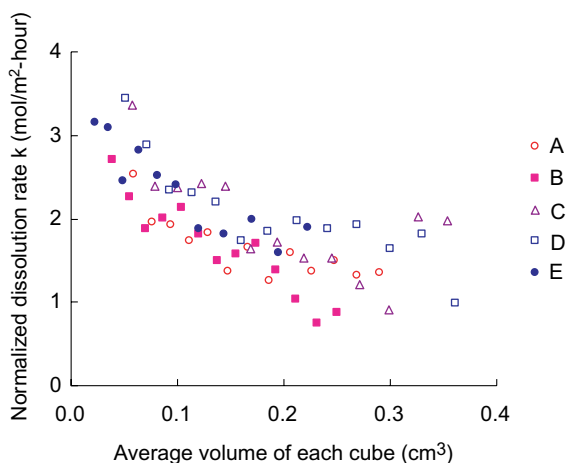


Fig. 3. Relations of the normalized dissolution rate (k) and the average volume of each glass cube.

Contrarily, the long-term results display a considerable difference in the dissolution percent of the glasses (Fig. 2). For instance, accumulated dissolutions are

nearly 50% for the glasses A and B in 60 days, nearly 60% for the glass C in 60 days, nearly 100% for the glass D in 40 days, and nearly 100% for the glass E about 10 days. It is noted that the dissolution behavior of the glass E is similar in both the short-term and long-term experiments, while others show a lot of differences (Fig. 4).

In the short-term experiments, etched pits and hills have been observed (Plate 1) on glass surfaces, and the results of EDS analyses on them are illustrated in Fig. 5. Evidently, it is shown that the ratios of CaO are greater than 1, while those of Na₂O and SiO₂ are less than 1 on both etched pits and hills. Moreover, the CaO ratios on hills are smaller than those in pits, but the Na₂O and SiO₂ ratios are in reverse. In addition, the Na₂O ratios are lower than SiO₂ both in hills and pits. It also indicates a higher dissolution rate, and the depletions of Na₂O and SiO₂ are more deeply in the pits.

In the long-term experiments, the treated glass cubes were cut in halves and the inner part of each half was smoothly polished by diamond paste for electron microprobe analyses. The results of the glass C are illustrated in Figs. 6 and 7 for different durations of reaction. It is

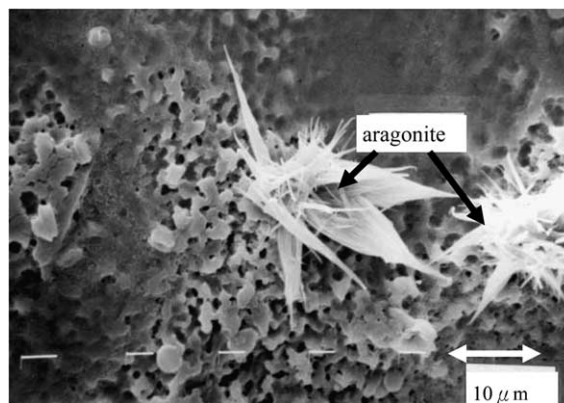


Plate 1. Etched pits and hills, and aragonite precipitated on a treated glass surface (150 °C for 25 h of glass A).

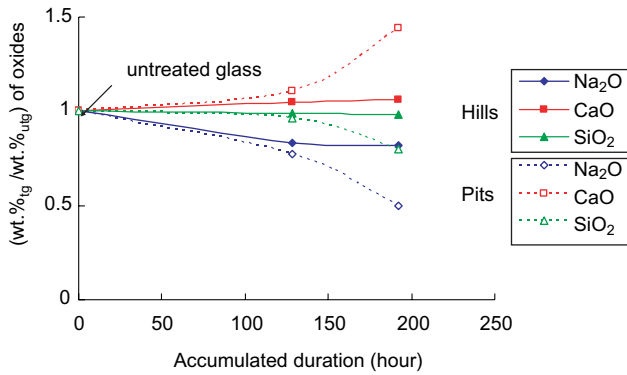


Fig. 5. Relations between weight percent ratios of oxides and accumulated durations on pits and hills of the glass B (wt%_{ig}: weight percent of treated glass; wt%_{utg}: weight percent of untreated glass).

