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ABSORPTION AND FIXATION OF CARBON DIOXIDE BY ROCK WEATHERING

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ABSTRACT

The weathering of alkaline rocks, such as alkaline or alkaline earth silicate is thought to have played a great role in the historical reduction in the atmospheric CO_2 of this planet. To enhance the process artificially, we should increase the surface area of the rocks. However, some additional pulverization energy is necessary, which leads to the additional CO_2 emission. In the present paper, first, we reviewed the possibilities of the utilization of the reaction as a countermeasure against the CO_2 problem from the view points of resources and global carbon circulation. Second, we report the experimental results on weathering kinetics conducted for various kinds of silicates. Lastly, the amounts of pulverization energy of wollastonite and olivine sand were evaluated using industrial data of their pulverization. It was concluded that the CO_2 absorption by rock weathering is one of the most promising measures for CO_2 problem.

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KEY WORDS

Carbon Dioxide, Rock Weathering, Silicate, Carbonate, Dissolution Kinetics, Pulverization Energy

INTRODUCTION

The weathering of alkaline rocks, such as alkaline or alkaline earth silicate is thought to have played a great role in the historical reduction in the atmospheric CO_2 of this planet. The initial CO_2 pressure on the planet is thought to have been several tens atm, but recently, it is less than several hundreds ppm. It is usually believed that the overall chemistry of the CO_2 absorption by wollastonite, a typical silicate, is given by the following equation

$$CaSiO_3 + CO_2 \rightarrow CaCO_3 + SiO_2 \qquad (1)$$

and the produced $CaCO_3$ is stored as limestone like a coral reef. Thus, the coral reef has so far been believed as a carbon stock. This is superficially true. However, the intrinsic reaction of the coral reef formation is expressed as

$$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3 + CO_2 + H_2O \qquad (2)$$

which means that in this process, a part of the carbon dioxide is again released to the atmosphere (Kojima, 1994) from the ocean surface. Instead of the reaction (2),

we should focus attention on the reaction of rock weathering,

$$CaSiO_3 + 2CO_2 + H_2O \rightarrow Ca^{2+} + 2HCO_3^- + SiO_2 \qquad (3)$$
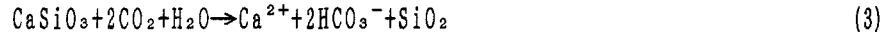
which occurs on land. Thus two moles of CO_2 are absorbed. They produce two moles of bicarbonate ions that are transported with one mole of calcium ion to the ocean, but one mole of CO_2 is again released with the formation of one mole of calcium carbonate (exactly, 0.6 mole of carbon dioxide is released with one mole of calcium carbonate deposition under the present ocean surface alkaline condition, Kojima, 1994). Thus the overall CO_2 fixation by eq. (1) is one mole (or a little more) per one mole of silicate.

In the present paper, first, we review the possibilities of the utilization of the reaction as a countermeasure against the CO_2 problem from the view points of resources and global carbon circulation. Second, we report the experimental results on the weathering kinetics conducted for various kinds of silicates. Lastly, the amounts of pulverization energy of silicates are evaluated using their industrial operation data.

PRELIMINARY EVALUATION

Resources. First of all, the amount of the silicate resources is discussed. The composition of the earth crust is shown in Table 1. It is clearly observed that alkaline silicates are abundant in the crust.

Table 1 Composition of Crust in vol% (Nesbitt and Young, 1984)

Minerals and representative Composition	Crust	Cont. Crust	Exposed Crust
Quarts, SiO_2	18	23.2	20.3
Plagioclase, $NaAlSi_3O_8$ or $CaAl_2Si_2O_8$	42	39.9	34.9
Glass, SiO_2	–	0.0	12.5
Potassium feldspar, $KAlSi_3O_8$	22	12.9	11.3
Olivine, $(Mg, Fe)_2SiO_4$	1.5	0.2	0.2
Pyroxene, Pyroxenoid, $(Ca, Mg, Fe)SiO_3$	4	1.4	1.2
Amphibole, $(Ca, Mg, Fe)_7Si_8O_{22}(OH)_2$	5	13.7	12.0
Phyllosilicate, $K_2Al_6Si_6O_{20}(OH)_4$	4	8.7	7.6
Magnetite, Fe_3O_4	2	1.6	1.4

Order of Magnitude Estimation of Rate. To utilize the weathering process artificially, the most important factor is its rate. To enhance it, we should increase the surface area of the rocks, however, some additional pulverization energy is necessary, which leads to the additional CO_2 emission. To evaluate the necessary degree of pulverization, we roughly evaluated its rate from the view point of global change in atmospheric CO_2 concentration.

