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Mineral Surface after Reaction with Aqueous Solution at High Temperatures and Pressures

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Abstract   This work presents new experimental results on surface chemistry of reacting minerals and interface kinetics between mineral and aqueous solutions. These experiments were carried out using a flow reactor (packed bed reactor) of an open system as well as a continuous stirred tank reactor, CSTR. The authors measured reaction rates of such minerals as zeolite, albite and carbonate (rhodochrosite, dolomite) in various solutions, and tested corresponding mineral surface by using SEM, XPS, SIMS, etc. This paper mainly presents the experimental results of zeolite dissolution in water and in low pH solutions at room temperature, and dolomite dissolution at elevated temperatures. The results show that the release rates of Si, Al and Na of zeolite are different in most cases. The incongruent dissolution of zeolite is related to surface chemical modifications. The Na, Al and Si release rates for dissolution of albite and zeolite in water and various solutions were measured as a function of temperature, flow velocity, pH and solution composition in the reaction system. In most cases, dissolutions of both albite and zeolite are incongruent. Dissolution of dolomite is also incongruent in most cases and varied with T, pH, and nature of aqueous solutions. For dolomite dissolution, the release rates of Mg are less than those of Ca at high temperatures as T increases from 25 to 300°C. SIMS study indicates that the contents of Al, Na and Si in the leached layer of zeolite or albite surface, change with the distance from the surface, exhibiting a non-linear behaviour within a thickness range of 1000%. The distributions of Ca, Mg, Mn, H and Cl in the leached surface layer of carbonate have a non-linear behaviour too.

Key words: mineral surface, kinetics, liquid/solid interface, reaction

1   Introduction

In order to understand the mechanism of rock (or mineral) and water (or aqueous solutions) interaction in the lithosphere, it is necessary to test mineral dissolution rates under the surface condition of the earth (Xu et al., 1997; Zhang Ligang et al., 1996; Zheng et al., 1995; Zhou et al., 1997). On the other hand, mineral surface takes an important role in water/rock interaction processes.

Previous kinetic experiments of minerals in hydrothermal solutions involving mineral dissolutions of feldspar, calcite, fluorite, kaolinite, gibbsite, etc, were performed. The results suggest that the dissolution rates of many minerals are affected by temperature, pH and solution composition. Incongruent dissolution of minerals is still an interesting problem. Some reports emphasize the congruent dissolution dominance at lower temperatures (<100°C) under conditions far

from equilibrium (Alekseyev, 1992; Alekseyev et al., 1993). Experimental studies suggest that the changes of mineral dissolution in stoichiometry can be treated as a function of time when the mineral is dissolved in constant physical and chemical conditions (Hellmann et al, 1989; Zhang et al, 1992; Hellmann, 1995). In these studies, the time evolution of the stoichiometry for albite was determined by the aqueous release rates of Sodium (Na), Aluminum (Al), and Silicon (Si) measured from the initial stages (non-steady state kinetics) to the establishment of steady state of kinetic conditions. In recent years, the authors have observed zeolite, albite, dolomite and $MnCO_3$ dissolution in water and in acidic solutions. These minerals have a behavior of incongruent dissolution in most cases. Albie dissolution is always incongruent in most cases except at 300°C. The release ratio of Al/Si (or Na/Si) for albite in water changed from positive to negative as T rises at from 25 to 400°C.

The maximum release rates of Na, Al and Si of albite dissolution in water under different flow velocities are always obtained at 300°C, which also depends on the nature of aqueous solutions (pH) and solution compositions.

The authors measured dissolution rates of zeolite and carbonate and investigated their incongruent dissolution behaviors with the purpose of understanding water/rock interaction in the nature.

2 Experimental Approach

The devices for the laboratory experiments were once used in previous studies, including a CSTR reactor, liquid pump, back pressure regulator, temperature controller, heat source (furnace), pressure gauge, electric conductivity detector and computer.