noted that the change of weight percentage ratios of the oxides is more obvious in glass margin, and a leached layer can possibly be defined by the change of weight percent ratios and by the change of weight percent of total oxides as indicated in Figs. 6 and 7. Thus, leached

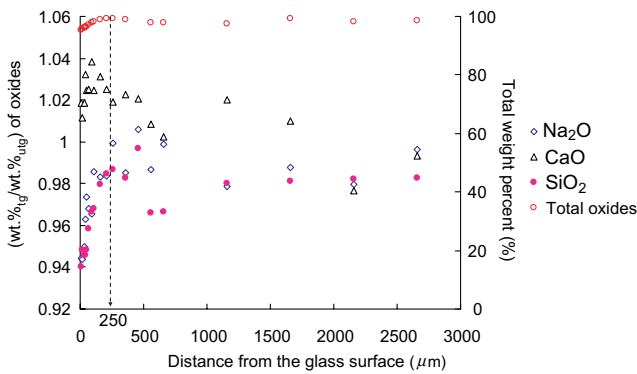


Fig. 6. Weight percent ratios of oxides in the interior of the glass C for 10 days (wt%_{ig} and wt%_{utg} the same as in Fig. 5).

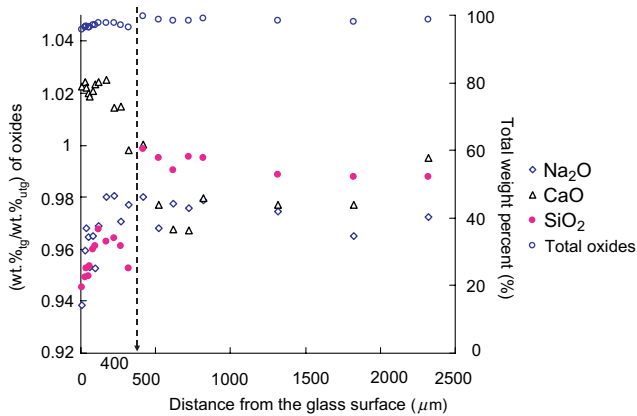


Fig. 7. Weight percent ratios and the total weight percent change of oxides in the interior of the glass C for 25 days (wt% and wt%_{utg} the same as in Fig. 5).

layers are about 250 μm for 10 days' treatment and about 400 μm for 25 days' as marked in the figures. Meanwhile, chemical analyses suggest that Na and Si are leached more easily than Ca as the experiments proceeded, and the depletion of Si is faster than Na (Figs. 6 and 7).

In summary, the phenomena of Ca-enrichment and Na/Si depletion in the reaction layer of glass exist both in short-term and long-term experiments.

3.3. Precipitated phases

In the long-term experiments, the precipitated minerals include aragonite (CaCO₃), pectolite (Na₂O · 4CaO · 6SiO₂ · H₂O), Na–Ca-silicates, and quartz (SiO₂). Their XRD patterns are shown in Fig. 8, which include the precipitated phases and the residual layer of reacting glass. The XRD data of amorphous glass in Fig. 8(a) was run under the scanning speed of 1°/min and the pattern was raw without computer smoothening, while the other minerals were run under the speed of 5°/min and the patterns of Fig. 8(b) had been smoothened by computer program. Among them, three different Na–Ca-silicate minerals have been identified by Treor program and their compositions were analyzed by EMP, namely, Na–Ca-silicate (1) (0.1Na₂O · CaO · 4SiO₂ · nH₂O), (2) (0.2Na₂O · CaO · 4SiO₂ · nH₂O), and (3) (0.3Na₂O · CaO · 4SiO₂ · nH₂O). The following mineral associations have been found: pectolite only for the glass A; pectolite and Na–Ca silicate (2) for the glass B; pectolite, Na–Ca-silicate (1) and (2) for the glass C; Na–Ca-silicate (1)–(3), and quartz for the glasses D and E. It is noted that aragonite of the first precipitation (Plate 1) grew on the glass surface after 25 h. All precipitated minerals display lower Na₂O content than their initial glasses. In addition, these secondary minerals have also been reported in previous workers [21,23].

