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LIMITATIONS IN APPLYING SILICA GEOTHERMOMETERS FOR GEOTHERMAL RESERVOIR EVALUATION

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ABSTRACT

Decrease in the existing experimental silica solubility data along the water-vapor saturation curve after 300ºC is due to analytical error associated with neglecting the effect of vapor proportion in the reaction vessel. This effect is very pronounced at high temperatures as the specific volume of water and vapor are of same order of magnitude. Therefore the existing solubility data could be considered as reliable only up to 300ºC. The respective regression expressions for quartz and amorphous silica are

$$\log SiO_2(ppm) = -\frac{1175\cdot 7(\pm 31.7)}{T(K)} + 4.88(\pm 0.08)$$

$$\log SiO_2(ppm) = -\frac{724.68(\pm 81.0)}{T(K)} + 4.50(\pm 0.13)$$

A combined evaluation of quartz solubility data along the water-vapor saturation and in the compressed liquid region together with the PVT characteristics of water suggests that these regression expressions are valid of whole range of temperature from 0 to 374ºC. It is concluded that the fundamental limitation to use these equations as geothermometers is the correction of total discharge silica composition from a well for the vapor fraction in the geothermal reservoir. For knowing the vapor fraction there is indirectly need of knowing the reservoir temperature. Therefore, the use of these equations is more likely to know the state of silica-water interaction in the reservoir.

INTRODUCTION

Silica solubility geothermometers are extensively used to estimate deep reservoir temperature during exploration and exploitation of geothermal systems. White et al. (1956) noticed for the first time that the silica concentration in hot springs at Steamboat, Nevada was very close to the experimental solubility of amorphous silica. Enormous contributions have been made on the silica solubility geothermometer development. The methodology applied for this development was based on gathering field evidences and creating an experimental temperature dependence silica solubility database (Fournier, 1973). Silica is found in many stable phases in natural and engineered earth systems including quartz, chalcedony, tridymite, moganite, cristobalite, coesite, stishovite, lechatelierite (silica glass), opal and amorphous silica (Drees et al., 1989). The dissolution-precipitation equilibration of such multi-phase minerals depends upon the solution-mineral contact time, and it requires an understanding of mineral solubility kinetics (Stumm and Morgan, 1981). Quartz is the most stable phase and has the lowest solubility, whereas amorphous silica is the least stable phase and has the highest solubility. Thus quartz and amorphous silica must represent two extreme cases of silica dissolution-precipitation equilibria in hydrothermal systems. The solubility of others silica phases will be in between the two extreme solubilities. It has been emphasized that the resident time for geothermal reservoir fluid is high enough to reach in equilibrium with quartz (Fournier and Rowe, 1966; Mahon, 1966; Fournier and Truesdell, 1970; and Arnorsson, 1970, 1975). Recently, in case of CP-M-19A well, Verma (1999) observed that the calculated concentration on silica in the deep reservoir fluid was substantially higher than the quartz solubility at the reservoir temperature. Therefore, we will here be concerned here for the two extreme solubilites of silica (i.e., solubility of quartz and amorphous silica).

Fournier (1977) derived the first geothermometer equation from the experimental quartz solubility data. Henley et al (1984) compiled all the existing silica geothermometers for many silica phases, including the effects of adiabatic and conductive cooling processes. Fournier and Potter (1982) deduced the most acceptable geothermometer regression equation valid up to 330ºC. Ragnarsdóttir and Walther (1983) determined the pressure dependence of quartz solubility at 250ºC and concluded that pressure had significant effect on calculated quartz equilibrium temperatures from silica contents in waters from deep geothermal reservoirs. Verma and Sontoyo (1997) found that the quartz solubility data (Fournier and Potter, 1982) for temperatures higher than 300ºC were outlier according to their statistical data treatment method and theory of error propagation.