Natural zeolite crystals were obtained from a pegmatite vien in the Xinqiang district. Mineral particles were crashed in a shatter box and sieved to 20 to 40 mesh, then the pure zeolite crystals were handpicked under the microscope. After that in mineral particles were crashed again in a shatter box and sieved to 20 to 120 mesh. These particles were cleaned ultrasonically using acetone to remove fine particles, rinsed with distilled water and dried at 70–80°C. Then the surface areas of representative samples were determined by the single-point (Kr-He) BET method.

The chemical compositions of the zeolite sample were analyzed and are listed in Table 1.

Mineral particles were put into a nylon string bag, which was then placed in a pressure vessel. De-ionized and de-gassed water was injected into the vessel from the bottom to the top at different flow rates (0.5–3 ml/min). Output solutions were sampled and the compositions of these solutions were analyzed. The flow reactor incorporates a continuous input of aqueous solutions through the sample bag and a resulting continuous fluid output.

Within the CSTR reactor, a transient material balance is given by:

$$dU\text{i} / dt = Rate\ v\text{i}\ A/V - q/V(U\text{i}-U\text{i}^0)$$

where the U_i refers to the output concentration, $U\text{i}^0$ the initial concentration of input solutions, A total surface area, V the volume of pressure vessel, q the flow flux (could be flow velocity in some cases), r the reaction rate (mol/min or mol/m^2). vi is the stoichiometric coefficient of the ith reaction. The output solutions pass through an electric conductivity detector, and a computer monitor displays the continuous variation of electric conductivity of the fluids in the reaction system, which indicates if the system is at a steady state or not. As $\dfrac{\partial C}{\partial t} = 0$ (i.e. dU$_{i/dt}$), the system is at a steady state. At this time, the liquid product of the system is sampled (Zhang et a, 1990, 1992, 1998).

The current experiments for zeolite were carried out under a uniform condition in a temperature range of 15° to 18°C, a constant pressure of 1 bar, and a flow velocity varying from 0.5 to 3.0 ml/min.

Samples of output solutions were taken at a constant pressure, temperature and flow velocity. In order to obtain an aqueous sample at a steady state, fluid samples were normally taken one or two hours after the flow rate or input solution was changed. For each aqueous sample, the authors analyzed the concentrations of Na, Al and Si. Analysis was also conducted for the surfaces of solid (zeolite) prior to and following the procedure. The chemical compositions of zeolite were also analyzed. Through examination of the residence time, mineral surface area, and the concentration of dissolved materials in the input and output solutions, the authors are able to measure the reaction rates. Dissolution experiments for dolomite and albite were performed using the packed bed reactor of an open system with a temperature range from 25 to 400°C.

3 Results and Discussion

The experimental results are presented in term of release rates of Na, Al, Si for zeolite dissolution. The release rates of Na, Al, and Si were obtained at a constant temperature and pressure and under a variety of hydrodynamic condition, i.e. varied flow velocities.

Table 1   Chemical compositions of zeolite

SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	FeO	MgO	CaO	Na$_2$O	K$_2$O
46.57	26.82	0.04	0.07	0.19	–	15.88	0.2

TiO$_2$	P$_2$O$_5$	MnO	H$_2$O	Li$_2$O	CO$_2$	Sum	
0.01	0.1	0.09	9.27	9.89	0.24	99.72	

3.1   Release rates of Na, Al and Si in zeolite dissolution

The experiments were carried out using a CSTR reactor (continuous stirred tank reactor) in an open system. Zeolite dissolution rates in the flow system of the different aqueous solutions, regardless of different flow rates, were repeatedly measured. Results indicate that zeolite dissolution rates vary with pH of the input solutions and the flow velocities.

Na, Al and Si release rates in aqueous solutions were measured as functions of flow rate in the reaction system. The zeolite dissolution is described by plotting the output concentration of dissolving species (Na, Al and Si) against temperature or by plotting the release rate against temperature at each flow velocity.