On the other hand, SEM observation shows layered growth of the precipitated minerals from the outer to the inner part of the treated glasses (Plates 2 and 3). This phenomenon indicates the nucleation occurs on the outer layered minerals and an interval exists between glass surface and precipitated layers after appearance of the first mineral precipitation. It implicates the solute had been dissolved in the solution then precipitation occurred on the outer mineral layers, but is not transferred from the glass directly. Besides, the leached layer of glass is still amorphous phase (Fig. 8(a)), so no proof can suggest minerals are produced from glass surface. In another word, dissolution and precipitation did happen in the long-term experiments, and the secondary minerals were not produced from the solid diffusion of glass. Besides, the residual glasses can be separated easily from the precipitated mineral layers by tapping, and the easiness of separation is decreasing from the glasses E to A. In addition, the texture of precipitation layers appears to be in the order of loose to close arrangements

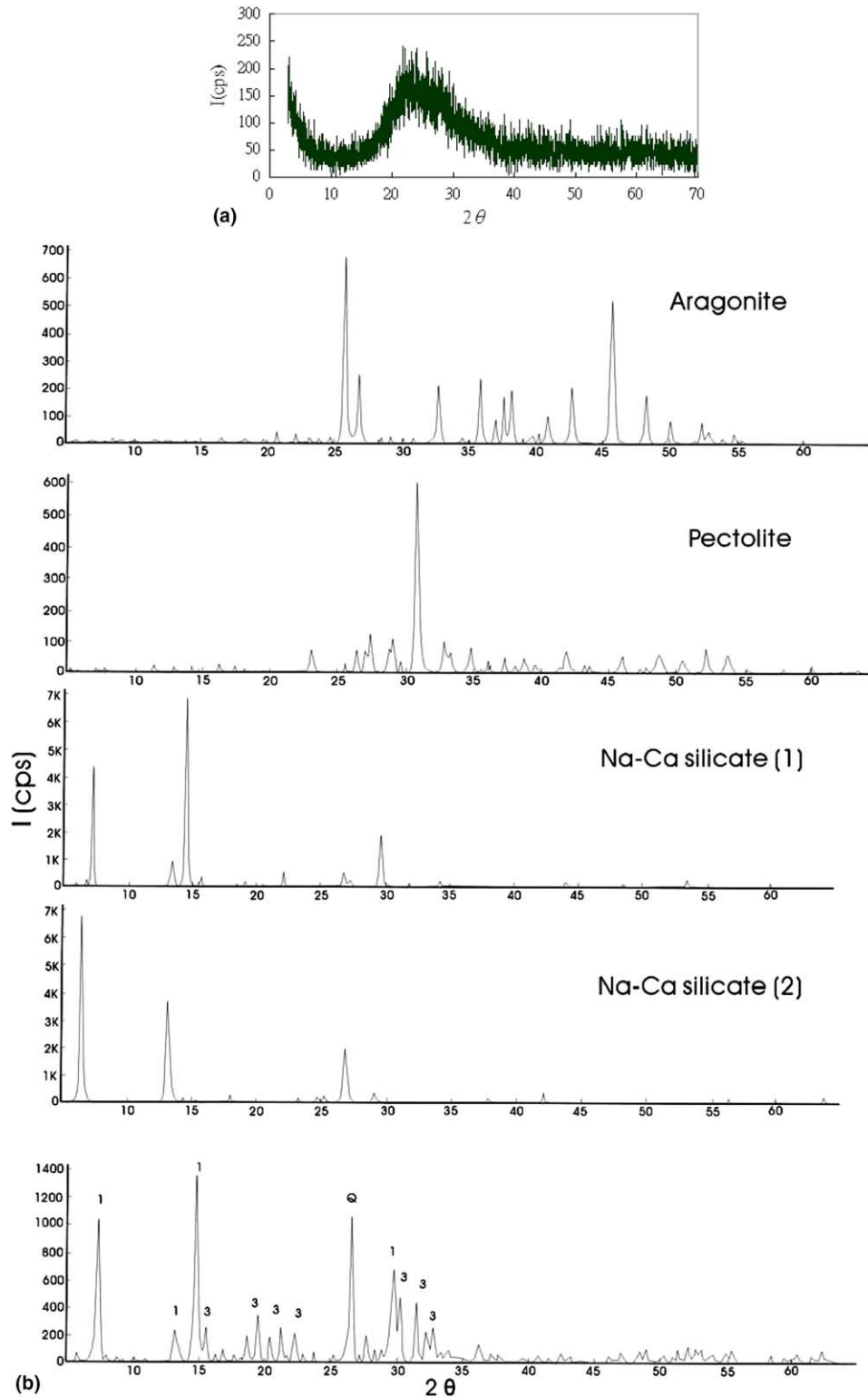