Verma (1999) presented the chemical thermodynamic calculation for quartz solubility for a wide range of temperature and amount of water in the reaction vessel. It was observed a wide difference between calculated and experimental solubility. He concluded a need of creating internal consistent thermodynamic data for aqueous silicic species and reevaluation of quartz solubility data at higher temperatures along water-vapor saturation curve. Recently, it is found that there is no internal consistency between thermodynamically calculated and the experimental values of dissociation constant of water at high temperature (Verma, 2000). The dissociation of water is a prime reaction in all the aqueous solutions. This inconsistency implies that the thermodynamic calculation of equilibrium constant for any aqueous system including H^+ or OH^- ion may not be in agreement with the experimental values at high temperature. Therefore, the experimental quartz solubility data will only be considered here.

Rimstidt (1997) compiled all the quartz solubility data along the water-vapor saturation curve and derived a regression expression that is valid up to 300ºC. In other words the existing experimental quartz solubility along the water-vapor saturation are incorrect for temperature higher than 300°C. Many hydrothermal reactions in geological environment take place at temperatures higher than 300°C. The reservoir temperature in many geothermal fields has been measured above than 300ºC and silica is one of the major constituents of hydrothermal fluids.

In this article all the quartz solubility data along the water-vapor saturation curve and in the compressed liquid will be analyzed. The causes of decrease in the solubility values in the existing quartz data along the water-vapor saturation after 300ºC will be discussed. On this basis, the regression equations for quartz and amorphous silica will be derived for whole range of water-vapor saturation temperature (0-374ºC). Similarly, the limitations to use this equation as a geothermometer for geothermal fluids will be presented.

EXPERIMENTAL SILICA SOLUBILITY

Figure1 shows the PT relations for water along different isochores. These curves have been constructed with using the steam tables of Haar et al. (1984) and are useful to understand the temperature dependence of silica solubility. For the cases when the total specific volume (i.e. the total volume of container divided by the total weight (mass) of water and vapor) is greater than the critical specific volume of water (3.106 cm^3/g), there is only vapor at a certain high temperature and vice versa. On the other hand, if the total specific volume of water is just equal to the critical volume of water, there will be water and vapor along the water-vapor saturation curve up to the critical point. After the critical point there will not be any distinction between water and vapor along the V=3.106 cm^3/g line, but there will be compressed liquid at any point above this line and superheated steam below it even in the supercritical region. Therefore there are two extreme cases when there will always be water in the reaction vessel at high temperature: i. When the vessel is just filled equal to the critical volume of water (V=3.106 cm^3/g) and ii. When the vessel is completely filled at the initial room temperature (V=1.00 cm^3/g). And there could be any proportion of water and vapor along the saturation curve.

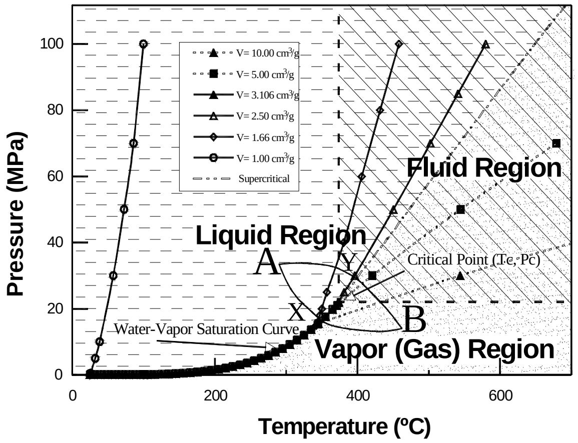

Fig. 1. The PT characteristics of water for different total specific volumes in a closed vessel (modified after Verma, 1999).

