

Wollastonite from Susan and Its Dissolution Behaviors

수산 지역의 규회석과 그 용해 거동

Soo Jin Kim (김수진) · Sung Pil Hyun (현성필) · Sung Keun Lee (이성근)

Department of Geological Sciences, Seoul National University, Seoul 151-742, Korea
(서울대학교 지질학과)

ABSTRACT : Wollastonite from Susan occurs as intercalations in limestone beds of Lower Paleozoic Joseon Supergroup. It is a thermal metamorphic product of impure limestone. Electron microprobe analysis shows that it is considerably pure wollastonite. It has triclinic cell with $a=7.932\text{\AA}$, $b=7.328\text{\AA}$, $c=7.069\text{\AA}$, $\alpha=89.995^\circ$, $\beta=95.255^\circ$, and $\gamma=103.367^\circ$.

Dissolution behaviors of wollastonite have been studied conducting three different dissolution experiments; two different reactions with HCl (one batch and one re-initialization experiment) and one reaction with distilled water. In the batch type powder wollastonite-HCl reaction, pH of the solution rapidly increases in the early stage and then its rate of increase slows down to reach plateau resulting in parabolic relationship with time. It is represented by the early rapid rise and fall in pH giving a sharp pH-edge and succeeding slow rise in the re-initialization experiment. The early rapid rise in pH is due to the rapid sorption of H^+ in solution to oxygens on the reactive surface of wollastonite and the fall in pH means that all reactive surface sites are occupied by H^+ ions and no more H^+ adsorption occurs. The slow rise in pH following the pH-edge is due to the dissolution of wollastonite as evidenced by the correlation of pH variation and cation concentration. Dissolution of powder wollastonite in HCl shows linear trend with time. Si is dissolved predominantly over Ca at a constant rate. Ca is dissolved predominantly in the very early stage. Dissolution rate of coarse-grained wollastonite fragments in distilled water is parabolic with time showing a rapid reaction in the early stage and a slow reaction in the advanced stage. The Ca/Si ratio in solution is high in the case of coarse-grained wollastonite fragment as compared with powder wollastonite. The coarse-grained wollastonite fragment-water (acid) reaction resulted in the solution with an elevated constant pH value (alkaline) giving an important significance on the environmental view point.

요약 : 수산 지역의 규회석은 고생대 하부 조선누층군의 석회암 층에 협재하여 산출된다. 이는 불순물을 함유한 석회암의 열변성작용 산물이다. 전자현미분석 결과 거의 순수한 규회석을 알 수 있었다. 이는 삼사정계에 속하며 $a=7.932\text{\AA}$, $b=7.328\text{\AA}$, $c=7.069\text{\AA}$, $\alpha=89.995^\circ$, $\beta=95.255^\circ$, $\gamma=103.367^\circ$ 의 격자 상수를 가진다.

세 종류의 용해 실험을 통해서 규회석의 용해 거동을 관찰하였다; 염산을 사용한 두 가지의 실험 (하나의 배치 실험과 하나의 재초기화 실험) 과 그리고 증류수를 사용한 한 가지 실험. 규회석 분말과 염산의 반응에 있어서 pH 변화 양상은 배치형 실험에서 시간에 대해 급격히 증가한 후 증가 속도가 감소하여 대지에 도달하는 포물선을 보여 준다. 이는 재초기화 실험에서는 pH가 반응 초기에 급격히 증가하였다가 감소하여 명확한 pH-급변대를 보여주며 그후에는 서서히 증가하는 양상으로 나타난다. 초기의 급격한 pH 증가는 용액 중의 수소 이온이 규회석 표면에 급속히 흡착되는데 기인하며 이후의 pH 감소는 표면의 반응 site가 완전히 수소 이온으로 덮여 더 이상 수소 이온이 흡착되지 못 하는 것으로 해석되며 pH-급변대 이후의 느린 증가는 pH 변화와 양이온 농도 변화 양상을 종합해 볼 때 규회석의 용해에 의한 것으로 생각된다.

