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# Thermodynamic modeling of solubility and speciation of silica in $H_2O$-$SiO_2$ fluid up to 1300°C and 20 kbar based on the chain reaction formalism

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**Abstract:** Recent systematic studies of mineral solubilities in water to high pressures up to 50 kbar call for a suitable thermodynamic formalism to allow realistic fitting of the experimental data and the establishment of an internally consistent data base. The very extensive low-pressure (< 5 kbar) experimental data set on the solubility of $SiO_2$ in $H_2O$ has in the last few years been extended to 20 kbar and 1300°C, providing an excellent experimental basis for testing new approaches. In addition, solubility experiments with different $SiO_2$-buffering phase assemblages and in *situ* determinations of Raman spectra for $H_2O$-$SiO_2$ fluids have provided both qualitative and quantitative constraints on the stoichiometry and quantities of dissolved silica species. We propose a thermodynamic formalism for modeling both absolute silica solubility and speciation of dissolved silica using a combination of the chain reaction approach and a new Gibbs free energy equation of water based on a homogeneous reaction formalism. For a given $SiO_2$-buffer (*e.g.*, quartz) and the coexisting $H_2O$-$SiO_2$ fluid *both* solubility *and* speciation of silica can be described by the following two reactions:

- monomer-forming standard reaction: $SiO_{2(s)} + 2(H_2O)L = (SiO_2)\bullet(H_2O)_2$ (A)
- polymer-forming chain reaction: $(SiO_{2)n-1}\bullet(H_2O)_n + (SiO_2)\bullet(H_2O)_2 = (SiO_2)_n\bullet(H_2O)_{n+1} + (H_2O)_L$, (B)

where $2 \leq n \leq \infty$, and $(H_2O)_L$ stands for "liquid-like" (associated, clustered) water molecules in the aqueous fluid. We show that reactions (A) and (B) lead to the simplified relationships $\Delta G°_{(mono),r,P,T} = \Delta H°_{(mono),r} - T\Delta S°_{(mono),r} + \Delta Cp°_{(mono),r}\,[T - 298.15 - T\ln(T/298.15)] + \Delta V°_{(mono),r}(P - 1)$, and $\Delta G°_{(poly),r,P,T} = \Delta H°_{(poly),r} - T\Delta S°_{(poly),r} + \Delta V°_{(poly),r}\,(P - 1)$
(where the $\Delta G°_{r,P,T}$, are the standard molar Gibbs free energy changes in reactions (A) and (B) as a function of pressure $P$ and temperature $T$; the $\Delta H°_r$, $\Delta S°_r$, $\Delta Cp°_r$ and $\Delta V°_r$ are standard molar enthalpy, entropy, isobaric heat capacity and volume changes, respectively, in reactions (A) and (B) at reference temperature $T_o$ = 298.15 K and pressure $P_o$ = 1 bar) that provide excellent descriptions of the available $H_2O$-$SiO_2$ data set in terms of both $SiO_2$ solubility and silica speciation. Discrepancies between directly determined solubility data and data obtained from *in situ* Raman spectra are ascribed to (i) possible experimental problems of equilibration and (ii) inherent difficulties of interpreting Raman spectra of dilute $H_2O$-$SiO_2$ solutions. In agreement with recent findings, our model indicates that dissolved silica in quartz-buffered aqueous solutions is considerably polymerized, exceeding 20-25 % at all temperatures above 400°C.

**Key-words:** silica solubility, silica speciation, chain reaction, high pressure, thermodynamics.

## Introduction

Aqueous solutions rich in dissolved rock-forming silicates constitute one of the most important types of fluid in the Earth's crust and upper mantle, for the latter specifically in or near subduction zones (*e.g.*, Manning, 2004). At depth, such fluids can approach and attain the composition and the properties of hydrous melts (*e.g.*, Shen & Keppler, 1997; Audetat & Keppler, 2004). Until recently, systematic experimental studies on the solubilities of minerals and other materials relevant to natural rocks have been limited, mainly due to experimental constraints, to pressures below ~ 5 kbar. Such data have been used in various compilations, for instance in a series of many articles extending over more than 30 years by Helgeson and coworkers (*e.g.*, Walther & Helgeson, 1977; Helgeson *et al.*, 1981; Sverjensky *et al.*, 1997), for modeling and predicting phase equilibria and thermodynamic properties of aqueous species. However, as discussed in detail by Manning (1994), these models do not allow rigorous extrapolation to depths beyond those corresponding to 5 kbar. More recent

