

ALTERATION ZONATION OF SILICA MINERALS IN A GEOTHERMAL SYSTEM - A NUMERICAL SIMULATION BASED ON REACTION-TRANSPORT MODEL

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SUMMARY - Dissolution and precipitation of silica polymorphs (amorphous silica, cristobalite and quartz) were incorporated into a geothermal reservoir simulator based on reaction kinetics. Reaction kinetics are simplified as follows; silica minerals are always precipitated from or dissolved into the solution without a direct solid phase transition among them. Only inorganic processes are considered and the effect of salinity is neglected. Modeling of reaction surface area was devised for both precipitation and dissolution of all silica minerals. Based on these assumptions and published experimental data of rate constants and solubilities, two dimensional numerical simulations of geothermal system development were performed. Alteration zoning of silica minerals was reproduced in the simulations as observed in natural geothermal systems. Sensitivity of silica alteration zoning to formation permeability and reaction surface area was also examined. The present model is preliminary, but the results show that numerical simulations incorporating chemical processes are promising for geothermal modeling, especially for reducing the non-uniqueness of the models.

1. INTRODUCTION

Natural state modeling for geothermal reservoir simulation always involves arbitrary assumptions. The information of geothermal alteration is one choice for constraining the geothermal model. Silica minerals (quartz, cristobalite and amorphous silica) are common alteration minerals. They form a one component system, dissolve congruently, and many data of solubility and dissolution / precipitation kinetics are published (Walther and Helgeson, 1977; Bohlmann et al., 1980; Rimstidt and Barnes, 1980; Fournier, 1982, 1983; Brady and Walther, 1990; Dove, 1994; Renders et al., 1995; Rimstidt, 1997). These characteristics of silica minerals are suitable for coupling chemical reaction with geothermal reservoir simulation in a reaction-transport system. Furthermore, understanding the behavior of silica minerals is useful to elucidate the development of the silica alteration zone as well as in estimating the influence of self-sealing or sealing by reinjection.

The studies on numerical simulation of the reaction-transport of silica involve one dimensional (Walder and Nur, 1984; Lowell et al., 1993) and two dimensional (Yano, 1994) flow models with silica in equilibrium with

quartz, a one dimensional flow model with amorphous silica reaction kinetics (Malate and O'Sullivan, 1992), a one dimensional flow model with quartz and amorphous silica reaction kinetics (Rimstidt and Barnes, 1980; Wells and Ghiorso, 1991), and a two dimensional flow model with quartz or amorphous silica reaction kinetics (Cathles, 1983; White, 1997). Takeno et al. (1998) tried to incorporate dissolution / precipitation kinetics of silica minerals, quartz, cristobalite and amorphous silica, in a geothermal reservoir simulator, called RIGHTS, and applied this simulator to a simple geothermal system based on a simple reaction surface model as a preliminary study. In this study, we revised the reaction surface model of RIGHTS and performed numerical simulation of the development of silica alteration zones to examine the effect of permeability, and reaction surface area.

In geothermal systems, many polymorphs of silica minerals are observed such as quartz, α -cristobalite, β -cristobalite, a-tridymite, and β -tridymite (Kimbara, 1977). In this study, we will treat dissolution and precipitation of three common silica polymorphs, a-quartz, α -cristobalite, and amorphous silica (hereafter simply called quartz, cristobalite, and amorphous-silica, respectively). We neglect direct solid-solid

phase transition among the minerals. Although biomineralization of silica minerals in some hot springs (Akabane et al., 1997; Tazaki, 1995) and the influence of salinity and pH on silica mineral solubility (Fourinier, 1983) as well as on precipitation / dissolution kinetics (Dove, 1994; Bohlmann et al., 1980) are known, for simplicity we neglect these effects. We also neglect dissolution of other minerals such as feldspar. Plagioclase has a higher dissolution rate than quartz so that its effect on aqueous silica transport is important. We think that this should be treated in future assessments.