In summary the fluid (supercritical) region is composed of compressed liquid and superheated vapor for pressure and temperature higher than the critical pressure and temperature (i.e., P> P_C and $T>T_C$). Thus supercritical fluid is not a homogeneous phase. It can be compressed liquid or superheated vapor depending on the condition of pressure and temperature. Thus there will be no phase change if a system moves from the liquid region to the fluid region unless crossing the vaporization curve or the extended dashed and dotted line in the fluid region (see the curves corresponding to V=1.66 and 2.50 cm^3/g for liquid region and V=5.00 and 10.00 cm^3/g for gas region in the Figure 1). It is interesting to note if a system passes from the liquid region to the gas region across the extended dashed and dotted line, the phase change will be gradual while an abrupt phase change across the vaporization curve.

All the quartz solubility data from literature are divided in two groups (Figure 2): a) along the water-vapor saturation (compiled data from Rimstidt, 1997 and Verma, 1999) and b) in the compressed liquid region (Compiled data from Verma, 1999). Let us first analyze the quartz solubility along the water-vapor saturation curve. In very early works the quartz solubility at room temperature (25ºC and 0.1 MPa) is reported as 12 ppm (Brisco et al., 1936-7; van Lier et al., 1960). Fournier and Potter (1982), and Flemingo

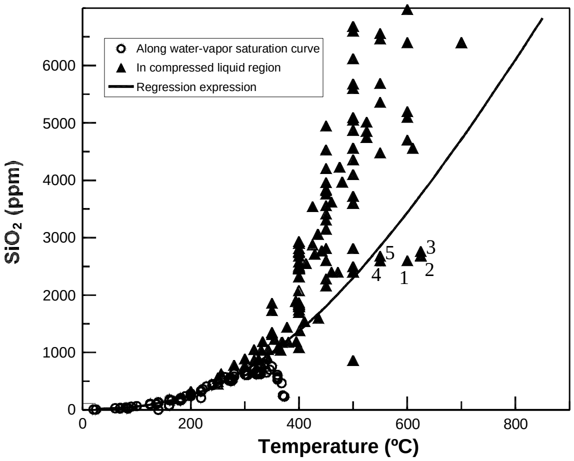

Fig. 2. Experimental quartz solubility data along the water-vapor saturation curve and in the compressed liquid region. Data are from Verma (1999).

and Crerar (1982) accepted the value 6.6±1 ppm. But recently Rimstidt (1997) conducted the solubility determination experiments for a long period and got the value of 11.0±1.1 ppm. To attain equilibrium between water and quartz at room temperature requires doing experiments for geological time period without supersaturating the solution at any instant, to prevent equilibrium with other silica phases. If the limitations involved in the quartz solubility determinations are considered, it is justify considering all the values within analytical errors (Gerardo-Abaya et al., 1997).

Rimstidt (1997) critically analyzed the solubility data and fitted the regression expression up to 300ºC. He did not consider the quartz solubility data from Fournier and Potter (1982), because those data were obtained by regression. He himself measured quartz solubility at four temperatures 21, 50, 74, and 96°C, but he considered ten values for his quartz solubility regression: 2 for 21, 2 for 50, 2 for 74 and 4 for 96°C. Similarly he also took repeated datasets by other authors from literature (Siever, 1962; Crerar and Anderson, 1971). Therefore, the solubility data are refitted here removing the duplicated values given by the same author (Figure 3). The refitted expression is more or less same as proposed by Rimstidt; but it is more realistic, because a biased statistical evaluation of the dataset due to repetition of data points is avoided. Here I have included all the existing values of quartz solubility at 25ºC between 6.6 to 12 ppm. It is also surprising to know that the actual analytical errors in the silica determination have never been reported in the literature. Therefore the errors in the coefficients of the following regression equation are only the statistical errors of ±1 σ (standard deviation). The regression expression is