Fig. 8. (a) The amorphous XRD pattern of the leached layer on the glass surface with the scanning speed of 1°/min. (b) The XRD patterns of other minerals (1: Na–Ca silicate (1), 3: Na–Ca silicate (3), Q: quartz). They are smoothed by computer programs and the scanning speed is 5°/min.

from glasses E to A. Based on the morphology and texture of mineral growth, the pectolites are aggregated together with closer fibers in glasses A and B, and all

Na–Ca silicate minerals are of a platy form and gathered loosely (Plate 3); however, the precipitation of quartz (SiO₂) from glasses D and E suspends in the liquid

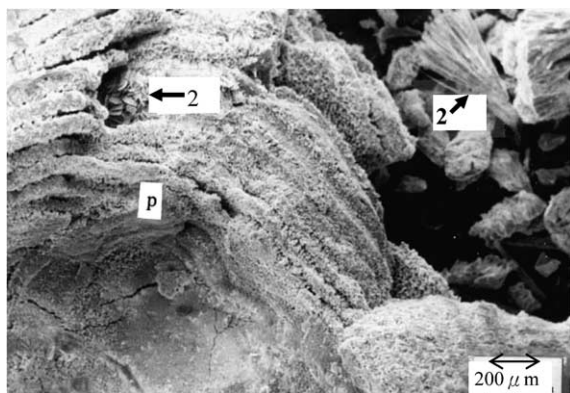


Plate 2. Layered growth of the precipitated minerals (2: Na–Ca silicate (2); p: pectolite) separated from the treated glass C.

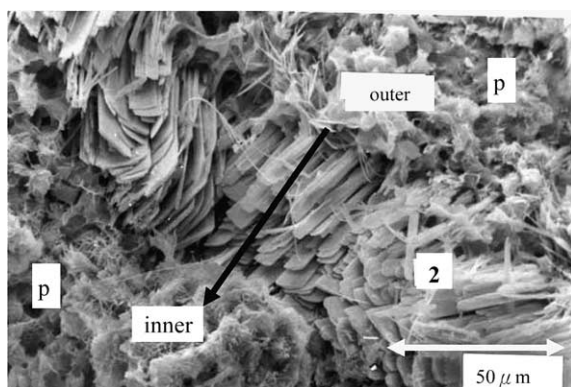


Plate 3. A closer view of a layered growth of the precipitated Na–Ca silicate mineral (2) and pectolite (p) from the outer to the inner part. The arrow means the crystal growth direction from the outer layer to the inner.

and is not attached to the other minerals. This also can explain why the glass dissolution rates decrease from E to A in long-term experiments (Fig. 2).

