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The Role of Silica Precipitation in the Permeable-Impermeable Boundary within the Earth's Crust

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ABSTRACT

Silica is one of the dominant constituents of the Earth's crust, and dissolution and precipitation of silica minerals have a significant role on the hydrological properties of the Earth's crust. However, the role of dissolution and precipitation of silica minerals on fracture permeability is still unclear.

In this study, the hydrothermal flow-through experiments were conducted to reveal the mechanism and kinetics of silica precipitation in the crustal conditions. Large amount of silica precipitation occurred only in the supercritical conditions of water. The strong temperature dependence of silica precipitation can be explained by the homogeneous nucleation of quartz. With increasing Al and Na concentrations in the solution, the dominant precipitates changed systematically from amorphous silica to cristobalite to quartz, and precipitation rate increased.

The Kakkonda geothermal field, Japan, has a deep well that penetrated the boundary between the hydrothermal convection zone and the heat conduction zone. Calculation of quartz solubility revealed that the depth of a local minimum of quartz solubility corresponds to that of the permeable-impermeable boundary at the Kakkonda geothermal field.

These experimental and calculation results suggest that the rapid quartz precipitation plays a significant role in forming and sustaining the permeable-impermeable boundary within the Earth's crust, especially at geothermal fields.

1. INTRODUCTION

Silica-water interaction is one of the dominant geochemical reactions and has a role on the hydrological properties within the Earth's crust. Precipitation of silica polymorphs (e.g., quartz, cristobalite, amorphous silica) has been observed ubiquitously as quartz vein, silica sinter, and silica scale. The major component of silica scale is amorphous silica, whereas veins consists of quartz without amorphous silica. Stretched-crystal and elongate veins (Bons 2000) show the epitaxial growth of quartz from the surfaces of quartz crystals in the wall rocks. Blocky veins filled by equant quartz grains have been considered to form via nucleation of amorphous silica and diagenesis of silica polymorphs, which is the change of amorphous silica → cristobalite → quartz (Williams *et al*. 1985). The high rate of ascent fluids is also expected to realize the high SiO_2 concentrations in the fluid, nucleation of silica minerals, and bringing of precipitated products from the deeper part to the shallower part (Okamoto and Tsuchiya 2009). The variety of precipitation of silica polymorphs leads to the expectation that dissolution and precipitation of silica polymorphs could control the distribution of fluids, the process of fracture sealing, and the spatial and temporal change of the permeability within the Earth's crust. However, the effect of silica-water interaction on the hydrological properties of the Earth's crust is still unclear.

At greater depths in the crust, permeability tends to be lower than that at shallower part. The transition from the permeable zone to the impermeable zone is at around 10–15 km depth (Ingebritsen and Manning 2010). The transition zone of permeability corresponds to that of the rock strength that has been known as the brittle-plastic transition (BPT) at 300–450 °C (Scholz 2002), and that of pressure and seismicity. Within faults and fractures, the fluid pressure fluctuation between lithostatic and hydrostatic in response to the seismic-interseismic cycle (Sibson 1992) is one of the possible driving forces of quartz vein formation (Rusk and Reed 2002). Actually, in some deep wells, abundant quartz veins were observed at around the permeable-impermeable boundary, indicating that large amount of silica precipitation could be a major geochemical reaction that would lead the self-sealed zone of the BPT (Fournier 1999).

In this study, the significant effect of dissolution and precipitation of silica minerals on the permeable-impermeable boundary of the Earth's crust is suggested by the calculation of silica solubility and the hydrothermal experiments of silica precipitation. At the Kakkonda geothermal field, Japan, the deep-drilling-well penetrated the boundary between the hydrothermal convection (permeable) zone and the heat conduction (impermeable) zone at 3100 m depth (Doi *et al*. 1998). The boundary is at 380 °C and 24 MPa, and in the supercritical conditions of water. Based on the detailed observations of the Kakkonda geothermal field, the quartz solubility at the Kakkonda geothermal field is calculated as a function of depth. In addition, hydrothermal flow-through experiments of silica precipitation were conducted to reveal the dependences of temperature and minor components in the solution on silica precipitation. The results of calculation and experiments suggest that the large amount of silica precipitation could seal fractures rapidly and control the depth of the permeable-impermeable boundary within the Earth's crust, especially in geothermal fields.

