Analysis of the mechanism of hydrothermal carbon dioxide fixation into serpentine with estimation of equilibrium of chemical species

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Abstract

Developing CO_2 storage technology is attracting attention as a reduction of the concentration of greenhouse gases. Serpentinite ($Mg_3Si_2O_5(OH)_4$) is widely distributed in the ground and one of the agents for CO_2 capture because CO_2 can be immobilized as magnesite ($MgCO_3$) in hydrothermal condition. In this study, we examined the fixation of CO_2 in serpentine under hydrothermal condition. The equilibrium composition of species in this system under hydrothermal condition was calculated and the effect of temperature and pH on CO_2 fixation is discussed.

 CO_2 fixation experiment was conducted with batch type reactor by introducing the serpentine powder, water and pressurizing with CO_2. A certain concentration of nitric acid and sodium hydroxide aqueous solution was used for changing pH of solution. After the reaction, the recovered powder was analyzed with TG-DTA and XRD. The equilibrium composition was calculated using PHREEQC software with llnl.dat database. The initial amount of gas, liquid (solvent) and solid species, initial temperature and pressure was given. Thermodynamically stable species were determined at each temperature to satisfy the mass balance. In the experiment, the yield of magnesite was below 15% based on magnesium atom and once decreased and increased with initial pH of solution at 7.1 MPa of initial pressure of CO_2 for 6 h. The reaction mechanism was proposed by the main species in the calculated equilibrium composition. The dissolution of serpentine was enhanced by the contribution of H^+ in low pH region and synthesis of magnesite was enhanced by OH^- in high pH region based on the mechanism and these factors probably promoted the formation of magnesite.

Keywords

Hydrothermal, Carbon dioxide, Serpentine

1. Introduction

The fixation of CO_2 in minerals in natural rock abundant is one of the methods for carbon dioxide capture and storage. Serpentine ($Mg_3Si_2O_5(OH)_4$) is a suitable feedstock for capturing and sequestering CO_2 as a carbonate mineral. The carbonation of serpentine generally produces magnesite ($MgCO_3$), which is stable and thus ensures long-term CO_2 fixation. The development of the process for hydrothermal CO_2 fixation to serpentine by using heat from CO_2 exhausting industrial production process is expected for effective CO_2 capture higher reaction rate than ambient condition.

Hydrothermal serpentine carbonation occurs and one of the main products is magnesite [1-5]. To develop a hydrothermal serpentine carbonation process, the effect of temperature and pH needs to be evaluated experimentally. Further, it is difficult to measure the concentration of chemical species during the hydrothermal reaction, the estimation of chemical species is also important to understanding the phenomena in the reactor. In particular, the effect of temperature and initial pH are basic information for considering hydrothermally CO_2 fixation process. This study examined the fixation of CO_2 in serpentine under hydrothermal condition. The equilibrium composition of species in this system under hydrothermal condition was calculated and the effect of temperature and pH on CO_2 fixation is discussed [6].

2. Experimental

2.1. Materials

Serpentine was sieved to less than 500 μm and calcinated at 903 K for 6 h. The estimated chemical formula from XRF analysis was $Mg_3Si_2O_5(OH)_4 \cdot 0.16Fe_2O_3 \cdot 0.10Al_2O_3 \cdot 0.11CaO$. The amount of magnesium in serpentine was calculated from this chemical formula. The purity of CO_2 was greater than 99.5%. Distilled water was obtained from a water purifier.

2.2. Apparatus and Procedure

The batch reactor (10 cm³) made from a titanium alloy and purchased from ACRAFT was used for the reaction. The 0.38 g serpentine and 5.0 g water were loaded into the reactor and was then connected a high pressure valve (SS-3NBF2, Swagelok). After purging with CO_2, CO_2 was introduced into the reactor by a high-pressure CO_2 pump (SCF-Get, JASCO Corporation). For the experiment of controlling initial pH, a certain concentration of nitric acid and sodium hydroxide aqueous solution was used instead of water. The reactor was submerged in a sand bath (ACRAFT) that was heated to the reaction temperature. After 6 h of reaction time, the reactor was cooled in a water bath. The solid product was recovered by filtration with a 0.1 μm PTFE filter, dried overnight, and weighed. The solid product was analyzed using a

TG-DTA (Thermo Plus Evo II, Rigaku Corporation) under nitrogen atmosphere from room temperature to 1273 K and by XRD (Ultima IV, Rigaku Corporation) and observed by SEM (JSM-5610LV, JEOL Ltd.). The yield of carbonated products was defined as the molar ratio of magnesium in the carbonated products to total magnesium in the recovered sample.