It is well known that the carbon dioxide concentration was drastically reduced in the order of 1 Gy. Now it is required that the present CO_2 concentration is reduced in the order of 100y. Here, one layer of the silicate rocks with diameter of 100m was assumed to suffer the natural weathering process, though definite value of the equivalent diameter is unknown. When we use these rocks to absorb CO_2 from the atmosphere, the rocks should be pulverized into the order of diameter of

(100m) (100y)$\angle$(1Gy)=10μm under the assumption of linear rate to the concentration of CO_2. If we capture 10-20% CO_2 in flue gas from power station, and select most suitable rocks, the rate is increased by three orders of magnitude because of higher concentration of CO_2 in the flue gas. Therefore if 0.1 % of the exposed silicate resources is mined, pulverized to 10 μm or larger, and used for CO_2 absorption from flue gas, the increase in atmospheric CO_2 is prevented for the order of 100 y. The rate will be larger in the CO_2 saturated water than under the natural, usually dry condition.

Possibility of Increase of Net CO2 Fixation Using Deep Ocean and Utilization of Weathering of CaCO3. Though net fixation of carbon dioxide is possible even by eq. (1), i.e., combination of eqs. (3) and (2), the carbon dioxide fixation becomes more efficient by preventing the process of eq. (2). When we dispose the product from eq. (3) into the deep ocean, eq. (2) does not occur under the chemical equilibrium condition. Furthermore, the acidification of deep sea water, which is worrysome in case of direct injection of liquefied CO_2, does not occur. (Even if eq. (2) occurred in the deep ocean, the produced CO_2 would be dissolved into the oceanic water by its high pressure and would not be released into the atmosphere for the order of thousand years of ocean water circulation.)

The products from eq. (3) are expected to contain fine SiO_2 powder. This causes the increase in density of the produced slurry, which enhance its sedimentation rate into the deep ocean, without any additional energy input. The unreacted fine minerals also contribute to increase the apparent density.

Taking the above possibility into account, the weathering of calcium carbonate,

$$CaCO_3 + CO_2 + H_2O \rightarrow Ca^{2+} + 2HCO_3^- \tag{4}$$

the reverse reaction of eq. (2), is also thought to contribute to the net CO_2 fixation. In the present study, calcium carbonate was therefore also chosen as a sample.

EXPERIMENTAL EVALUATION OF RATE

Next, we conducted the experimental rate evaluation for various kind of silicates; wollastonite, olivine sand, potassium and sodium feldspars (orthoclase, albite and nephelite with cyanite), talc and calcium carbonate.

Preliminary Experiments on Direct Carbonation at High Temperature. In a recent publication (Lackner *et al.*, 1995), it was pointed out that CO2 could be absorbed by eq. (1) using same kinds of minerals as in the present study, directly at high temperature. They indicated that eq. (1) progresses at the temperature less than 554 K for wollastonite and

$$1/2 \cdot Mg_2SiO_4 + CO_2 \rightarrow MgCO_3 + 1/2 \cdot SiO_2 \tag{5}$$
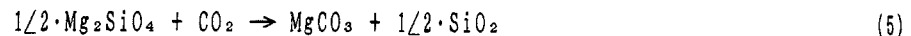
eq. (5) under 515 K for olivine at 1 atm, from the thermodynamic consideration of $\Delta G < 0$. Therefore, we tried to examine the possibilities of the reaction by using TGA and to compare with our results shown below, because they did not conduct any experimental demonstration. However our TGA results indicated no apparent

weight change for several hours under the temperature range shown above while the following aqueous absorption rate by eq. (3) was obviously higher than the high temperature reaction of eq. (1). Therefore, in the present paper, we only focused on the aqueous absorption.

Experimental. The expected chemical reaction schemes for the various kinds of rocks are shown in Table 2. The dissolution kinetics of minerals suspended in water (mostly 0.1 wt% of solid) was measured for 0 - 600 hr at 25°C. The 500 cm^3 of deionized water presaturated with pure CO_2 was employed and sufficient amount of CO_2 (2 cm^3/s) was continuously introduced with mechanical stirring at 600 rpm. The experimental apparatus is shown in Fig. 1. The filtered aqueous solution was acidified and then analyzed for the main metal element of the mineral by ICP-AES (Kyoto Koken, UOP-1 MKII).