2. THE CONDITIONS OF THE KAKKONDA GEOTHERMAL FIELD, JAPAN

The Kakkonda geothermal field within the Hachimantai volcanic zone, NE Japan, is one of the most extensive liquid-dominated geothermal fields nationwide. The heat source of the hydrothermal system of the Kakkonda geothermal field is the Kakkonda granite (Kato *et al*. 1993; Doi *et al*. 1998). The K-Ar ages of K-feldspars in the hydrothermal veins at the Kakkonda areas are 0.2 ±

0.1 Ma (Koshiya *et al*. 1993). In the geothermal reservoirs recognized in the well WD-1a, the vertical permeability values are approximately from 10^{-14} to 10^{-16} m^2 (Hanano and Takanohashi 1993).

Figure 1 shows the cross-section through the Kakkonda geothermal system. In 1995, the well WD-1a was drilled into the Kakkonda field. Measured temperature in the well WD-1a exceeded the hydrostatic boiling-point curve with a maximum of >500 °C at a depth of >3.7 km (Ikeuchi *et al*. 1998; Fig. 1, 2a). A depth of 3.1 km (380 °C and 24 MPa) within the Kakkonda granite was regarded as the boundary between the hydrothermal convection zone and the heat conduction zone because the temperature gradient changed (Doi *et al*. 1998; Ikeuchi *et al*. 1998; Fig. 2a). The core samples recovered from the base of the hydrothermal convection zone have permeability values of 10^{-17} m^2 (at room temperature; Fujimoto *et al*. 2000). By the logs of formation micro-imager (FMI), high concentrations of fractures and closed fractures with low angles were observed from 1.8 to 2.9 km depth (Muraoka *et al*. 1998; Fig. 2b). The strong reflectors in prestack time-migrated multi-channel seismic data were identified at or near the 350 °C isotherm (Matsushima *et al*. 2003).

In this paper, the hydrothermal convection zone and the heat conduction zone are expressed as the permeable zone and the impermeable zone, respectively (Fig. 1, 2).