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Table 1. Summary of thermodynamic variables.

| **Variable** | **Definition** | **Units** |
|---|---|---|
| $\phi$ | parameter characterizing attractive forces between all $H_2O$ molecules | bar |
| $\gamma_i$ | activity coefficient of fluid component *i* | |
| $\mu_i$ | chemical potential (partial molar Gibbs free energy) of fluid component *i* | J/mol |
| $a_1$ | activity of monomers | |
| $a_{H_2O}$ | activity of $H_2O$ | |
| $a_i$ | activity of fluid component *i* | |
| $a_L$ | activity of "liquid-like" $H_2O$ | |
| $a_n$ | activity of polymers of dimension n | |
| $a_{SiO_2 \bullet nH_2O(aq)}$ | activity of $SiO_2 \bullet nH_2O(aq)$ | |
| $c_1$, $c_2$ | empirical parameters for the vibrational part of the Gibbs free energy of water | |
| $\Delta C_P{}^{\circ}{}_{Liq\text{-}Gas}$ | difference in standard isobaric molar heat capacity of $H_2O$ in "liquid-like" and "gas-like" states at reference pressure ($P_o$ =1 bar) and temperature ($T_o$ = 298.15 K) | J/(K mol) |
| $\Delta Cp^{\circ}{}_{(mono),r}$ | standard molar isobaric heat capacity change for the monomer-forming reaction at reference pressure ($P_o$ =1 bar) and temperature ($T_o$ = 298.15 K) | |
| $f_{H_2O}{}^{\circ}$ | fugacity of pure $H_2O$ at given temperature and pressure | |
| $\Delta G^{\circ}{}_{(1),r,P,T}$ | standard molar Gibbs free energy change for reaction 1 at given pressure and temperature | J/mol |
| $\Delta G^{o}{}_{(Buffer\text{-}Quartz),P,T}$ | standard molar Gibbs free energy change for the quartz buffer at given pressure and temperature | J/mol |
| $G_{H_2O}$ | molar Gibbs free energy of pure $H_2O$ | J/mol |
| $G_m$ | the part of the Gibbs free energy of pure $H_2O$ related to the association (clustering) of molecules | J/mol |
| $\Delta G^{\circ}{}_{(mono),r,P,T}$,<br>$\Delta G^{\circ}{}_{(poly),r,P,T}$ | standard molar Gibbs free energy change for the monomer- and polymer-forming reactions at given pressure and temperature | J/mol |
| $G^{o}{}_{Qtz}$ | standard molar Gibbs free energy of quartz | J/mol |
| $G_s$ | standard molar Gibbs free energy of water in the pure "liquid-like" state | J/mol |
| $H_{298,1}$ | standard enthalpy of formation from elements of pure "liquid-like" water at reference pressure ($P_o$ = 1 bar) and temperature ($T_o$ = 298.15 K) | J/mol |
| $\Delta H^{\circ}{}_{Liq\text{-}Gas}$ | difference in standard molar enthalpy of $H_2O$ in "liquid-like" and "gas-like" states at reference pressure ($P_o$ = 1 bar) and temperature ($T_o$ = 298.15 K) | J/mol |
| $\Delta H^{\circ}{}_{(mono),r}$,<br>$\Delta H^{\circ}{}_{(poly),r}$ | standard molar enthalpy change for the monomer- and polymer-forming reactions at reference pressure ($P_o$ = 1 bar) and temperature ($T_o$ = 298.15 K) | J/mol |
| $\Delta H_{s1}{}^{o}$ | empirical parameter for the vibrational part of the Gibbs free energy of water | J |
| $(H_2O)_G$ | "gas-like", unassociated, free water molecules in fluid | |
| $(H_2O)_L$ | "liquid-like", associated, clustered water molecules in fluid | |
| $K_{(mono)}$, $K_{(poly)}$ | equilibrium constant of the monomer- and polymer-forming reactions | |
| $m_{SiO_2(aq)}$ | molality of dissolved $SiO_2$ in $H_2O$ | mol/kg |
| n | dimension of polymer | |
| $P$ | pressure | bar |
| $P_o$ | reference pressure (1 bar) | bar |
| $S_{298,1}$ | standard entropy of pure "liquid-like" water at reference pressure ($P_o$ = 1 bar) and temperature ($T_o$ = 298.15 K) | J/(K mol) |
| $\Delta S^{\circ}{}_{Liq\text{-}Gas}$ | difference in standard molar entropy of $H_2O$ in "liquid-like" and "gas-like" states at reference pressure ($P_o$ = 1 bar) and temperature ($T_o$ = 298.15 K) | J/(K mol) |
| $\Delta S^{\circ}{}_{(mono),r}$,<br>$\Delta S^{\circ}{}_{(poly),r}$ | standard molar entropy change for the monomer- and polymer-forming reactions at reference pressure ($P_o$ = 1 bar) and temperature ($T_o$ = 298.15 K) | J/(K mol) |
| $SiO_{2(s)}$ | silica in solid form | |
| $SiO_2 \bullet nH_2O(aq)$ | silica in dissolved form in water | |
| $T$ | temperature | K |
| $T_o$ | reference temperature (298.15 K) | K |
| $\Delta V^{\circ}{}_{(mono),r}$,<br>$\Delta V^{\circ}{}_{(poly),r}$ | standard molar volume change for the monomer- and polymer-forming reactions at reference pressure P = 1 bar and temperature T = 298.15 K | J/(bar mol) |
| $\Delta V^{\circ}{}_{s1}$ | empirical parameter for the vibrational part of the Gibbs free energy of water | J/bar |
| $W^{Cp}$, $W^{H}$, $W^{S}$ | heat capacity, enthalpy and entropy Margules parameters for the interaction of “liquid-like” and “gas-like” water molecules | J/(K mol) |
| $X_G$ | mole fraction of "gas-like" $H_2O$ in $H_2O$-$SiO_2$ fluid | |
| $X_{Gas}$ | mole fraction of "gas-like" $H_2O$ in pure $H_2O$ | |
| $X_1$ | mole fraction of monomer in $H_2O$-$SiO_2$ fluid | |
| $X_L$ | mole fraction of "liquid-like" $H_2O$ in $H_2O$-$SiO_2$ fluid | |
| $X_{Liq}$ | mole fraction of "liquid-like" $H_2O$ in pure $H_2O$ | |
| $X_n$ | mole fraction of polymer of dimension n in $H_2O$-$SiO_2$ fluid | |
| $X_{SS}$ | sum of the mole fractions of all dissolved silica species in $H_2O$-$SiO_2$ fluid | |
| $Y_{SiO_2}$ | bulk concentration of $SiO_2$ in $H_2O$-$SiO_2$ fluid, *i.e.*, $SiO_2/(H_2O+SiO_2)$ | |