3. Experimental Results

XRD profiles of products indicate that the sample was almost antigorite that is one of the kinds of serpentine [7,8]. TGA results of products revealed that carbonated product was magnetite only and others were antigorite [4, 7-9]. The yield of magnetite was calculated by the decrease in weight related to decarbonation of magnetite.

Fig. 1(a) shows the yield of magnesite against temperature obtained at 7.1 MPa of initial CO_2 pressure for 6 hours in distilled water. In this condition, the loaded amount of CO_2 was 4.5 g, the molar ratio of CO_2 to CO_2+water was 0.27 and the molar ratio of CO_2 to Mg in serpentine was 2.9. The yield of magnesite once increased with increasing temperature and then slightly decreased. There is the optimal temperature in the case of constant loading.

Fig. 1(b) shows the yield of magnesite versus initial pH of loaded solution at 7.1 MPa of initial CO_2 pressure for 6 hours. The yield of magnesite decreased with increasing initial pH and then increased over pH=12. Acidic and basic conditions were preferred to the magnetite formation. The maximum yield of magnesite was 12.7% at pH=1.0, which means that acidic conditions was more advantageous than basic conditions. H_2SO_4 pretreatment of serpentine enhances the dissolution of magnesium [10], which is the same trend as the results in this study.

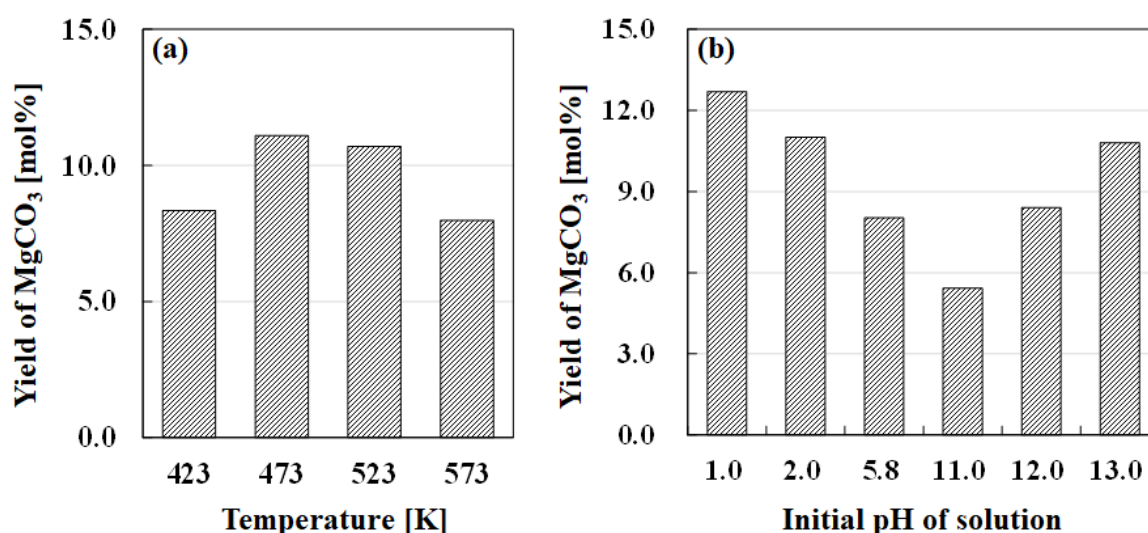

Fig. 1 Yield of magnetite in hydrothermal fixation of CO_2 to serpentine at 7.1 MPa of initial CO_2 pressure for 6 hours (a: In distilled water, b: At 573 K)

4. Estimation of equilibrium concentration

4.1 Method of calculation

The equilibrium was calculated using PHREEQC that is free software. The database used was llnl.dat database. This model calculates the concentration of chemical species derived from aqueous solution and can calculate at high temperature region up to 573 K [11].