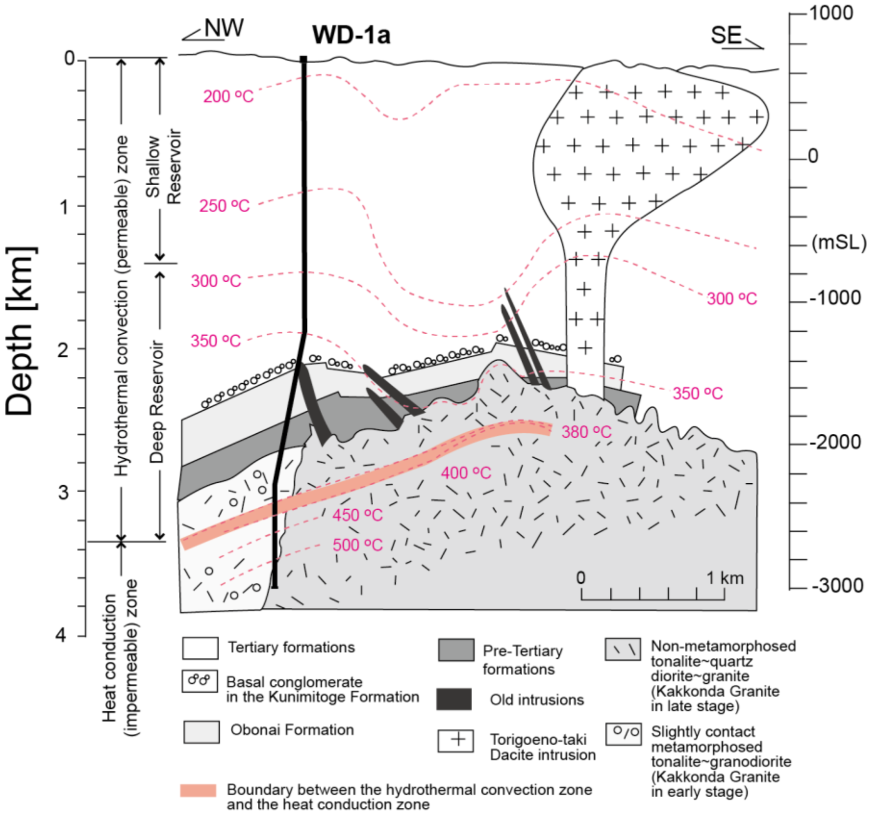

Figure 1: Schematic cross-section through the Kakkonda geothermal system (modified after Doi *et al*. 1998).

3. CALCULATION OF QUARTZ SOLUBILITY

3.1 Conditions of calculation

The quartz solubility was calculated along the well WD-1a at the Kakkonda geothermal field by using the program LonerAP (Akinfiev and Diamond 2009). Pressure and temperature at each depth were referred the observation data in Hanano and Takanohashi (1993) and Ikeuchi *et al*. (1998) (Fig. 2a), respectively. Based on the low salinity of the geothermal fluids in the Kakkonda geothermal field (Muramatsu *et al*. 2000), the condition of the fluid in the calculation was assumed to be pure H_2O.

3.2 Calculation results

The depth of a local maximum of quartz solubility is at around 2 km depth (Saishu *et al*. 2014; Fig. 2c). The local maximum of quartz solubility results in the dominant reaction being silica dissolution from both upward and downward fluids. The FMI logs showed that the fracture concentration increases from the depth of 1.5 km to the deeper part (Muraoka *et al*. 1998; Fig 2b). The strong seismic reflectors were also observed at around the 350 °C isotherm, which is also one of the evidences that fluid-filled fractures contribute at 2 km depth (Matsushima *et al*. 2003). These correspondences of the depth of the local maximum of quartz solubility and that of the observed fluid-filled fractures suggest that quartz dissolution leads the formation of the open fractures and affects the distribution of the relatively large amount of fractures.

The depth of a local minimum of quartz solubility correlates to the permeable-impermeable boundary (3.1 km depth) in the supercritical conditions of water (380 °C, 24 MPa) (Saishu *et al*. 2014; Fig. 2). The calculation result suggested that precipitation of silica minerals is a dominant reaction from both upward and downward fluids, and it could seal the fractures and control the depth of the permeable-impermeable boundary. The downwards decrease in silica solubility from 2.3 to 3.3 km is much greater than the upwards decline in solubility beneath the boundary (Fig. 2c). Downwards-moving fluids affect the amount of silica deposition more than that in the upwards-moving fluids.