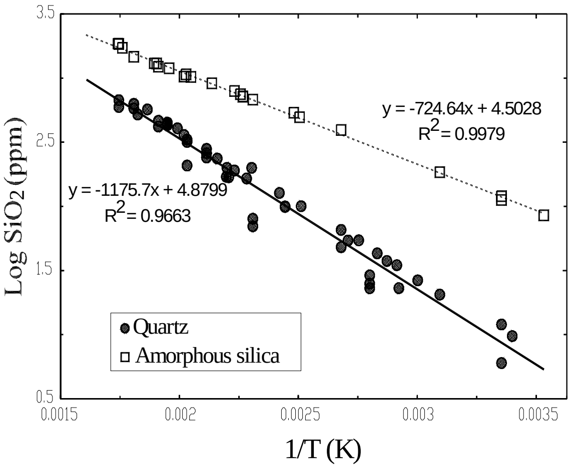

Fig. 3. A regression relation for quartz and amorphous solubility data along water-vapor saturation curve.

$$\log SiO_2(ppm) = -\frac{1175\cdot 7(\pm 31.7)}{T(K)} + 4.88(\pm 0.08).$$

Similarly the regression expression for amorphous silica is

$$\log SiO_2(ppm) = -\frac{724.68(\pm 81.0)}{T(K)} + 4.50(\pm 0.13)$$

Figure 2 also shows the temperature dependence of quartz solubility along the water-vapor saturation curve as well as in the compressed liquid. The decrease in the existing quartz solubility data along the water-vapor saturation curve after 300ºC can be explained with taking into account the PVT characteristics of water and the details on the solubility measurement techniques. As mentioned above, at a specified temperature or pressure along the water-vapor saturation curve, there could be any amount of vapor from 0 to 100%. The specific volume of vapor at low temperatures is very high; therefore the volume of vapor doesn't affect significantly the solubility of any mineral like quartz, which is only soluble in the liquid phase. But at higher temperatures (above 300ºC) it does affect as the specific volumes of water and vapor are of same order of magnitude. Most of the quartz solubility determinations were performed with the weight loss method or by rapid quenching of reaction vessel to room temperature. In both the cases the solution after quenching has condensed vapor which indirectly modifies (rather decreases) the concentration of silica in the solution. Therefore, knowledge of proportion of water and vapor is vital to solubility determination along the saturation curve at temperatures higher than 300^{o}C. Unfortunately, it has been ignored in the quartz solubility determinations in the literature.

Under this circumstances a combined evaluation of quartz solubility data along the water-vapor saturation curve and in the compressed liquid region will be helpful in understanding the behavior of quartz solubility data after 300°C (Figure 2). Let us suppose a point on the water-vapor saturation curve at 370°C. Any point above this curve will be in the compressed liquid region. It can be considered that a point just above the curve near to 370°C will be in compressed liquid region, but the thermodynamic properties of this compressed liquid will be very similar to the saturated water at 370°C. Similarly, the solubility of quartz in this compressed liquid will be nearly equal to the solubility of quartz in the saturated water at 370°C. Now let us concentrate on a point along the "critical line" (i.e. temperature and pressure higher than the critical point of water). Suppose the amount of water in a reaction vessel is such that the total specific volume is just less than critical volume of water. On heating this vessel, the values of pressure and temperature will be very close to those of the saturation curve and the "critical line", but there will always be water (compressed liquid) even at 1000°C (see Steam Tables). The solubility of quartz in this compressed liquid will be very close to the extrapolated saturated water solubility at the same temperature.

The values of pressure and temperature for all the solubility experiments in the compressed liquid region together with the theoretical PT curves for the two above mentioned extreme cases are plotted in Figure 4. All the experimental pressure and temperature data lie between the theoretical curves. Therefore the pressure and temperature during all these solubility studies were probably controlled by the different amount of water in the reaction vessel. It can be observed that all the data points in the supercritical region are in compressed liquid region. There is not even a single point in gas region. It clearly shows that silica is only soluble in liquid phase. According to above argument, the quartz solubility of the points, which are near to the saturation curve and the extended line in supercritical region in the Figure 4, could be used to define the tendency of the solubility data along saturation curve after 300ºC.