2 GOVERNING EQUATIONS

The basic governing equations used in this simulation are mass balance, momentum balance, and energy conservation. Chemical reactions are implemented as add-on packages that are independent of the physical parameters. Governing equations for physical parameters are solved first, then the equations for chemical reactions and silica mass transport are solved. Dissolution or precipitation of silica minerals gives feedback to the change of porosity, permeability, and reaction surface area. Then the governing equations for physical parameters of the next step are solved. Calculations are performed at each step in this way.

Dissolution and precipitation rate for the *i*th silica mineral is given as follows. The left side is positive for dissolution and negative for precipitation.

$$\frac{\partial m_{H_4SiO_4}}{\partial t} = k_{+i} \frac{A_i}{M} \left(1 - \frac{Q}{K_i}\right)$$

where

$$Q = m_{H_4SiO_4}$$

m is molality of aqueous silica species (in this study, only H_4SiO_4 is considered), *t* is time, k_{+i} is dissolution rate constant of *i*th silica mineral, A_i is reaction surface area of *i*th silica mineral, *M* is mass of solution, and K_i is solubility constant of *i*th silica mineral. Activities of silica minerals and water are assumed as unity, and the activity coefficient of $H_4SiO_4(aq)$ is assumed as unity. Solubility constants K_i are calculated as follows:

Quartz (Rimstidt, 1997)

$$\log K = -0.0254 - 1107.12 / T$$

α -cristobalite (Rimstidt and Barnes, 1980)

$$\log K = -0.0321 - 988.2 / T$$

Amorphous silica (Rimstidt and Barnes, 1980)

$$\log K = 0.3380 - 7.889 \times 10^{-4} T - 840.1 / T$$

T is absolute temperature. Rate constants k_{+i} are given by Rimstidt and Barnes (1980); we used a rate constant for quartz recalculated from the data revised by Rimstidt (1997):

$$\log k_{+(qtz)} = -0.7324 - 3705.12 / T$$

$$\log k_{+(\alpha-crist)} = -0.739 - 3586 / T$$

$$\log k_{+(am.silica)} = -0.369 - 7.890 \times 10^{-4} T - 3438 / T$$

T is absolute temperature. We neglected pressure effects for these constants and regarded them to be the same as on the vapor-liquid saturation curve. Many empirical or theoretical functions of grain size or porosity are known for permeability (Domenico and Schwartz, 1990). We used the following equation derived from Kozeny-Carman relation:

$$\frac{\text{current-permeability}}{\text{initial-permeability}} = \left(\frac{\text{current-porosity}}{\text{initial-porosity}} \right)^3$$

We also assumed the following relationship between porosity and total reaction surface area.

$$\frac{\text{current-area}}{\text{initial-area}} = \left(\frac{\text{current-porosity}}{\text{initial-porosity}} \right)^{0.5}$$

In this study, we revised the reaction surface area model used in Takeno et al. (1998) in which the constant ratio of surface area for silica minerals was used. The principles of the new model are as follows. 1) Primary minerals, when undersaturated in rock dissolve into solution. 2) Secondary minerals, when oversaturated, precipitate only in pore spaces from the solution, and cover the pore wall, and redissolve into the solution when undersaturated. For precipitation, the total surface area *A* is partitioned into A_i in proportion to the precipitation rate of *i*th silica mineral. 3) Covering of secondary minerals on pore walls inhibits the dissolution of primary minerals in the rock. However, we consider that perfect blocking of soluble minerals in the rock by trace amounts of insoluble precipitates is not realistic owing to roughness of the pore surface. For this reason, we introduced a parameter F^* ($0 < F^* < 1$) and we virtually subdivided total surface area into surface area of precipitated secondary silica minerals *A*, and surface area of

rock A_i which is composed of primary silica minerals and inert minerals. Then following equations are imposed.