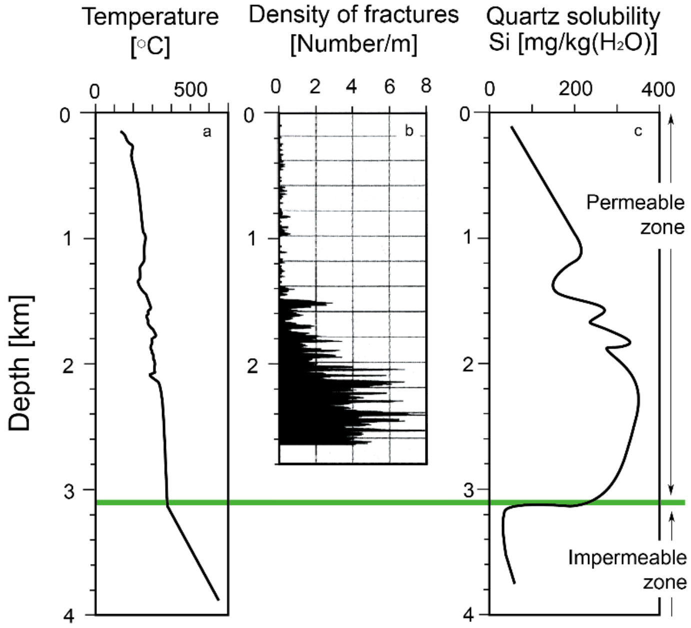

Figure 2: (a) Temperature-depth curve obtained for the drillhole WD-1a (Ikeuchi *et al.* 1998). (b) The FMI logs of the well WD-1a (modified after Muramatsu *et al.* 1998). (c) Quartz solubility with depth (modified after Saishu *et al.* 2014). Calculation of quartz solubility was by using the program LonerAP (Akinfiev and Diamond 2009). The green line shows the boundary between the permeable (hydrothermal convection) zone and the impermeable (heat conduction) zone at 3.1 km depth.

4. HYDROTHERMAL EXPERIMENTS OF SILICA PRECIPITATION

4.1 Experimental methods

The hydrothermal flow-through experiments were conducted to investigate (1) the temperature dependence of silica precipitation and (2) the effect of minor components in the solution on silica precipitation. No rock/mineral substrate was set in the precipitation vessel in all experiments. The Si-supersaturated input solution was made by dissolution of rock/minerals to simulate the crustal fluids. The concentrations of components in the input and output solutions (before and after passing through the precipitation vessel, respectively) were observed by using ICP-AES. The precipitates were observed by using XRD, SEM, and EPMA.

Seven experiments of temperature dependence were conducted at 24 MPa, which was same as the pressure at the permeable-impermeable boundary of the well WD-1a. Temperature was set as 200, 250, 300, 380, 390, 400, and 430 °C in each experiment. The input Si-supersaturated solution was made by dissolution of granite sand at 350 °C. Concentrations of Si and minor components (Al, Na, and K) in the input solutions were 332–348 and 1.3–3.7 mg/kg(H_2O). Values of pH ranged from 6.9 to 7.4 at room temperature in each experiment. The details of the experiments are expressed by Saishu *et al*. (2014).

In the experiments of minor components in the solution, pressure and temperature for precipitation were at 30 MPa and 430 °C, in the supercritical conditions of water. The Si-supersaturated solution was made by dissolution of quartz and albite sand. Quartz was dissolved at 280–360 °C. Si concentrations in the input solution was 268–375 mg/kg(H_2O), which was higher than the solubility of not only quartz but also amorphous silica at 30 MPa and 430 °C (Akinfiev and Diamond 2009; Okamoto *et al*. 2010). Dissolution temperature of albite varied from 170 to 350 °C. Al concentrations in the input solutions were 0, 0.4, 1.2, 2.3, 3.0, 5.6, and 6.7 mg/kg(H_2O). The Na concentration had a linear correlation with Al concentration in the input solutions (Na/Al molar ratio of ~1.48). Values of pH ranged from 5.5 to 8.2 at room temperature in each experiment. The details of the experiments are expressed by Saishu *et al*. (2012).

4.2 Experimental results

4.2.1 Temperature dependence on silica precipitation

At >390 °C, Si concentration in the solution decreased under 100 mg/kg(H_2O), in other words, the amount of precipitated Si in the precipitation vessel increased to >250 mg/kg(H_2O) (Saishu *et al.* 2014; Fig 3). The trend of increasing of difference of Si concentration between input and output solutions correlates to the drastic decrease of quartz solubility at 24 MPa (Fig 3). The experimental results suggested that large amount of silica precipitation occurs only in the supercritical conditions of water, whereas less precipitation of silica minerals occurs in liquid phase.