염산에 의한 규회석 분말의 용해는 시간에 대해 선형적인 경향성을 보여준다. 규소는 일정한 속도로 칼슘에 비해 우세하게 용해되었다. 칼슘은 반응의 매우 초기 단계에서 우세하게 용해된다. 증류수에 의한 조립질 규회석편의 용해 속도는 초기의 빠른 반응과 연이은 느린 반응에 의해 시간에 대해 포물선을 보여준다. 용액 중의 칼슘/규소 농도비는 조립질 규회석의 경우에 분말 규회석에서보다 높다. 조립질 규회석편과 증류수 (산)의 반응은 용액의 pH를 높여 주며 이는 환경적인 측면에서 중요성을 가진다.

INTRODUCTION

Wollastonite is a common constituent mineral of thermally metamorphosed impure limestone. In most of its occurrence, it is the result of the reaction $\text{CaCO}_3 + \text{SiO}_2 \rightarrow \text{CaSiO}_3 + \text{CO}_2$ (Goldschmidt, 1912). Physicochemical environment of the formation of wollastonite has been studied by Goldschmidt (1912), Danielsson (1950), Ellis and Fife (1956) and Harker and Tuttle (1956). Harker and Tuttle (1956) show that in certain circumstances the CO_2 pressure may be effectively reduced, either by a dilution by some volatile component or by the escape of CO_2 through fissures. They also show that wollastonite may form at somewhat lower temperatures than those indicated and that at atmospheric pressure the reaction takes place at or slightly below 400°C .

The present work aims to characterize the mineralogical properties of wollastonite and to study its dissolution behaviors by HCl and water. Wollastonite-water reaction has been studied to know the possibility of its use as a neutralizer of the acid deposition. Wollastonite occurrence is found about 500m NE from Sucheonggeori, Susan-myeon, Jecheon-gun, Chungcheongbug-do.

OCCURRENCE

Geology of the wollastonite occurrence in this study consists of limestone and dolostone of Lower Paleozoic Joseon Supergroup and the Jurassic granite intrusion. Wollastonite occurs as thin or thick intercalations in the gray limestone beds showing roughly concordant but partly discordant relation to the bedding of wall rocks. The

wollastonite intercalations are not continuously developed. This wollastonite locality is about 500m apart on the surface from the granite intrusion. Therefore the formation of wollastonite may be related to the intrusion of granite.

The thickness of wollastonite intercalations varies from several ten centimeters to a few meters. The contact between limestone and wollastonite intercalation is considerably sharp in the field. However, the rosette-shaped wollastonite is often found in limestone near the wollastonite intercalations.

Under the microscope, wollastonite shows elongated or acicular aggregates in association with calcite (Fig. 1). The size of wollastonite crystals are 5-15 mm in length. Small amounts of diopside, vesuvianite and sphene are associated with wollastonite.

MATERIALS

Wollastonite is closely associated with calcite. Therefore it is very hard to get pure wollastonite sample. In order to prepare pure sample for dissolution experiment, first of all, the wollastonite-rich part was crushed to powder and sieved using 230 mesh sieve. The powder has been then leached with 6N HCl three times to remove the calcite impurity and then rinsed with distilled water for eight times in the centrifuge at 3000rpm. The electrical conductivity of finally rinsed water was $3.2\mu\text{mho/cm}$. It is expected that the reactive sites of particles and ultrafines are dissolved by such an acid treatment.

Electron microprobe analyses (Table 1) show that the wollastonite sample used for this study is

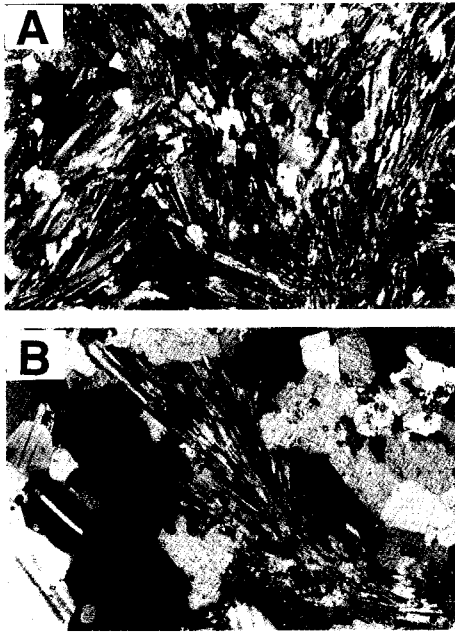


Fig. 1. Photomicrograph of wollastonite from Susan. A: Fibrous wollastonite aggregates. B: Wollastonite fibers in crystalline limestone.

considerably pure except a few samples containing about 0.25% FeO. X-ray diffraction analysis shows that wollastonite from Susan has triclinic cell with $a=7.932 \text{ \AA}$, $b=7.328 \text{ \AA}$, $c=7.069 \text{ \AA}$, $\alpha=89.995^\circ$, $\beta=95.255^\circ$, and $\gamma=103.367^\circ$.