$$F = \frac{V_p}{F^*(V_p + V_l)}$$

$$G = \frac{A_f}{A}$$

so that

$$A_f = GA$$

$$A_i = (1-G)A$$

$$G = (1-F)^2 \quad \text{for } F < 1$$

$$= 0 \quad \text{for } F \geq 1$$

V_p is the volume occupied by secondary silica, and V_l is the volume occupied by liquid. For the dissolution of secondary silica minerals, A_i is given from A_f by volume-weighting among the silica minerals. For the dissolution of primary silica minerals, A_i is given from A_f by volume-weighting among the silica and inert minerals. The simulation code **RIGHTS** solves the above equations by the finite difference method. In this simulation, we treat discontinuous phenomena such as appearance and disappearance of minerals so that we cannot use a large time step. In this regard, there is no advantage for using implicit method, so we use the explicit method for solving the equations.

3. GEOTHERMAL MODEL-BOUNDARY CONDITION AND INITIAL CONDITION

We examined a two dimensional porous square 2 km wide and 2 km deep uniformly subdivided into a computational grid of 80 by 80. Two basic types of geothermal model were assessed. One is a homogeneous system (model I) in which all grids have the same rock properties, and the other (model II) has a cap rock, a fracture (represented by vertical high permeable zone), and a reservoir. One example of model II is illustrated in Fig. 1. The common rock properties for both models are density (2500 kg/m^3), heat capacity (1000 J/kg/deg), and thermal conductivity (2 W/m/deg). All boundaries (bottom, top, left, and right) are insulated. The bottom, left, and right boundaries are impermeable. The top blocks are open to free pure water at 10°C and 1 bar. Heat sources were given within bottom layer blocks as ranging continuously from $80 \times 10^{-5} \times (350-T)$ (at the left

corner) to $0 \times (350-T)$ (at the right corner) W/m^3 . Heat sinks for so called "radiative / convective condition" were given as $0.08 \times (T-10) \text{ W/m}^3$ within top layer blocks. T is temperature in centigrade. Thermal equilibrium between rock and fluid was always assumed. All blocks consist of rock containing 20 weight% quartz (the other part is inert) with pores filled with pure water at 10°C in the initial state. From the preliminary simulation, the results were not sensitive to the variation of F^* , because only the most insoluble mineral, quartz, was included in the rock as a primary mineral. Therefore, F^* is fixed as 0.01 for all cases. Simulation was carried out for up to 50,000 years.

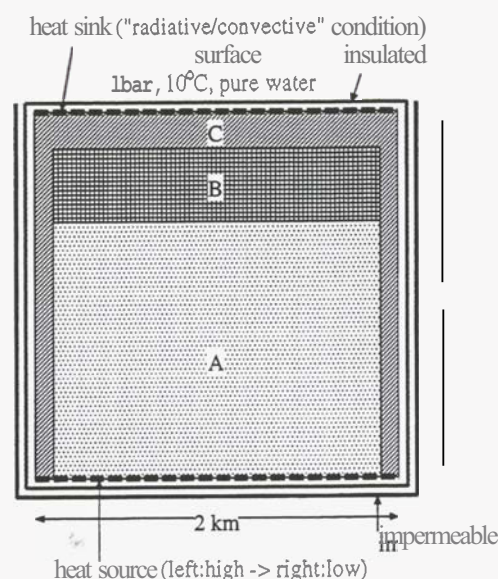


Figure 1 - Model for the simulation. A (reservoir): porosity = 0.05, permeability = $5 \times 10^{-15} \text{ m}^2$, surface area = $100 \text{ m}^2/\text{m}^3$, B (cap rock): porosity = 0.01, permeability = $1 \times 10^{-15} \text{ m}^2$, surface area = $10 \text{ m}^2/\text{m}^3$, C (two vertical fractures and shallow horizontal permeable formation): porosity = 0.05, permeability = $1 \times 10^{-14} \text{ m}^2$, surface area = $10 \text{ m}^2/\text{m}^3$.