In the Figure 2 the solubility regression expression is also plotted with extrapolation up to 850ºC. It can be observed in the figures 4 and 2 that there are clusters of compressed liquid solubility data points near to the saturation curve and to the regression expression in the temperature range 300-400ºC, respectively. Similarly there is closeness of the same points to the curves around 600°C in both figures.

It can also be observed that there is no decrease in the silica solubility values with temperature in the data for the compressed liquid region. Thus it can be concluded that the extrapolation of the quartz solubility regression expression is valid for the interoperation of silica chemistry in the natural high temperature hydrothermal systems. In summary the above regression equation for quartz solubility along the water-vapor saturation curve can be used for whole range of temperature 0-374°C.

CRITIQUE ON SILICA GEOTHERMOMETRY

The silica geothermometers have been applied extensively to estimate geothermal reservoir temperature from the silica concentration of the fluid obtained from natural manifestations and drilled wells. Unfortunately, the predicted temperatures generally show a wide dispersion even when applying a single geothermometer to all the wells in a geothermal field. Many reasons have been proposed to justify the discrepancies, including gain or loss of steam phase in the reservoir, mixing of different types of fluids, re-equilibration during ascension to superficies, precipitation-dissolution, etc. (Fournier and Truesdell, 1974; Truesdell and Fournier, 1977).

Verma and Santoyo (1997) improved the silica geothermometer equation proposed by Fournier and Potter (1982) and applied their equation to demonstrate reasonable agreement between the estimated and measured reservoir temperatures in the Cerro Prieto geothermal reservoir. They took the chemical data for the reservoir liquid from Fausto et al. (1979). One way to calculate deep-liquid composition is by knowing reservoir enthalpy and temperature. Probably, Fausto et al. (1979) used the silica temperature for this purpose. They do not state clearly the procedure that they used for the reservoir fluid concentration calculation. In the same proceedings Truesdell et al (1979) presented results indicating that the silica temperature in all the wells in Cerro Prieto is always lower than the measured, NaKCa and enthalpy temperatures.

Enormous works have been done on improving the geothermometer equation and its applications. But there is a fundamental question to be answered on the correction of silica total-discharge concentration for vapor fraction in the geothermal reservoir fluid in order to use silica content in geothermal fluids as a chemical geothermometer. Similarly, it is also needed to justify that the silica in the quartz phase is in the equilibrium with the geothermal fluid. In case of natural manifestations there are still more complications in determining the dilution component, re-equilibration, steam loss or gain, etc. Therefore, we will limit ourselves to geothermal wells.

Verma (1997) presented a two-phase flow approach to calculate the fluid thermodynamic parameters including chemical speciation, pressure, and temperature in a geothermal reservoir from the parameters measured in the geothermal fluid (vapor and liquid) at the wellhead separator. Using this approach the geothermal reservoir fluid parameters were calculated in the well M-19A at Cerro Prieto. The concentration of silica is 666 ppm and the reservoir temperature is 248ºC. The data point is shown in Figure 5. It can be observed that the value is higher than the experimental quartz solubility, but is lower than the amorphous silica solubility. Thus the fluid is supersaturated with respect to quartz, or the solubility of silica is controlled by other phase.

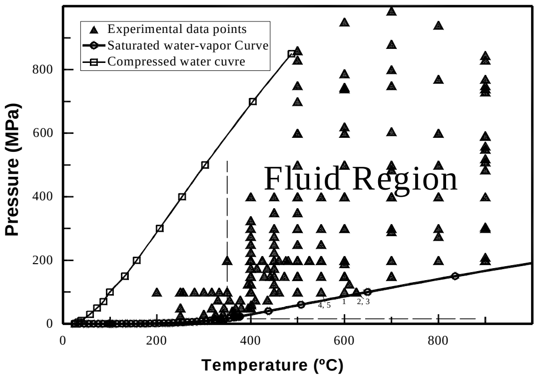

Fig. 4. *The pressure and temperature values for all the experimental determinations of quartz solubility data in the compressed liquid region together with theoretical curves for the two extreme cases for existence of water in the reaction vessel.*