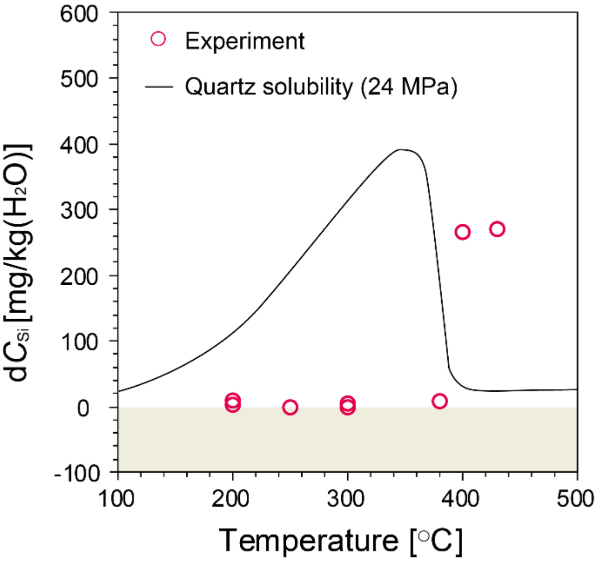

Figure 3: Temperature of precipitation and difference of Si concentrations between the input and output solutions (modified after Saishu *et al.* 2014). The red circles show the difference of Si concentrations between the input and output solutions, dC_{Si}, in the experiment. The line shows the solubility of quartz at 24 MPa calculated by LonerAP (Akinfiev and Diamond 2009).

4.2.2 The effect of minor components in the solution on silica precipitation

Figure 4 shows the XRD results of the precipitated products in the experiments of minor components in the solution. The observed precipitated products by XRD were quartz (Q) and cristobalite (X). Calcite at 2θ = 29.4° was used as the standard (STD) material to estimate the relative intensity. The main compositions of the precipitates changes systematically with increasing Al concentration in the input solution (Saishu *et al.* 2012). In the materials precipitated from the solution of Al concentration of <1 mg/kg(H_2O), no peak was observed by XRD, indicating that amorphous silica precipitated dominantly (Fig. 4). In the solution of Al concentration >1 mg/kg(H_2O), cristobalite and quartz precipitated (Fig. 4). In the experiments of Al concentration in the input solution of 5.6 and 6.7 mg/kg(H_2O), almost all of precipitates was quartz (Fig. 5) and no relics of precipitation of amorphous silica was found within quartz crystals. The correlation of (1) the difference in Al and Na concentrations (mol/L) between the input and output solutions and (2) the Al and Na contents (mg/kg) in quartz precipitated in the experiments of Al concentrations of 3.0–6.7 mg/kg(H_2O) indicates that Al coupled with Na is incorporated into quartz (Saishu *et al.* 2012). The amount of precipitates increased from 13 to 61 mg/h linearly with increasing Al concentration in the input solution from 0 to 6.7 mg/kg(H_2O) (Saishu *et al.* 2012).