The dissolution rates increase as the flow velocities change from lower to higher. However, under a constant hydrodynamic condition (flow velocity is constant) dissolution rates rise as pH decreases.

Dissolution rates increase as the pH of input solutions decrease from 7 to 2.45 and rise when the flow velocity increases. Such strong dependence on pH in zeolite hydrolysis can be expressed by

$$-r=kS(a_H^+)^m/(a_i)^n$$

where -r is the dissolution rate (in mol/min), k the rate

constant; s the surface area of minerals, m and n are the order of the rates, a_H^+ hydrogen ion activity in the solution, a_i the activity of aqueous species, such as Si, Al and Na in the solutions.

It can be seen in Fig. 1   that the release rates of Si, Al and Na are different. Zeolite dissolutions in water and in acidic solutions are incongruent in most cases. The dissolution rates of zeolite in a steady state were measured in a CSYR reactor of an open - flow system as the pH of input (or output) solutions, and such rates can be considered as a function of the concentrations of aqueous silica, aluminum and sodium.

At a far-from-equilibrium condition, dissolution rates are found to vary linearly with a_i^n, where a_i were designated as the activity of aqueous silica, aluminum and sodium, n is the rate order.

Because of incongruent dissolution, the release rate of Si is different from that of Al or that of Na in most cases. The n of Si-release rate is different from those of the release rates of either Al or Na.

The measured dissolution rates, which were obtained in a far-from-equilibrium condition, are consistent with what are expressed by

$$-r = k \Pi a_i^n$$

where -r refers to the dissolution rate, k the rate constant.

Zeolite dissolution rates in water and acidic solutions, pH=2.45 and pH=3.26) respectively, were measured with a CSTR open-flow reactor. Dissolution rates of albite are affected by changing flow velocity of the reaction system, i.e. by varying the average residence time. Therefore, different dissolution rates can be obtained at the same temperature. Increase in flow velocity leads to the increase of zeolite dissolution rates.

Based on the relation between the dissolution rate (release rate for Na, Al and Si) and the concentration of the output solution and the relations between logarithm values of dissolution rates and pH values, the zeolite dissolution rate law can be worked out. The simplified expression is
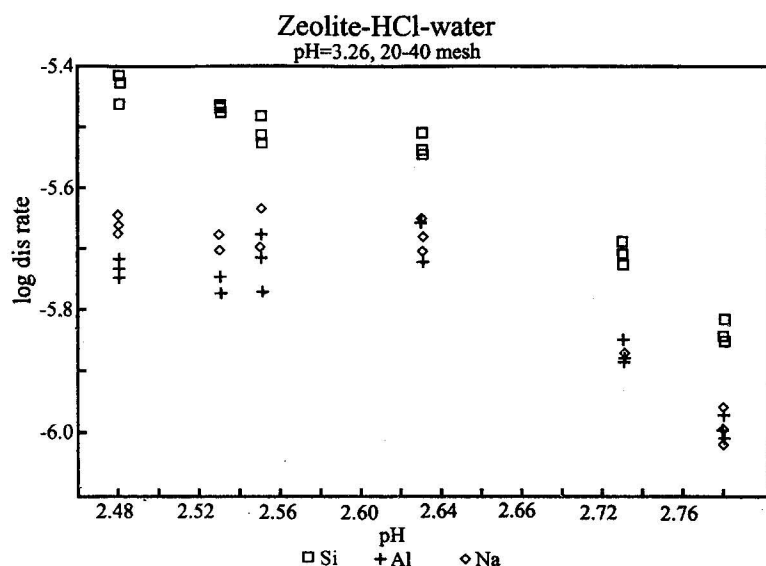

Zeolite-HCl-water
pH=3.26, 20-40 mesh

Fig. 1.   Logarithms of the release rates of Si, Al and Na vs pH of the output solutions when zeolite reacts with low-pH solutions.
□–release rate of Si; +–release rate of Al, and ◇–rate of Na.