At first, the initial amount of CO_2, water, liquid species, solid species, initial temperature, initial pressure, and final temperature were input. PHREEQC calculated thermodynamically stable gas, liquid and solid species to satisfy the mass balance and charge balance at the desired temperature. The calculation was conducted with the fixed volume mode. In this study, the volume of the gas phase and liquid phase were assumed to be always equal and constant and the solubility of CO_2 in water was calculated using the Peng–Robinson equation of state. Further, due to the limitation of calculation, the gas phase was assumed to be CO_2 only. The environment in the calculation was probably different from the actual reaction condition, however, the estimated equilibrium was useful for understanding the reaction mechanism.

The initial condition considering the actual reaction was 0.0168 mol/kg of antigorite as a serpentine, water, and 7.1 MPa of CO_2 were introduced into the reactor at 289 K. The compositional formula of antigorite ($Mg_{48}Si_{24}O_{85}(OH)_{62}$) was almost the same as standard formula of serpentine ($Mg_3Si_2O_5(OH)_4$). The initial pH of the aqueous solution changed by introducing HNO_3 or $NaOH$ into the system. The equilibrium concentration was expressed in unites of mol/kg-water.

4.2 Calculated results

At first, the dependence of equilibrium on temperature was calculated at 7.1 MPa of initial CO_2 pressure for 6 hours in distilled water. Fig. 2(a) shows the amount of species in solid phase against temperature. Magnesite ($MgCO_3$) and quartz (SiO_2) were main species from antigorite. Fig. 2(b), (c) and (d) shows the concentration of main species in liquid phase containing carbon atoms, magnesium atoms, and silicon atoms, respectively. The main species containing carbon atoms were dissolved CO_2, HCO_3^-, $MgHCO_3^+$, dissolved $MgCO_3$ and CO_3^{2-}. The concentration of ionic species decreased with increasing temperature. Interestingly, CO_3^{2-} was minor species. For magnesium containing species, Mg^{2+}, $MgHCO_3^+$ and dissolved $MgCO_3$ were main species and the concentration of these species decreased with increasing temperature. The trend of ionic species related to carbon and magnesium against temperature obeyed the principle that polarity of water decreases with increasing temperature. The main species containing silicon atoms were dissolved SiO_2, $HSiO_3^-$, $H_6(H_2SiO_4)_4^{2-}$ and $H_2SiO_4^{2-}$.