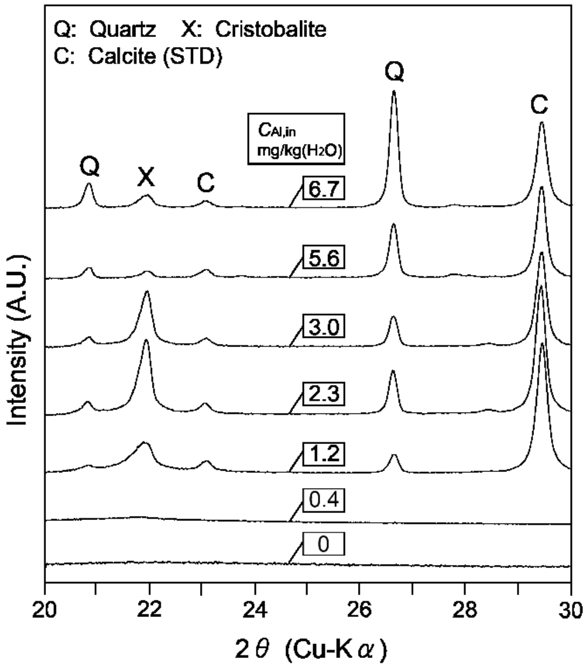

Figure 4: XRD results of the precipitated products in the experiments of Al concentration in the input solution, $C_{Al,in}$ = 0–6.7 mg/kg(H_2O) (modified after Saishu *et al.* 2012). The degree of XRD analysis was 2θ = 20–30°. Observed precipitated minerals were quartz (Q) and cristobalite (X), respectively. Calcite (C) at 2θ = 29.4° was used as the standard (STD) material to estimate the relative intensity.

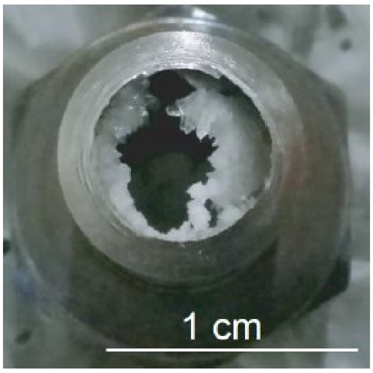

Figure 5: The cross-section of the precipitation vessel at 8 cm from the inlet in the experiment of Al concentration 5.6 mg/kg(H_2O).

5. DISCUSSION

Strong temperature dependence observed in the experiments can be explained by the homogeneous nucleation of quartz in the surface energy of quartz, σ = 130 mJ/m^2 (Saishu *et al.* 2014), which correlates with the value estimated from greenschist-facies metapelites (145 mJ/m^2) (Hiraga *et al.* 2002). Quartz precipitation via nucleation in the supercritical conditions of water is considered to be faster than that via growth on quartz surface in liquid phase. The sealing of fractures could be occurring effectively by quartz precipitation via nucleation at the permeable-impermeable boundary in the supercritical conditions of water rather than quartz growth at the shallower permeable zone.

Quartz and minor chalcedony form throughout the entire reaction vessel and that the impurities (Al, Na, and K) in the solutions inhibit the precipitation of opal and enhance the direct nucleation of quartz (Okamoto et al. 2010). The formation of Na-Al and Na-Al-Si complexing in solutions (Newton and Manning 2008) may be associated with quartz nucleation. In this study, the observations of Al and Na concentrations in the solutions and the precipitates suggested that the presence of Al^{3+} and Na^+ in solution could be one of the factors to reduce the energetic barrier of quartz nucleation. In addition, the increase of precipitation rate with increasing of Al concentration in the solution correlated to the change of precipitates of silica minerals from amorphous silica to quartz. Based on the observation that solubility of quartz is lower than that of amorphous silica in the same *PT* conditions, the amount of precipitates of quartz could be larger than that of amorphous silica in the solutions of the same Si concentration. Thus, the concentration of minor components in the solution is one of the important factors to control not only the phase of the precipitates of silica polymorphs but also the amount of them. The permeable-impermeable boundary of the Kakkonda geothermal field is in Kakkonda granite (Fig. 1), which leads the fluid at the boundary to include Si and minor components such as Al, Na, and K, as similar to that in the experiments of this study. The rapid precipitation of quartz via nucleation could affect to sealing of fractures and the formation of the permeable-impermeable boundary.