EXPERIMENTAL

Occurrence and mineral association of wollastonite have been studied both in the field and in the laboratory. Identification was made using Rigaku Geigerflex X-ray diffractometer. Mineral association was studied under the polarizing microscope.

Dissolution behavior of wollastonite was studied in three different modes of dissolution experiment; two different dissolution experiments with HCl (one batch type and one "re-initialization method"). Re-initialization method is a kind of re-action method used in studying mineral-water reaction, in which mineral sample is reacted with aqueous solution and after certain time, the min-

Table 1. Table 1. Electron microprobe analyses of wollastonite.

	w1742	w1519	w1817	w1823
SiO ₂	50.36	50.60	50.60	50.72
TiO ₂	0.03	0.00	0.00	0.06
Al ₂ O ₃	0.03	0.07	0.02	0.03
Cr ₂ O ₃	0.02	0.07	0.03	0.03
FeO	0.06	0.25	0.02	0.10
MnO	0.11	0.07	0.09	0.10
MgO	0.03	0.07	0.01	0.06
CaO	48.84	49.04	49.04	49.30
Na ₂ O	0.03	0.00	0.00	0.00
K ₂ O	0.04	0.04	0.03	0.04
Total	99.54	100.02	99.87	100.40

	w1829	w1841	w1919	w201
SiO ₂	51.02	50.67	50.81	51.04
TiO ₂	0.06	0.02	0.04	0.01
Al ₂ O ₃	0.02	0.03	0.01	0.03
Cr ₂ O ₃	0.05	0.11	0.00	0.00
FeO	0.07	0.12	0.10	0.06
MnO	0.05	0.13	0.11	0.08
MgO	0.00	0.15	0.02	0.01
CaO	49.21	49.61	49.43	48.93
Na ₂ O	0.00	0.00	0.01	0.00
K ₂ O	0.06	0.03	0.02	0.04
Total	100.53	100.77	100.55	100.20

eral sample is filtered and dried and used for further reaction with solutions of the same (or different) compositions again. This procedure is repeated again and again. This method aims to detect the changes in solid phase, especially in surfaces, between the two neighboring experimental steps by analyzing the solutions reacted with mineral. In this method solution composition can be maintained constant, and smaller amount of solid sample is needed than in the batch type experiment.

The pH 4 HCl and distilled water were firstly equilibrated with carbon dioxide in the air and then reacted with wollastonite. The variations of pH as well as the concentration of dissolved cations were periodically measured to know the process of interaction of wollastonite with HCl or

distilled water. The reacted solutions were filtered with a membrane filter of $0.2\ \mu\text{m}$ pore size and then measured for pH using an Orion EA 940 pH-meter and for cations using the inductively coupled plasma-atomic emission spectrometer (ICP-AES). The solid materials were dried and then X-rayed for identification. X-ray analysis was needed to check the phase of solid materials during or after the procedures. Dissolution experiments with HCl were done at ordinary environment. 1. 25 grams of pure wollastonite powders ($<62\ \mu\text{m}$) were reacted with 125 grams of pH 4 HCl at $25\ ^\circ\text{C}$ in the reaction bottle (by batch type) by continuous shaking water bath (Run 1), or by continuous shaking for ten minutes employing the re-initialization method (Run 2). In Run 2, the solid sample firstly reacted with pH 4 HCl at $20\ ^\circ\text{C}$ for ten minutes was filtered and then reacted again with pH 4 HCl for 10 minutes repeatedly. In another one experiment, coarse-grained wollastonite fragments were reacted for one hour with 125 gram of distilled water which was equilibrated with atmospheric carbon dioxide by employing the re-initialization method (Run 3). The solutions after reaction were analyzed for pH and cation concentrations in the same way as above.

RESULTS

pH variation

In Run 1 in which wollastonite powder was reacted with pH 4 HCl solution equilibrated with atmospheric carbon dioxide, pH shows rapid rise from 4.0 to 6.5 in 2.5 hours but after this slow rise reaching pH 7.6 in 120 hours (Fig. 2).