Next, the dependence of equilibrium on initial pH was calculated at 573 K and 7.1 MPa of
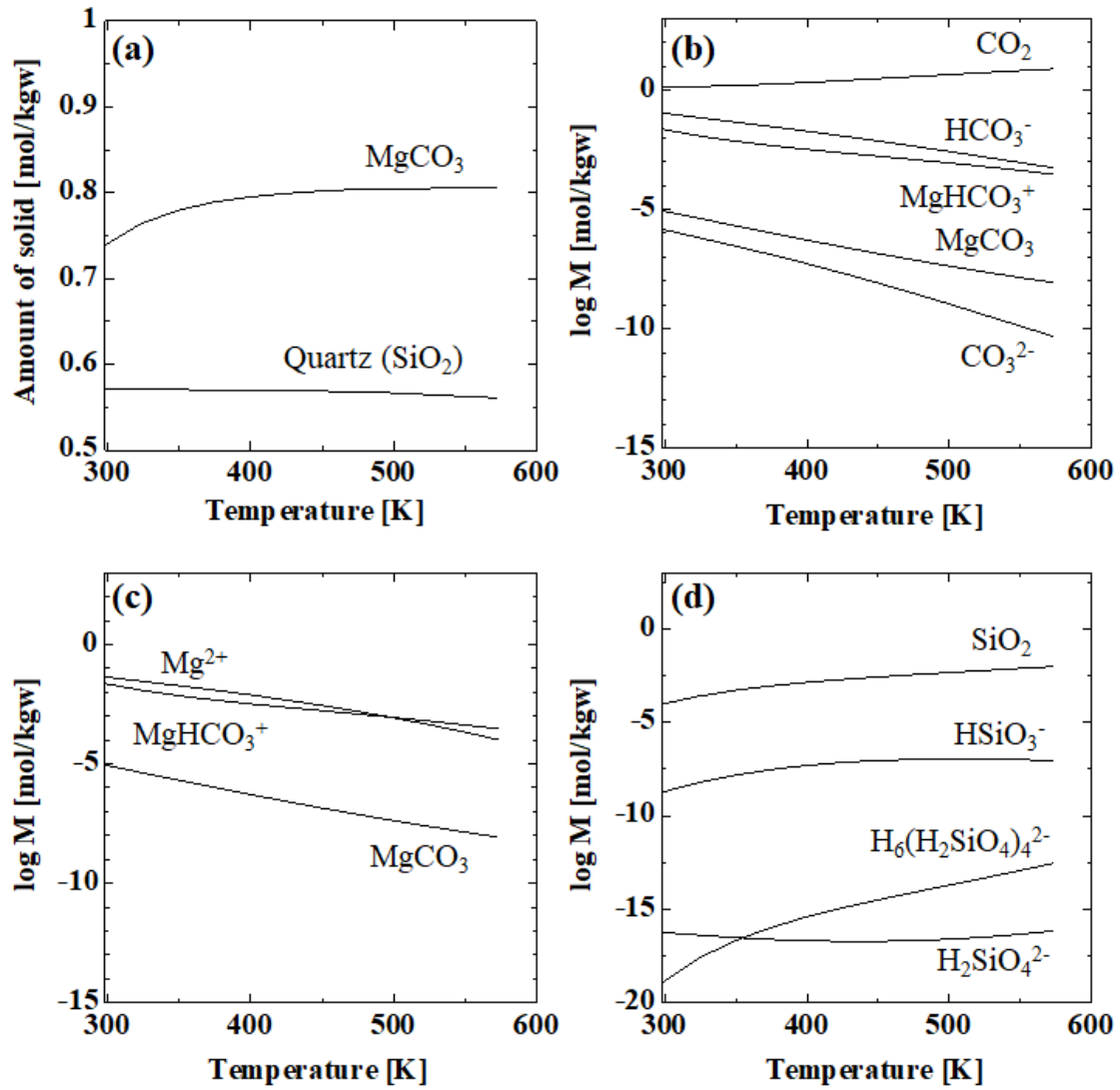
Fig. 2 Yield of $MgCO_3$ against temperature at 7.1 MPa of initial CO_2 pressure for 6 hours (a Solid phase, b: carbon containing species in liquid phase, c: magnesium containing species in liquid phase, b: silicon containing species in liquid phase)