In comparison, almost the same experiments were conducted under various conditions as follows, by keeping other factors same as the standard conditions; diameters for Sicatec, Olivine sand, and calcium carbonate K1; stirring speed; N_2 instead of CO_2; 1 wt% or 0.01 wt% instead of 0.1 wt%.

Table 2   Assumed Chemical Reaction Scheme

wollastonite $CaSiO_3 + 2CO_2 + H_2O \rightarrow Ca^{2+} + 2HCO_3^- + SiO_2$	$(Ca:CO_2=1:2)$
calcium carbonate $CaCO_3 + CO_2 + H_2O \rightarrow Ca^{2+} + 2HCO_3^-$	$(Ca:CO_2=1:1)$
olivine $Mg_2SiO_4 + 4CO_2 + 2H_2O \rightarrow 2Mg^{2+} + 4HCO_3^- + SiO_2$	$(Mg:CO_2=1:2)$
orthoclase $2KAlSi_3O_8 + 2CO_2 + 3H_2O$	
$\rightarrow 2K^{2+} + 2HCO_3^- + 4SiO_2 + Al_2Si_2O_5(OH)_4$	$(K:CO_2=1:1)$
albite $2NaAlSi_3O_8 + 2CO_2 + 3H_2O$	
$\rightarrow 2Na^+ + 2HCO_3^- + 4SiO_2 + Al_2Si_2O_5(OH)_4$	$(Na:CO_2=1:1)$
talk $Mg_3Si_4O_{10}(OH)_2 + 6CO_2 + 2H_2O$	
$\rightarrow 3Mg^{2+} + 6HCO_3^- + 4SiO_2$	$(Mg:CO_2=1:2)$

Table 3   Experimental results

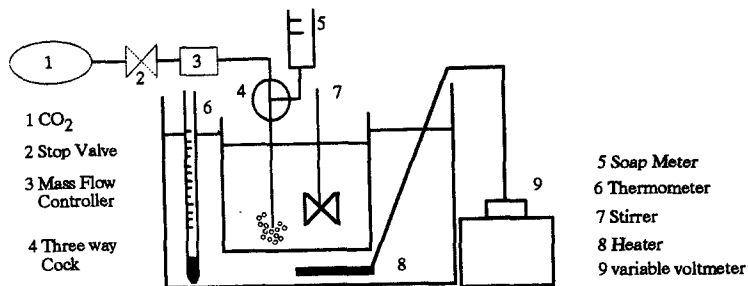|	metal wt % by EPMA	rep. d. SEM, μm	S. area SEM m^2/g	rate, mmol/m^{2}h metal,	CO$_2$
wollastonite ($CaSiO_3$)	CaO:48.3*				
LF-60 (China)	45.2	75.9	.0205	0.73	1.46
Sicatec (China) powder	37.0	44.2	.0355	0.52	1.04
olivine (chrysolite, Mg_2SiO_4)	MgO:57.3*				
Olivine sand, PAN	36.4	40.8	.0549	0.11	0.22
calcium carbonate ($CaCO_3$)	CaO:100.0*	(except CO$_2$)			
(Japan, Fukushima) K1	92.3	168	.0135	0.45	0.45
heavy calcium carbonate	97.2	1.72	1.35	0.37	0.37
orthoclase ($KAlSi_3O_8$)	K$_2$O:16.9*				
orthoclase (Australia)	12.5	11.8	0.207	.021	.021
indian orthoclase	14.5	18.8	0.132	.038	.038
nephelite ($NaAlSiO_4$)	Na$_2$O:19.8*				
with cyanite (Al_2SiO_5)	8.8**	9.67	0.267	.024	.024
albite ($NaAlSi_3O_8$)	Na$_2$O:11.8*				
indian soda feldspar	13.6	11.6	0.203	.034	.034
talk ($Mg_3Si_4O_{10}(OH)_2$)	MgO:31.9*				
99 talk (China)	34.1	18.3	0.298	.025	.050