In Run 2 in which wollastonite powder was reacted with pH 4 HCl solution for 10 minutes and then repeating the same procedure again and again, pH of solution showed very rapid rise from 4 to 5.5 in 10 minutes, then rapid fall in another 10 minutes and then to 4.15 in 50 minutes (Fig. 3), but after this point pH showed slow rise (Fig. 4).

In Run 3 in which coarse-grained wollastonite

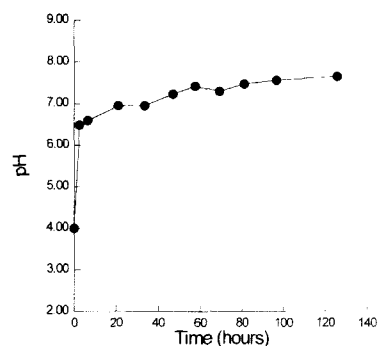


Fig. 2. pH variations in the reaction of powder wollastonite with pH 4 HCl in batch experiment (Run 1).

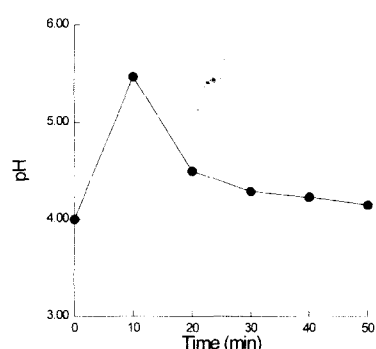


Fig. 3. pH variations in the reaction of powder wollastonite with pH 4 HCl employing the re-initialization method (Run 2).

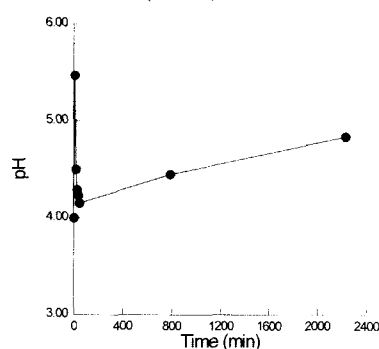


Fig. 4. pH variation of powder wollastonite with pH 4 HCl employing the re-initialization method (Run 2). Fig. 3 corresponds to the reaction of beginning stage of this figure.

fragments were reacted with distilled water employing the re-initialization method, pH of solution showed slow rise from 5.69 to 8.6 in two hours, and then nearly the same pH value (Fig. 5).

Wollastonite from Susan and Its Dissolution Behaviors

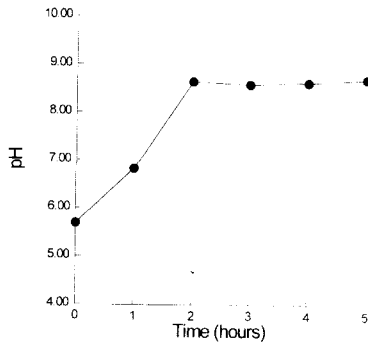


Fig. 5. pH variations in the reaction of coarse-grained wollastonite fragment with distilled water employing the re-initialization method (Run 3).

Cation Concentration

Concentrations of cations (Si and Ca) dissolved from wollastonite were measured for each run of reaction experiments. The Si and Ca concentrations in Run 1 are cumulative values throughout the experiment, whereas they are values for each 10 minutes and 1 hour reaction in Runs 2 and 3. Therefore direct comparison of curves is meaningless.

Fig. 6 shows that in Run 1 Si concentration increases very rapidly with time showing linear relationship up to 100 hours and then increases slowly showing a plateau of the curve. But Ca concentration reaches 3 ppm rapidly in the beginning of reaction and then remains nearly constant. It is remarkable that Ca concentration is not variable in contrast to the rapidly increasing concentration of Si in this dissolution experiment. Fig. 7 shows that Si concentration increases up to 18 ppm in 10 minutes in the experiment employing the re-initialization method, whereas Ca concentration is only 1 ppm in 10 minutes and then remains nearly constant. It suggests that the dissolving rates of Si and Ca be constant in every step of reaction. Fig. 8 shows the Si and Ca concentrations with time in Run 3 in which coarse-grained wollastonite fragments are reacted with distilled water employing the re-initialization method. This figure shows that Si and Ca concentrations in one hour's reaction are variable: high in the beginning and low in the later reaction. Si concentration was 2.2 ppm in the first one hour