4. RESULTS AND DISCUSSION

A representative result is shown in Fig. 2, with the boundary and initial conditions illustrated in Fig. 1. The boxed parts of the shallow area in Fig. 2 is enlarged in Fig. 3. Model I has a permeability of $5 \times 10^{-15} \text{ m}^2$ with a reaction surface area ranging from $10 \text{ m}^2/\text{m}^3$ to $100 \text{ m}^2/\text{m}^3$. In this model, a cristobalite zone at the surface and a secondary quartz zone along the up-flow path appeared, but amorphous silica was absent.

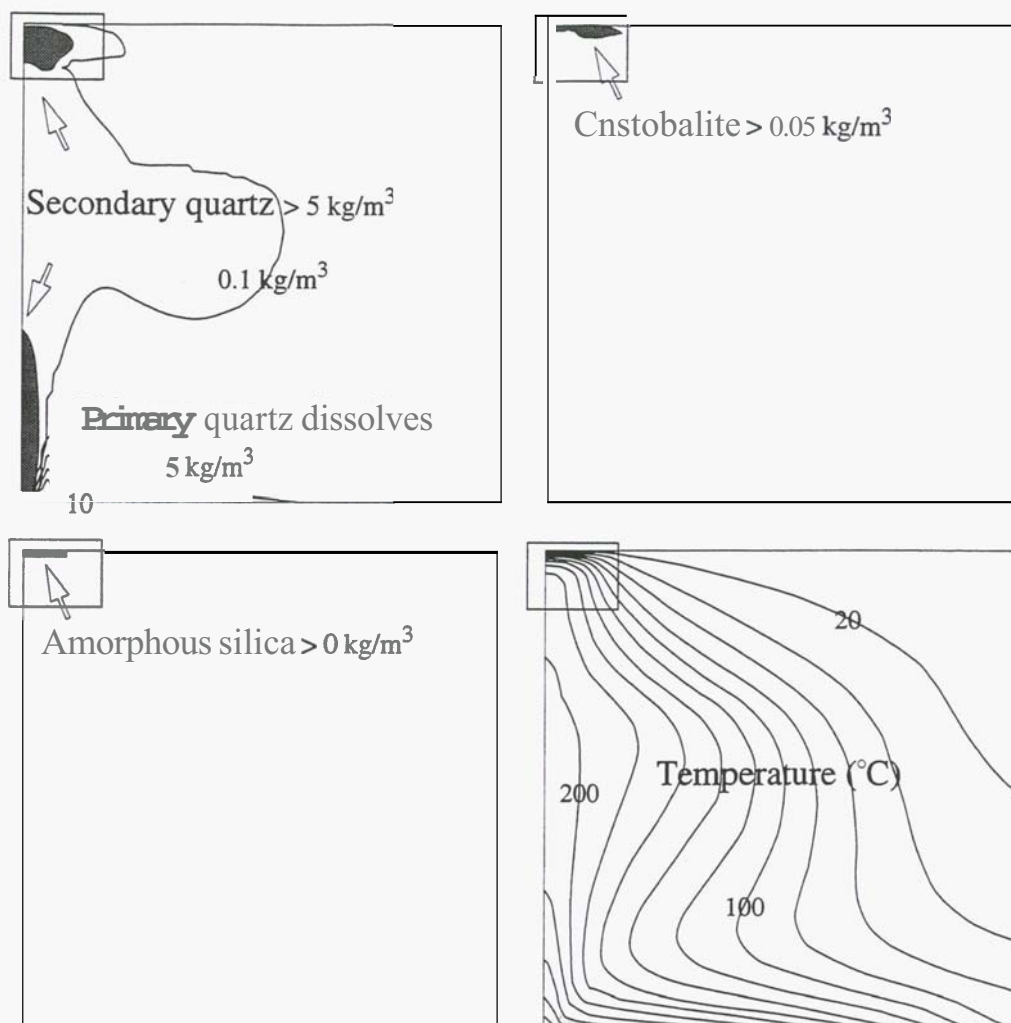


Figure 2 - Precipitation/dissolution of silica minerals and temperature distribution in 50,000 years. Areas with significant precipitation of quartz, cristobalite, and amorphous silica is shaded or enclosed. The amount of quartz dissolved is contoured in kg/m³. Boxed parts are enlarged in Fig. 3.