systematic studies on mineral solubilities to considerably higher pressures (*e.g.*, Manning, 1994, 2004; Zhang & Frantz, 2000; Newton & Manning, 2000, 2002, 2003; Fockenberg *et al.*, 2004) have raised the necessity of seeking a thermodynamic formulation for aqueous fluids up to at least 50 kbar.

Manning (1994), Zhang & Frantz (2000) and Newton & Manning (2002, 2003) have extended the available, very extensive low-pressure experimental data set on the solubility of $SiO_2$ in $H_2O$ to 20 kbar and 1300°C, thus providing an excellent data base for developing and testing alternative approaches to the problem. Manning (1994) also derived an empirical polynomial equation that describes the solubility of quartz in aqueous fluid well from 1 bar and 25°C up to 20 kbar and 900°C:

$$\log(\mathrm{m}_{SiO_2(aq)}) = 4.2620 - 5764.2/T + 1.7513 \times 10^6/T^2 - 2.2869 \times 10^8/T^3 + [2.8454 - 1006.9/T + 3.5689 \times 10^5/T^2] \times \log(\rho_{H_2O}),$$

where $m_{SiO_2(aq)}$ is the *molality* of $SiO_2$ in the fluid, mol/kg; $\rho_{H_2O}$ is the density of pure water in g/cm$^3$ at given pressure and temperature ($T$, K). Definitions of the thermodynamic variables used in this paper are summarized in Table 1.