The permeable-impermeable boundary of the well WD-1a is at 380 °C and 24 MPa, in the supercritical conditions of water. A drop in quartz solubility can be led by the downwords fluid flow, which is from the liquid region (higher density) into the supercritical region (lower density). The results of the calculation of quartz solubility and that of the precipitation experiments show that, at the permeable-impermeable boundary, high SiO_2 concentration in the solution and large amount of quartz precipitation via nucleation could be led by the phase change of H_2O and by minor components in the solution of supercritical conditions of water instead of the fluid pressure fluctuation. In the Kakkonda geothermal field, the evidences of significant formations of quartz veins are not clear in the core samples from around the hydrological boundary. However, in The Geysers geothermal field, the United States, abundant quartz vein was observed in a relatively impermeable barrier at 3.5–3.6 km depth at higher than 350–370 °C (Fournier 1991). Based on the correspondence of the conditions of the impermeable barrier between The Geysers and the Kakkonda geothermal fields, if quartz veins in the Kakkonda geothermal field are there, these would be missed by chance, or quartz creep affects the bottoming permeability as well as quartz precipitation (Fournier 1999).

In the field of high geothermal gradient (>~50 °C/km), the quartz solubility has a local maximum and minimum values in the range of the typical temperature of the BPT (300–450 °C) (Saishu *et al*. 2014). The compositions of the crustal fluid at the BPT could be similar to that of the experiments in this study because dissolution of granite is one of the common reactions in the continental crust. Precipitation of quartz via nucleation could lead the sealing of fractures around the hydrological boundary and the controlling depth of the BPT, especially in the geothermal systems.

6. CONCLUSIONS

The Kakkonda geothermal field has a deep well WD-1a that penetrated the permeable-impermeable boundary, which is in the supercritical conditions of water (380 °C and 24 MPa). The calculation of quartz solubility at the Kakkonda geothermal field showed that (1) dissolution of quartz is a dominant reaction at around 2 km depth where the density of the fluid-filled fractures is high, and that (2) the depth of precipitation-dominant of quartz corresponds to that of the permeable-impermeable boundary. The hydrothermal flow-through experiments of silica precipitation revealed that (1) silica precipitation via nucleation occurs only in the supercritical conditions of water (>400 °C and 24 MPa), and (2) with increasing of Al concentration in the solutions, precipitates changes from amorphous silica to quartz and precipitation rate of silica minerals increases. These results suggest that the rapid and large amount of silica precipitation could seal fractures and control the depth of the permeable-impermeable boundary within the Earth's crust, especially in the geothermal fields.

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REFERENCES

Akinfiev, N.N., and Diamond, L.W.: A simple predictive model of quartz solubility in water-salt-CO2 systems at temperatures up to 1000 °C and pressures up to 1000 MPa. *Geochimica et Cosmochimica Acta*, **73**, (2009), 1597-1608.

Bons, P.D.: The formation of veins and their microstructures. *Stress, Strain and Structure*, Journal of the Virtual Explorer, **2** (2000).

Doi, N., Kato, O., Ikeuchi, K., Komatsu, R., Miyazaki, S., Akaku, K., and Uchida T.: Genesis of the plutonic-hydrothermal system around quaternary granite in the Kakkonda geothermal system, Japan. *Geothermics*, **27**, (1998), 663-690.

Fournier, R.O.: The transition from hydrostatic to greater than hydrostatic fluid pressure in presently active continental hydrothermal systems in crystalline rock. *Journal of Geophysical Research Letters*, **18**, (1991), 955-958.

Fournier, R.O.: Hydrothermal Processes related to movement of fluid from plastic into brittle rock in the magmatic–epithermal environment. *Economic Geology*, **94**, (1999), 1193-1211.

Fujimoto, K., Takahashi, M., Doi, N., and Kato, O.: High permeability of Quaternary granites in the Kakkonda geothermal area, northeast Japan. *Proceedings*, World Geothermal Congress 2000, Kyushu, Japan (2000).

Hanano, M., and Takanohashi, M.: Review of recent development of the Kakkonda deep reservoir, Japan. *Proceedings*, Eighteenth Workshop on Geothermal Reservoir Engineering, Stanford University, Stanford, California (1993).

Hiraga, T., Nishikawa, O., Nagase, T., Akizuki, M., and Kohlstedt, D.L.: Interfacial energies for quartz and albite in politic schist. *Contributions to Mineralogy and Petrology*, **143**, (2002), 664-672.