shown as follows: (Aagaard & Helgeson, 1982)

$-r=k \, \Pi a_j^n [\, 1- exp \, (-A/\sigma RT)]$ (far from equilibroum)

$-r=k \, \Pi a_j^n$ (close to equilibroum)

where, $-r$ is the reaction rate (in mol/min or mol/min/m²), a_i is the activity of aqueous species, $-n_{ij}$ the stoichiometric coefficient of jth reaction; σ is the stoichimetric number. In fact, the value of exp $(-A/\sigma RT)$ could be negatiate in case st is far from the equilibrium state. The above equations are derived from the following equation:

Rate $= kSa\Pi \, a_i^n \, (1-Qj/Kj)$

Q_j stands for the activity product (experimental result) and K_j is the equilirium constant of the jth reaction (e.g. zeolite-water).

3.2 Incongruent dissolution of zeolite and surface chemistry

Zeolite dissolution is often incongruent in water and in acidic solutions. The current study bears out the hypothesis that dissolution moves from congruence to incongruent caused by the pH value of solution.

The release ratio is $\log \dfrac{(X/Si)_{aq}}{(X/Si)_{solid}}$, where X

refers to Na or Al, aq the aqueous solution, and solid to the original mineral material. A logarithm value of > 0 indicates positive incongruent dissolution; a logarithm value of 0 congruent dissolution; and a logarithm of < 0 negative incongruent dissolution. The release ratio (logarithm value) for Na/Si or Al/Si in a pH range from 2 to 7 shifts from positive to zero. In most cases, Na and Al easily enter into aqueous solution.

However, the shift of release ratio from zero to negative indicates that the Si release rate is higher than those of Na and Al. The release ratio at zero indicates congruent dissolution. The definition of release ratio can be used to investigate both albite and zeolite incongruent dissolution process. And also it can be used to describe dolomite dissolution.

Incongruent dissolution is usually caused by chemical modifications of mineral surfaces and changes in surface leached layers during a mineral-water reaction.

Correspondent observations were done between

fresh mineral surfaces and reacted surfaces by using SEM (Scanning Electronic Microscope), XPS (X-ray Photo Spectrometer) and SIMS (Second Ion Mass Spectroscopy). SEM study for zeolite and albite found that a smooth mineral surface appeares if zeolite (or albite) is reacted with acidic solution, while a roughly surface appears if reacted with water.
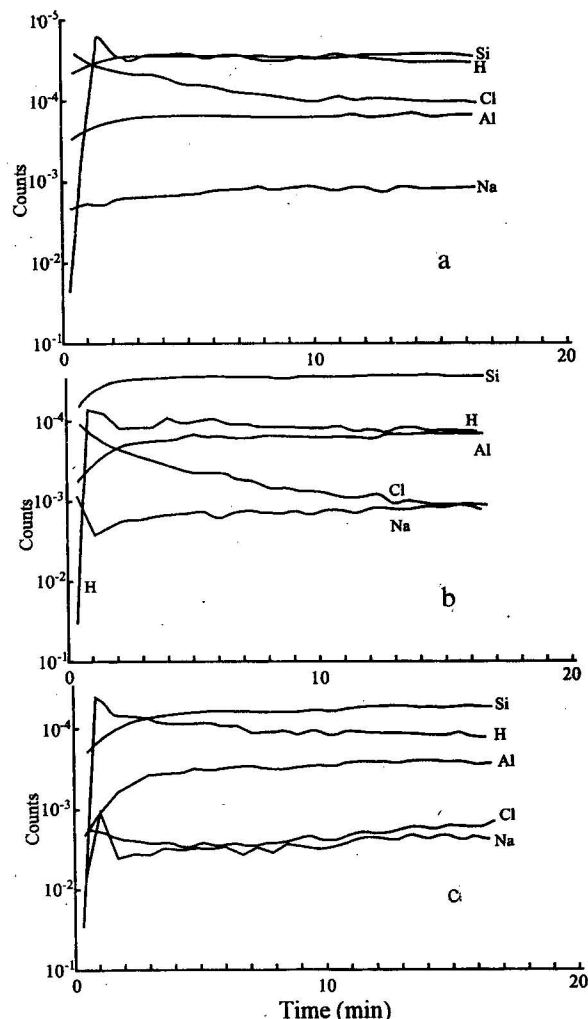