The results of the model II show that an amorphous silica zone appeared at and around the surface where fluid discharged from fracture, and that this zone overlaps with cristobalite. These zones correspond to subsurface up-flow. Secondary quartz is concentrated along the up-flow zone in a pattern that is mushroom shaped. In both models, primary quartz in the rock was dissolved from the bottom, and silica is transported along up-flow path to the top. Porosity change and permeability change by precipitation/dissolution of quartz were too small in 50,000 years of fluid circulation to influence the hydrology.

From the above results, we recognized that high permeability and a small reaction surface area were favorable for the precipitation of amorphous silica, and the results correspond well with the occurrence of a silica alteration zone in a natural geothermal system. It is also noted that temperature of disappearance of the cristobalite zone is less than 100°C. In an active geothermal

area, it is suggested that cristobalite disappears below 100°C (Hayashi, 1973; Browne, 1978; Kimbara and Ohkubo, 1978), however this could not be proved by thermodynamics based on chemical equilibrium. Our results might give insight to this empirical law. Compared to Takeno et al. (1998) in which the ratio of reaction surface area for each silica mineral was assumed to be constant, the redissolution rate of precipitated secondary silica minerals in this study is relatively slow. When the redissolution of secondary silica minerals becomes very small (1×10^{-14} kg/m³ order or less), the redissolution rate is much too slow due to volume weighting method for partitioning the reaction surface area.

5. CONCLUSION

From the numerical reservoir simulation incorporating silica dissolution / precipitation kinetics, we show that high permeability and small reaction surface area are favorable for the development of an amorphous silica zone. We

also show that this condition forms a geothermal reservoir with a cap rock and fracture (vertical permeable zone in this study) to the surface. Amorphous silica and cristobalite appear at the top where fluid discharges. Although the model could be further improved, we reproduced characteristics observed in natural geothermal systems by the numerical simulation using available kinetic data and a simple reaction model. The results also imply that numerical simulations incorporating chemical processes are promising for geothermal modeling, especially for reducing the non-uniqueness of the models.

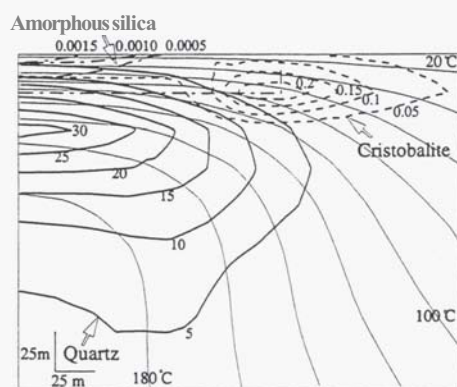


Figure 3 - Boxed parts in Fig. 2 are enlarged; thin line: temperature($^{\circ}\text{C}$), thick line: quartz (kg/m^3), broken line: cristobalite (kg/m^3), chain line: amorphous silica (kg/m^3).