4. Discussion

4.1. Congruent versus incongruent dissolution

The short-term experiments indicate that a complete dissolution may occur for all glasses (A–E) as the experiments proceeded to sufficient accumulated durations, for instance, approximately 270 h for glass A as extrapolated from Fig. 1. In addition, a leached layer has not been found clearly for the treated glasses. Obviously, these facts suggest a congruent dissolution behavior for the glasses in the short-term experiments. Chemical analyses, however, denote that $\text{wt}\%_{\text{tg}}/\text{wt}\%_{\text{utg}}$ ratios of the oxides are different on the pits and hills of the residual glass (Fig. 5). In this regard, the dissolution may be considered to be temporarily incongruent at glass surface.

On the other hand, the dissolution behavior of the glasses display differently in the long-term experiments (Fig. 2). It is shown that the dissolution rates of the glasses increase in the order of A, B, C, D and E. Complete and fast dissolutions have been reached for the glasses E and D in about 10 and 50 days, respectively, though a partial dissolution of only up to about 50 wt% was found for the other glasses as long as 60 days. In addition, Fig. 3 shows similar normal dissolution rates between the glasses A and E under the same surface areas in short-term experiments, but the accumulated dissolution percents in 5 days shows a lot of differences between long-term and short-term experiments (Fig. 4). In long-term experiments, the high-Si glasses dissolved faster than the low-Si ones at 5 days. It is worthy to note that the high-Si glasses have the similar dissolution behaviors in both two kinds of experiments, but the low-Si glasses own extremely delay in their dissolution rates.

From another point of view, chemical analyses denote that $\text{wt}\%_{\text{tg}}/\text{wt}\%_{\text{utg}}$ ratios of the oxides are evidently different in the leached layers (Figs. 6 and 7). It indicates that incongruent dissolution really happened in the long-term experiments and expanded with long time. Therefore, the dissolution behaviors of the glasses may be regarded as congruent in short-term experiments and incongruent depending on the different glasses in long-term ones, except in the case of glass E. What kind of mechanisms make these differences between the two systems? Did the precipitation occur or the saturated condition change?

4.2. Dissolution mechanism

The surface reaction seems to play an important role [17], while the solid diffusion may only plays a minor one if there is any during dissolution of the glasses in the short-term experiments. The former is suggested by pits and hills (Plate 1) left on the surfaces of treated glasses, and the latter is implied by lack of development of a detectable leached layer. On the other hand, the long-term experiments of glasses A, B, C, D are mainly controlled by solid diffusion inner the glasses.

In the preparing of the glasses, the distribution of Ca is not so homogeneous from the EMP analyses of fresh glasses. It is likely related to a little phase separation in the glasses. So, a different dissolution rates on the glass surfaces can be suggested, and disordered ‘pits and hills’ have occurred.

Chemical analyses show the dissolution rates increasing in the order of Ca, Si and Na during the surface reaction (Fig. 5). It implicates the dissolution rate of Na may be controlled by mass transport and surface reaction, because the 0.5 M Na_2CO_3 solution has not reached saturation yet under the renewing solution, and consequently caused the Na ion dissolving faster

than Si. However, this order may change somewhat with the change of pH value of the solution as suggested by many previous studies [4,17,24,25]. Possibly, this may be due to the effect of H^+ and OH^- concentrations of the solution as proposed by Douglas and EL-Shamy [10]. These authors consider that H^+ ions replace cations of Na^+ and Ca^{2+} , whereas OH^- ions break the Si–O bond of silicates during dissolution. So, the order of easiness of elemental migration of the glasses during dissolution should be related with the characteristics of solution. In the Na_2CO_3 solution, the first minerals growing on the glass surface is aragonite ($CaCO_3$) (Plate 1), which makes supersaturation on the glass surface and the dissolution of Ca ion would be obstructed. So, the concentration of Ca will be concentrated on the glass surface in this alkaline solution of CO_3^{2-} .