initial CO_2 pressure for 6 hours. Fig. 3(a) shows the amount of species in solid phase against pH. Magnesite ($MgCO_3$) and quartz (SiO_2) were main species and the concentration of these species was almost constant against pH. Fig. 3(b), (c) and (d) shows the concentration of main species in liquid phase containing carbon atoms, magnesium atoms, and silicon atoms, respectively. The main species containing carbon atoms were dissolved CO_2, HCO_3^-, $MgHCO_3^+$, dissolved $MgCO^3$, and CO_3^{2-}. The concentration of dissolved CO_2 was always the highest and dissolved CO_2 was probably the source of CO_2 in liquid phase. The concentrations of HCO_3^- and $MgHCO_3^+$ were relatively high. The concentrations of HCO_3^- and CO_3^{2-} increased with
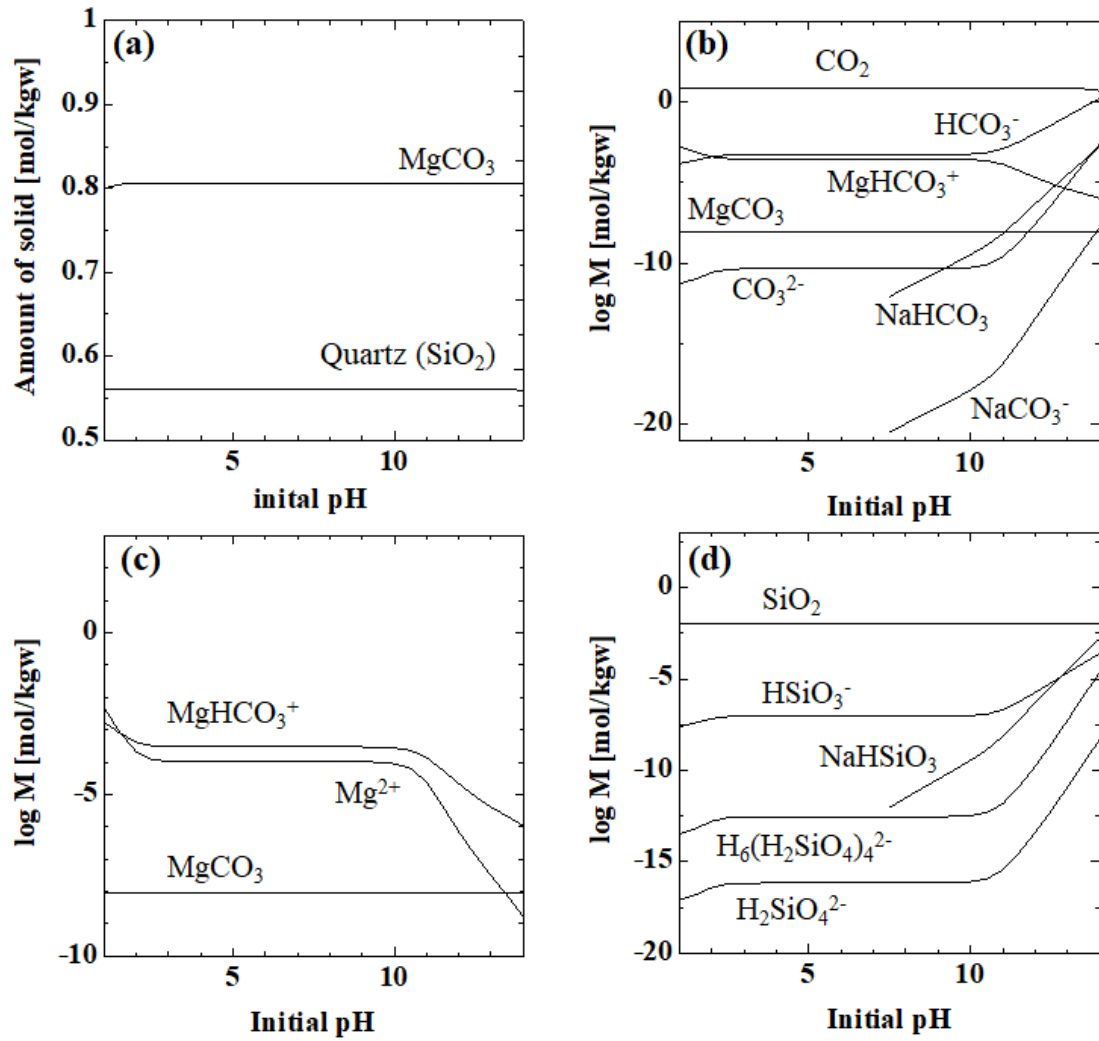
Fig. 3 Yield of $MgCO_3$ against pH at 573 K and 7.1 MPa of initial CO_2 pressure for 6 hours (a Solid phase, b: carbon containing species in liquid phase, c: magnesium containing species in liquid phase, b: silicon containing species in liquid phase)

increasing initial pH. In high pH region, $NaHCO_3$ and $NaCO_3^-$ appeared due to additional NaOH for adjusting pH and increased with increasing initial pH. For magnesium containing species, the main species were $MgHCO_3^+$ and Mg^{2+} and decreased with increasing initial pH over pH=10. The main species containing silicon atoms was dissolved SiO_2 and almost constant regardless of initial pH. The concentration of $HSiO_3^-$, $NaHSiO_3$, $H_6(H_2SiO_4)_4^{2-}$ and $H_2SiO_4^{2-}$ increased as the initial pH especially above pH=10.

5. Reaction pathway

In the calculation of equilibrium, the main species in solid phase were magnesite ($MgCO_3$) and quartz (SiO_2). These in liquid phase were dissolved CO_2, SiO_2, HCO_3^-, Mg^{2+} and $MgHCO_3^+$.