Secondly, if we use these regression expressions for quartz and amorphous silica as geothermometers. The reservoir temperature at Cerro Prieto will be 299 and 168ºC, respectively. Vapor fraction in the reservoir was 0.244 by weight (Verma, 1997). Therefore the total discharge concentration of silica at the wellhead was 517 ppm. If we apply the above geothermometers on the total discharge concentration, the reservoir temperatures will be approximately 265 and 132^{o}C, respectively. Thus there is a difference 34^{o}C for quartz and 36ºC for amorphous, when there is only 22.4% by weight vapor in the reservoir. As it is well established that there could be any amount of vapor from 0 to 100% along the water-vapor saturation curve. Therefore, the independent estimation of reservoir vapor fraction is essential in the application of silica geothermometry. The two-phase flow approach gives the values of vapor fraction and the temperature without using any empirical geothermometer equation. Therefore the silica solubility data could be useful to understand the state of silica-water equilibrium.

The solubility of silica is also function of pH, which has been well studied at 25ºC. Therefore, it is also required to calculate the deep reservoir fluid pH and its dependence on the quartz solubility at high temperature. In summary the temperature dependence regression equation for quartz solubility is not a geothermometer for geothermal reservoir evaluation.

CONCLUSIONS

The quartz and amorphous silica solubility regression expressions are derived by a critical scrutiny of all the existing experimental data along the water-vapor saturation and in the compressed liquid region. The reported experimental solubility data after 300ºC are incorrect as the proportion of water and vapor in the reaction vessel was not taken into account during experimental determinations. A thermodynamic evaluation of all the quartz solubility data along the water-vapor saturation and in compressed liquid region justifies the extrapolation of the low-temperature solubility regression expression. Thus the present expressions are valid for whole range of temperature from 0 to 374ºC.

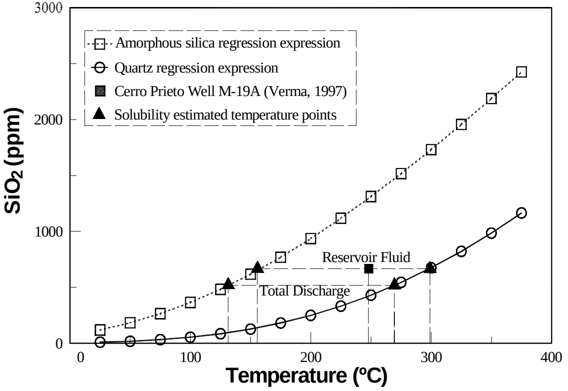

Fig. 5. *The calculated concentration of silica in the liquid phase in the reservoir and in the total concentration at wellhead for the well M-19A at Cerro Prieto.*

The unknown value of reservoir vapor fraction is a fundamental limitation in using the quartz solubility expression as a chemical geothermometer on the total discharge composition of a well. In case of the CP-M-19A well at Cerro Prieto it has been calculated that the reservoir temperature is 248ºC and a vapor fraction 0.224 by weight with a two-flow approach. There could be a wide range of silica concentration in geothermal fluids depending on the silica phase in equilibrium at a specified temperature. Additionally, there is a difference of 34ºC for quartz and 36ºC for amorphous silica between the temperature obtained by applying the solubility expressions on the total discharge and the reservoir fluid silica concentration. The reservoir fluid is supersaturated with respect to quartz, but sub-saturated with respect to amorphous silica according to the two-phase flow calculations.

It can be concluded that the silica solubility equation even along the water-vapor saturation curve is not a *chemical geothermometer* for geochemical evaluation of geothermal systems. Additionally, the silica solubility is a function of pH of the solution. The experimental quartz data for the pH dependence are only available at low temperatures. Similarly the procedures for the pH calculation of geothermal reservoir fluid are also need updating (Verma, 2000).

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