Ikeuchi, K., Doi, N., Sakagawa, Y., Kamenosono, H., and Uchida, T.: High temperature measurements in well WD-1a and the thermal structure of the Kakkonda geothermal system, Japan. *Geothermics*, **27**, (1998), 591-607.

Ingebritsen, S.E., and Manning, C.E.: Permeability of the continental crust: dynamic variations inferred from seismicity and metamorphism. *Geofluids*, **10**, (2010), 193-205.

Kato, O., Doi, N., and Muramatsu, Y.: Neo-granitic pluton and geothermal reservoir at the Kakkonda geothermal field, Iwate prefecture, Japan. *Journal of the geothermal research society of Japan*, **15**, (1993), 41-57.

Koshiya, S., Okami, K., Kikuchi, Y., Hirayama, T., Hayasaka, Y., Uzawa, M., Honma, K., and Doi, N.: Fracture System Developed in the Takinoue Geothermal Area. *Journal of the Geothermal Research Society of Japan*, **15**, (1993), 109-139 (in Japanese).

Matsushima, J., Okubo, Y., Rokugawa, S., Yokota, T., Tanaka, K., Tsuchiya, T., and Narita, N.: Seismic reflector imaging by prestack time migration in the Kakkonda geothermal field, Japan. *Geothermics*, **32**, (2003), 79-99.

Muramatsu, Y., Komatsu, R., Sawaki, T., Sasaki, M., and Yanagiya, S.: Geochemical study of fluid inclusions in anhydrite from the Kakkonda geothermal system, northeast Japan. *Geochemical Journal*, **34**, (2000), 175-193.

Muraoka, H., Uchida, T., Sasada, M., Yagi, M., Akaku, K., Sasaki, M., Yasukawa, K., Miyazaki, S., Doi, N., Saito, S., Sato, K., and Tanaka, S.: Deep geothermal resources survey program: Igneous, metamorphic and hydrothermal processes in a well encountering 500 °C at 3729 m depth, Kakkonda, Japan. *Geothermics*, **27**, (1998), 507-534.

Newton, R.C., and Manning, C.E.: Solubility of corundum in the system Al2O3-SiO2-H2O-NaCl at 800 °C and 10 kbar. *Chemical Geology*, **249**, (2008), 250-261.

Okamoto, A., Saishu, H., Hirano, N., and Tsuchiya, N.: Mineralogical and textural variation of silica minerals in hydrothermal flow-through experiments: Implications for quartz vein formation. *Geochimica et Cosmochimica Acta*, **74**, (2010), 3692-3706.

Okamoto, A., and Tsuchiya, N.: Velocity of vertical fluid ascent within vein-forming fractures. *Geology*, **37**, (2009), 563-566.

Rusk, B., and Reed, M.: Scanning electron microscope–cathodoluminescence analysis of quartz reveals complex growth histories in veins from the Butte porphyry copper deposit, Montana. *Geology*, **30**, (2002), 727-730.

Saishu, H., Okamoto, A., and Tsuchiya, N.: Mineralogical variation of silica induced by Al and Na in hydrothermal solutions. *American Mineralogist*, **97**, (2012), 2060-2063.

Saishu, H., Okamoto, A., and Tsuchiya, N.: The significance of silica precipitation on the formation of the permeable–impermeable boundary within Earth's crust. *Terra Nova*, (2014). DOI: 10.1111/ter.12093.

Scholz, C.H.: *The Mechanics of Earthquakes and Faulting (2nd edition)*, Cambridge University Press, Cambridge (2002).

Sibson, R.H.: Implications of fault-valve behavior for rupture nucleation and recurrence. *Tectonophysics*, **211**, (1992), 283-293.

Williams, L.A., Parks, G.A., and Crerar, D.A.: Silica diagenesis; I, Solubility controls. *Journal of Sedimentary petrology*, **55**, (1985), 301-311.