*theoretical, **10.3% of K$_2$O is also included.
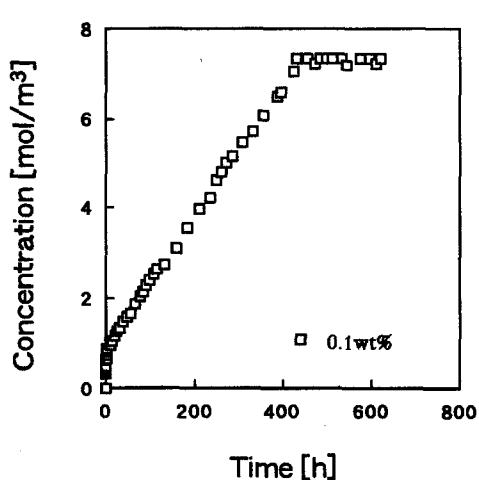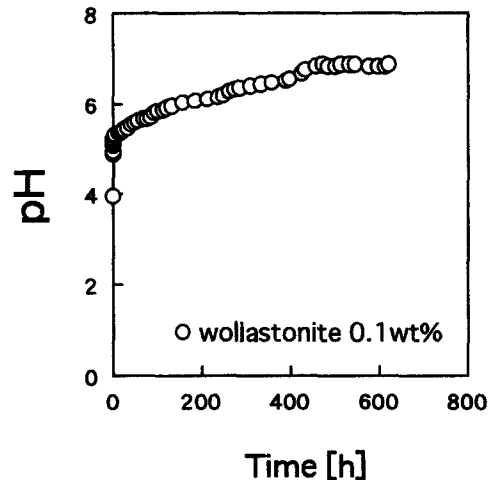
Fig. 1 Experimental apparatus.

1 CO_2

2 Stop Valve

3 Mass Flow
   Controller

4 Three way
   Cock

5 Soap Meter

6 Thermometer

7 Stirrer

8 Heater

9 variable voltmeter

Fig. 2 Time variation of Ca^{2+} concentration.   Fig. 3 Time variation of pH.

Characterization of Samples. The characterization of samples was done by SEM with EPMA. From SEM photographs, mean representative diameter and surface area were determined. The surface area was determined regarding particles as pillars for wollastonites. Their chemical composition was also determined by EPMA. The results are shown in Table 3.

Results. The time variation curves of calcium ion concentration and pH are shown in Figs. 2 and 3 respectively, for wollastonite (0.1 wt%) as examples with CO_2 introduction, while no obvious increase in the metal ion concentration was found when nitrogen was introduced instead of CO_2. After an initial rapid increase in the metal concentration, it linearly increased with time and then attained a plateau value as reported previously (Nagamine *et al.*, 1994). The initial rapid increases in concentration and pH were thought to be caused by rapid ion exchange between surface metal ions and aqueous protons. The plateau concentration was found to be determined by the dissolution equilibrium. From the linear dissolution stage, the intrinsic dissolution rate of the mineral was determined. The rate was found not to be affected by the stirring speed or gas flow rate under the conditions employed. The rate was also found to be proportional to the surface area of the sample, irrespective of the wt. ratio of sample to water, or its average diameter. Thus the concentration attained to the plateau value more rapidly (within several tens hr) for the case of 1 wt%. The dissolution rate per unit area, of

particles once utilized for the experiment was almost same as that of fresh particles. It was concluded that the dissolution kinetics was controlled at the mineral surface area. The calculated linear rates per unit surface area are shown in Table 3. The dissolution rates of wollastonite and calcium carbonate were found to be faster than others.

PULVERIZATION ENERGIES

Lastly, the pulverization energies of wollastonite and olivine sand were evaluated using industrial data of their pulverization. The required amounts of electricity of the pulverizers for 6t/h of wollastonite from 200 mm to 75μm are 55 kW for a single crusher, 100 kW for a hammer crusher, and 100 kW for a roller mill, in series. The CO_2 emission from pulverizers is given as 18.7 kg-CO_2/t-wollastonite using average CO_2 emission from power plants, 0.44 kg-CO_2/kWh, while the CO_2 uptake by wollastonite is theoretically 758 kg-CO_2/t from eq. (3). Thus the the CO_2 emission from pulverizers was 2.47 % of the fixed amount of CO_2 by rock weathering. When the wollastonite is pulverized to 10μm, the pulverizatio energy will be increased to 6.76 %, according to the Bond's theory. On the other hand, when more efficient pulverization process is employed, its energy can be saved. In case of olivin sand, pulverization energy to 41μm for a 30,000 t scale plant using 10 crushers or mills, was given as 32 kWh/t and 14.1 kg-CO_2/t while CO_2 uptake is 1251 kg-CO_2/t from table 2. Thus the the CO_2 emission from pulverizers was 1.13 % of the fixed amount of CO_2 by rock weathering for 41μm and 2.28 % for 10μm though its rate is 15% of that of wollastonite.

CONCLUSION

It was concluded that the CO_2 absorption by rock weathering is one of the most promising measures for CO_2 problem from the present experimental and energy evaluation. Wollastonite was found to be most reactive among the minerals tested in the present study.

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