REFERENCES

- Akabane, H., Yasuda, I., Miyajima, H., Goto, K., Honoki, H. (1997). Precipitation of silica sinter in hot spring water*. *Jour. Geol. Soc. Japan*, Vol. 103(2), 154-162.
- Bohlmann, E. G., Mesmer, R. E. and Berlinski, P. (1980). Kinetics of silica deposition from simulated geothermal brines. *Soc. Petrol. Engineers Jour.*, Vol. 20(4), 239-248.
- Brady, P. V. and Walther, J. V. (1990). Kinetics of quartz dissolution at low temperatures. *Chem. Geol.*, Vol. 82(3/4), 253-264.
- Browne, P. R. L. (1978). Hydrothermal alteration in active geothermal fields. *Ann. Rev. Earth Planet. Sci.*, Vol. 6, 229-250.
- Cathles, L. M. (1983). An analysis of the hydrothermal system responsible for massive sulfide deposition in the Hokuroku basin of Japan. *Econ. Geol. Monograph*, Vol. 5, 439-487.
- Domenico, P. A. and Schwartz, W. F. (1990). Physical and Chemical Hydrogeology, 824p., John Wiley & Sons, New York, p.76.
- Dove, P. M. (1994). The dissolution kinetics of quartz in sodium chloride solutions at 25° to 300°C . *Am. Jour. Sci.*, Vol. 294(6), 665-712.
- Fournier, R. O. (1982). An equation correlating the solubility of quartz in water from 25° to 900°C at pressures up to 10,000 bars. *Geochim. Cosmochim. Acta*, Vol. 46(10), 1969-1973.
- Fournier, R. O. (1983). A method of calculating quartz solubilities in aqueous sodium chloride solutions. *Geochim. Cosmochim. Acta*, Vol. 47(3), 579-586.
- Hayashi, M. (1973). Hydrothermal alteration in the Otake geothermal area, Kyushu*. *Jour. Japan Geotherm. Energy Assoc.*, 10(3), 9-46.
- Kimbara, K. (1977). Some cristobalites and tridymites in geothermal area*. *Jour. Japan Geotherm. Energy Assoc.*, Vol. 14(1), 13-20.
- Kimbara, K. and Ohkubo, T. (1978). Hydrothermal altered rocks found in an exploration bore-hole (No. SA-1), Satsunan geothermal area, Japan*. *J. Assoc. Petrol. Mineral. Econ.*, 73(5), 125-136.
- Lowell, R. P., Cappellen, P. V. and Germanovich, L. N. (1993). Silica precipitation in fractures and the evolution of permeability in hydrothermal upflow zones. *Science*, Vol. 260, 192-194.
- Malat'ev, R. C. M. and O'Sullivan, M. J. (1992). Mathematical modeling of silica deposition in a porous medium. *Geothermics*, Vol. 21(3), 377-400.
- Renders, P. J. N., Gammons, C. H. and Barnes, H. L. (1995). Precipitation and dissolution rate constants for cristobalite from 150 to 300°C . *Geochim. Cosmochim. Acta*, Vol. 59(1), 77-85.
- Rimstidt, J. D. (1997). Quartz solubility at low temperatures. *Geochim. Cosmochim. Acta*, Vol. 61(13), 2553-2558.
- Rimstidt, J. D. and Barnes, H. L. (1980). The kinetics of silica-water reactions. *Geochim. Cosmochim. Acta*, Vol. 44(11), 1683-1699.
- Takeno, N., Ishido, T. and Pritchett, J. W. (1998). Numerical simulation of development of silica alteration zoning in geothermal system-preliminary study based on kinetic reaction-transport model*. *Jour. Min. Soc. Japan*, Vol. 27(3), 157-166.
- Tazaki, K. (1995). Electron microscopic observation of biomineralization in biomats from

hot springs*. *Jour. Geol. Soc. Japan*, Vol. 101(4), 304-314.

Walder, J. and Nur, A. (1984) .Porosity reduction and crustal pore pressure development. *Jour. Geophys. Res.*, Vol. 89(B13), 11539-11548.

Walther, J. V. and Helgeson, H. C. (1977) . Calculation of the thermodynamic properties of aqueous silica and the solubility of quartz and its polymorphs at high pressures and temperatures. *Am. Jour. Sci.*, Vol. 277(10), 1315-1351.

Wells, J. T. and Ghiorso, M. R. (1991) . Coupled fluid flow and reaction in mid-ocean ridge

hydrothermal systems:the behavior of silica. *Geochim. Cosmochim. Acta*, Vol. 55(9), 2467-2481.

White, S. P. (1997) .Modeling the dissolution and precipitation of quartz in a deep geothermal system. *Proceedings 19th New Zealand Geothermal Workshop*, 93-98.

Yano, Y. (1994) . Permeability change in the evolution of hydrothermal convection system due to silica dissolution/precipitation** (abstract). *Jour. Geothenn. Res. Soc. Japan*, Vol. 16(2), 218.

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