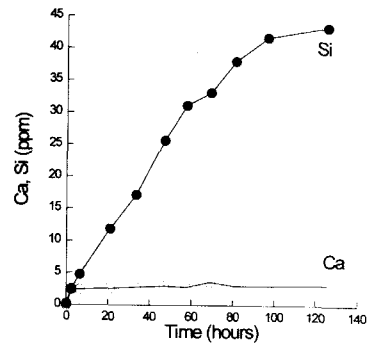


Fig. 6. Variation of Si and Ca concentration in the reaction of powder wollastonite with pH 4 HCl in the batch experiment (Run 1).

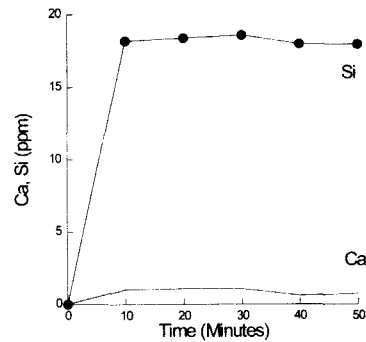


Fig. 7. Variation of Si and Ca concentration in the reaction of powder wollastonite with pH 4 HCl employing the re-initialization method (Run 2).

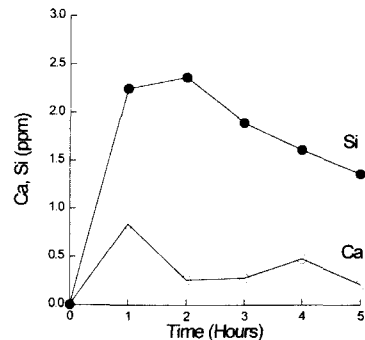


Fig. 8. Variation of Si and Ca concentration in the reaction of coarse-grained wollastonite fragment with distilled water (Run 3).

and 2.3 ppm in another one hour, but it decreased gradually to 1.5 ppm in 5 hours. But Ca concentration was 0.8 ppm in the first one hour and afterward it fluctuated around 0.3 ppm. This suggested that in the reaction employing the re-initialization method, dissolution of wollastonite

in distilled water in the case of coarse-grained fragments is fast in the beginning and slow in the late reaction.

DISCUSSION AND CONCLUSIONS

Wollastonite-HCl reaction in the batch type experiment shows a rapid rise in the very early stage and then slow rise in pH resulting a linear curve in the long periodic measurement (Fig. 2). However short periodic measurement of pH in the experiment employing the re-initialization method shows a rapid rise and a rapid fall in pH in the early stage showing a sharp pH-edges (Fig. 3), and then slow rise in pH showing a linear relation with time (Fig. 4). The early rapid rise is too fast to be the result of the dissolution of wollastonite. Correlation of pH variation and cation concentration of solution suggests such a conclusion. It might be due to the rapid sorption of H⁺ to oxygens at the reactive surface sites. The decrease of pH, following the early rise, to the initial solution pH, means that almost all available surface sites are occupied by H⁺ and no more sorption of H⁺ occurs. This variation pattern matches well with the parabolic pattern in the batch type experiment. Therefore, the re-initialization method is superior to the batch type experiment in interpreting the pH variation patterns.

It is significant to mention that Si and Ca are dissolved from wollastonite at different rate; Si at a high rate but Ca at a very low rate (Figs. 6, 7 and 8). However, Ca is dissolved at a high rate in the beginning but at a very low rate in the afterward reaction. The cause of the differential dissolution needs further more study. It might be partly due to the removal of Ca from wollastonite during the dissolution of calcite by acid treatment. Coarse-grained wollastonite-distilled water

reaction shows a parabolic dissolution curve in contrast to the linear curve in powder wollastonite-HCl reaction (Fig. 6).

The Ca/Si ratio in solution is high in the case of coarse-grained wollastonite, compared with powder wollastonite. It might be due to the smaller specific surface area in the coarse-grained sample compared with powder samples. Coarse-grained wollastonite-water reaction resulted in the solution with an elevated constant pH value of 8.6 after 2 hour's reaction with distilled water of pH 5.7 (Fig. 5). This is an important result because it can be used to neutralize the acid deposition.

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