Fig. 2. SIMS study on zeolite surface.

a. Fresh mineral surface; b. react with water; c. react with low-pH solution.

The SIMS is a new technique for testing mineral surfaces after reactions. Fig. 2 shows the results of SIMS analysis for fluorite reacted with water and with HCl solution (εpH=3.26). The same condition is also illustrated in Fig. 1. This plot represents the results of SIMS analyses for Cs ion-sputtering in different time intervals (in minute). In fact, this is a profile for the

comparison of chemical compositions in terms of depth. Fig. 2 expresses the comparison of the SIMS results between fresh zeolite and reacted samples, and also indicates that chemical modifications of mineral surfaces are different between zeolite (or albite) reacted with water and that with low pH solution.

Results of surface study indicate that surface dislocation and chemical modification (from surface to surface leached layer of zeolite) happen simultaneously.

It has been found that Cl^- and proton H^+ penetrate into the surface of zeolite after reaction and Si, Al and Na removed out of the surface layer, so that the Si, Al, Na and H^+, Cl^- distribution curves in the depth profile are characterized by non-lineation and wavy from the surface to the interior.

3.3 Incongruent dissolution of dolomite

Dissolution of dolomite is also incongruent in most cases and varied with T, pH, and the nature of aqueous solutions. Dissolution experiments of dolomite were carried out using a flow reactor (packed bed reactor) of an open system in a temperature range from 25 to 300°C and a constant pressure of 13.8 MPa. For dolomite dissolution, release rates of Mg are less than those of Ca at high temperatures as T increases from 25 to 300°C (see Fig. 3).
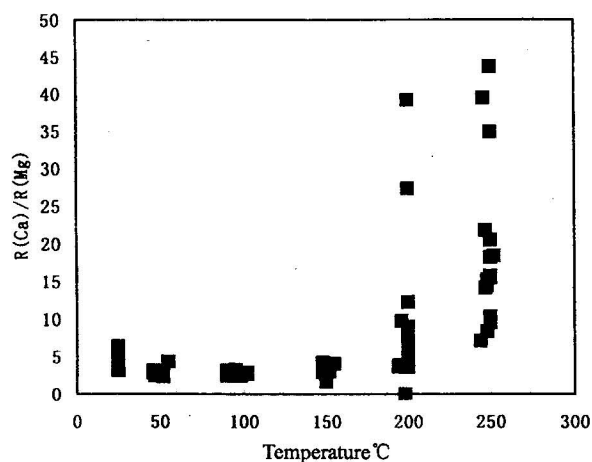

Fig. 3. Ratio of dissolution rates of Ca vs dissolution rates of Mg as a function of temperature.

Previous experimental results for silicate minerals suggested that the changes of mineral dissolution in

stoichiometry can be treated as a function of time in a particular condition and function of temperature and solution nature (pH). The current work presents the experimental results of zeolite dissolution in water and in low pH solutions at the room temperature. The results show that the release rates of Si, Al and Na of zeolite are different in most cases. The incongruent dissolution of zeolite is related to surface chemical modifications.

Acknowledgements

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Zhang Xuetong   Born in 1971; graduated from Material Science Department, Beijing Union University, 1996. She is working on chemical kinetics of mineral material-aqueous solutions interaction at elevated temperatures and pressures. And she joined the projects from the Ministry of Land and Resources and the Ministry of Sciences and Technology, working in the Open Research Laboratory of Geochemical Kinetics.