Fig. 4 shows the proposed main reaction pathway for this system. The dissolution of serpentine proceeded by the contribution of proton through Eq. 1 to form Mg^{2+}.
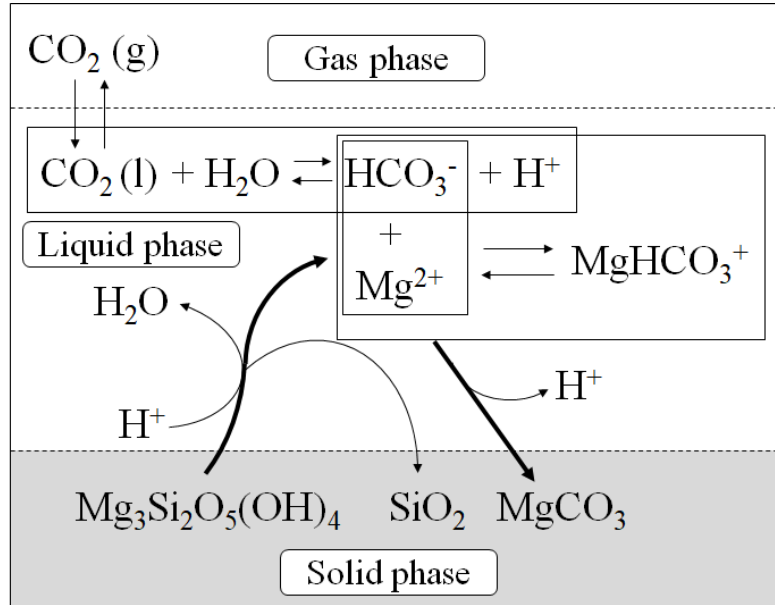
$$Mg_3Si_2O_5(OH)_4 \text{ (s)} + 6\ H^+ = 2\ SiO_2 \text{ (s)} + 3\ Mg^{2+} + 5\ H_2O \tag{1}$$
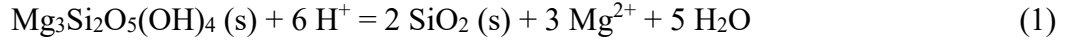
CO_2 in gas phase was dissolved in liquid phase and dissolved CO_2 reacted with H_2O to form HCO_3^- through Eq. 2.

$$CO_2 \text{ (l)} + H_2O = HCO_3^- + H^+ \tag{2}$$

Mg^{2+} derived from serpentine was reacted with HCO_3^- by Eq. 3 and 4 to produce $MgHCO_3^+$ and solid $MgCO_3$.

$$Mg^{2+} + HCO_3^- = MgHCO_3^+ \tag{3}$$

$$Mg^{2+} + HCO_3^- = MgCO_3 \text{ (s)} + H^+ \tag{4}$$

$MgHCO_3^+$ was deprotonated to form solid $MgCO_3$ by Eq. 5.

$$MgHCO_3^+ = MgCO_3 \text{ (s)} + H^+ \tag{5}$$

In the experiment, the yield of magnesite once increased with increasing temperature and then decreased. The reaction rate generally increased with increasing temperature while the concentration of ionic species containing carbon and magnesium atoms decreased with increasing temperature to suppress the reaction. The optimal temperature was probably determined from the balance of these factors. For the effect of initial pH in the experiment, both low pH region and high pH region were effective for the formation of $MgCO_3$. In low pH region, the dissolution of serpentine by Eq. 1 was enhanced with increasing of the concentration of proton to promote Mg^{2+} delivery. In high pH region, the reaction between Mg^{2+} and HCO_3^- (Eq. 4) and decomposition of $MgHCO_3^+$ (Eq. 5) was enhanced by neutralization of H^+ with OH^-. These reactions promoted the formation of magnesite in high pH region.

Conclusion

Hydrothermal fixation of CO_2 to serpentine was examined with batch type reactor. The magnetite was produced as a carbon containing product. From 473 K to 573 K, the yield of magnesite once increased with increasing temperature and then slightly decreased. At 573 K, the yield of magnesite decreased with increasing initial pH and then increased. The equilibrium composition was calculated using PHREEQC software with llnl.dat database. Thermodynamically stable species were determined at each temperature and to satisfy the mass and electric balance. The decrease in the yield of magnesite in high temperature region was probably due to the decrease of concentration of ionic species. In low pH region, the dissolution of serpentine was enhanced to produce Mg^{2+} from serpentine. In high pH region, the formation of magnesite and intermediate were enhanced by the contribution of OH^- for neutralization of H^+. The estimated equilibrium can be used for the explanation of the trends of experimental trends.

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