In addition to the surface reaction, the solid diffusion may play a different role. This can be proved by the development of a different thickness of leached layers inside the glasses during the long-term experiments. The thickness of leached layers can easily be identified by the chemical change and the total weight percent change of oxides from the outer to inner parts of the treated glasses through micro-analyses (Figs. 6 and 7). It is found that the leached layer became thicker obviously when the glass was less siliceous. So, the solid diffusion is likely to play a more important role in the less siliceous glasses.

Chemical analyses imply that the easiness of elemental migration through the solid diffusion increases in the order of Ca, Na, and Si which is denoted by the change of weight ratios of the oxides (Figs. 6 and 7). This phenomenon can be considered as Ca-enrichment and Na/Si depletion. It shows the solid diffusion of Si is slightly faster than Na in long-term experiments, which is opposite in the short-term ones (Fig. 5). Firstly, the Na_2CO_3 solution was renewed in short-term experiments. That make the Na concentration always far away from saturation, and the dissolution rate of Na is faster than Si. However, in the close system of long-term experiments, the concentration of Na was saturated, and the precipitation occurred to consume Si continuously. This also can be observed in Fig. 4, which displays a higher dissolution rate with the higher Si-glass. What kind of roles did the precipitation minerals play?

The bulk composition of Na–Ca silicates and quartz (SiO_2) all show the Si-enrichment in the precipitated processes. For example, the interlayer growth of the glass C (Plates 2 and 3) indicates the reaction was continuous, and both of Si and Na ratios of pectolite (Si/Na = 6) and Na–Ca silicate (2) (Si/Na = 20) are higher than the initial glass (Si/Na = 3.5). On the other hand, precipitated minerals anchored on the glasses inhibit them from dissolution as denoted by slower dissolution in the long-term than in the short-term experiments. Possibly, it may be due to a limited supply of the solu-

tion through covered precipitates to react with the glasses. It is worthy to be noted that the precipitated quartz and Na–Ca-silicate (3) on more siliceous glasses (i.e., D and E) grow loosely, whereas pectolite on less siliceous ones (i.e., A, B and C) intervenes tightly as stated previously (Plates 2 and 3). Naturally, the solution flowing through tightly aggregated precipitates is more limited than that of loosely aggregated ones. To sum up, the effects of controlling the slower dissolution of low-Si glass may be due to the prevention of reaction by the precipitated layers in long-term experiments. In addition, the fast solid diffusion rate of Si is controlled by the consuming Si of precipitated phases in long-term experiments.

5. Conclusions

In the short-term experiments, the accumulated dissolution rate increases slight with increasing silica-content of the glass, and a complete dissolution has been observed in all glasses within about 10 days. On the other hand, in the long-term ones, the dissolution rate has been found to increase quickly when increasing the silica-content of glasses, and though a complete dissolution has been reached for the glasses E and D in about 10 and 50 days, respectively, a partial dissolution of only up to about 50 wt% has been noted for the rest of the glasses even in 60 days.

The dissolution percent is greatly lower in the long-term than in the short-term experiments for the same glass in a given duration. This is essentially attributed to two points: in the short-term system, the solution of Na_2CO_3 was renewed, and in long-term system, the precipitated minerals affect the dissolution behavior.

We suggest that the dissolution behavior of the glasses may be regarded as congruent in short-term experiments, but as incongruent in the long-term ones. Our results indicate that the surface reaction seems to play an important role, while the solid diffusion may only act as a minor one in the short-term experiments. However, in the long-term experiments, the solid diffusion may play a significant role in addition to the surface reaction. It is worthy to note that Ca-enrichment and Na/Si depletion on the glass surface are the common phenomena both in these two systems under the alkaline solution, but the depletion degrees of Na and Si are different in these two systems. As the solution was renewed in short-term systems, the dissolution rate of Na is faster than Si, while the precipitation occurring, Si were consumed by the precipitated phases continuously and the depletion of Si is more obviously in long-term experiments. On the other hand, the fabrics of precipitation layer can prevent the reaction of glass and solution. So, the dissolution rate of low-Si glass is less than the high-Si glass in long-term experiments.

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