Experimental studies on the solubility of quartz in fluid mixtures (Walther & Orville, 1983), on the diffusion of dissolved silica (Applin, 1987) and *in situ* determinations of the Raman spectra of dissolved silica species in $H_2O$-$SiO_2$ fluids (Zotov & Keppler, 2000, 2002) up to 900°C and 14 kbar provide both qualitative and quantitative constraints on the stoichiometry and quantities of dissolved silica species. However, at present no precise, generally applicable thermodynamic treatment describing *both* the bulk solubility *and* the speciation of silica in aqueous silica-rich fluid has been developed. In the present paper we derive and test such a formalism for the $SiO_2 - H_2O$ system using a combination of the chain reaction approach and a new Gibbs free energy equation of water based on a homogeneous reaction formalism (Gerya & Perchuk, 1997; Gerya *et al.*, 2004).

## Thermodynamic formalism

As suggested by Dove & Rimstidt (1994), silica dissolves in water by the following general reaction

$$SiO_2(s) + \mathrm{n}\ H_2O = SiO_2 \bullet \mathrm{n}H_2O(aq). \qquad (1)$$

Accordingly, the thermodynamic equilibrium condition for the dissolution of quartz is

$$\Delta G^\circ_{(1),r,P,T} + RT\{\ln[a_{SiO_2 \bullet nH_2O(aq)}] - \mathrm{n} \times \ln(a_{H_2O}) - \mathrm{n} \times \ln(f_{H_2O}{}^\circ)\} = 0, \qquad (2)$$

where $\Delta G^\circ_{(1),r,P,T}$ is the standard molar Gibbs free energy change of reaction (1) as a function of temperature $T$ and pressure $P$, $a_i$ are activities of fluid components, and $f_{H_2O}{}^\circ$ is the fugacity of pure $H_2O$ at given pressure and temperature (*e.g.* Holland & Powell, 1998). In the case of low bulk silica concentrations ($Y_{SiO_2} < 0.05$ or $\mathrm{m}_{SiO_2(aq)} < 1$, where $Y_{SiO_2} = SiO_2/(SiO_2+H_2O)$ and m is molality in mol/kg), $a_{H_2O} \approx 1$ and $a_{SiO_2 \bullet nH_2O(aq)} \approx Y_{SiO_2}$. Then equation (2) can be rewritten as

$$\ln(Y_{SiO_2}) = \mathrm{n} \times \ln(f^\circ_{H_2O}) - \Delta G^\circ_{(1),r,P,T}/RT, \qquad (3)$$

implying an apparently simple thermodynamic treatment of this system. However, the available experimental data (Fig. 1a) indicate that the correlation of $\ln(f_{H_2O}{}^o)$ and $\ln(Y_{SiO2})$ along different isotherms is actually very nonlinear. Our test calculations have shown that equations (1)-(3) fail to provide a precise continuous description of experimental data on quartz solubility at both low and high pressure from 1 bar to 20 kbar with a reasonably small number of empirical parameters for the representation of $\Delta G^\circ_{(1),r,P,T}$ (*e.g.*, Walther & Helgeson, 1977). On the other hand, Manning (1994) has demonstrated a strong positive correlation between the logarithm of silica concentration in quartz-buffered $H_2O$-$SiO_2$ fluid and the logarithm of the density of pure $H_2O$ fluid along different isotherms (Fig. 1b). Our calculations have also shown a similar strong positive correlation between isothermal silica solubility and the degree of association or clustering of $H_2O$ molecules in pure $H_2O$ (Fig. 1c), which increases with increasing density (*e.g.*, Gorbaty & Kalinichev, 1995; Luck, 1980; Gerya & Perchuk, 1997; Gerya *et al.*, 2004). This strongly suggests that the dissolution of silica is directly related to the actual *proportion* of *associated* (*i.e.*, clustered, "liquid-like") $H_2O$ molecules in the aqueous fluid, and offers the possibility of deriving a general thermodynamic description for silica solubility in water.

It has been shown recently (Gerya & Perchuk, 1997; Gerya *et al.*, 2004) that from the viewpoint of thermodynamics pure $H_2O$ fluid (and many other gases) can be effectively treated as a mixture of molecules in two distinct states: (1) a "liquid-like" (associated, clustered) state (defined as $(H_2O)_L$ in this paper), and (2) a "gas-like" (unassociated, free) state (defined as $(H_2O)_G$). This phenomenological approach uses the concept of homogeneous reactions of $H_2O$ molecules leading to their liquid-like linkage (for a detailed discussion of the thermodynamic background and derivation of the association/clustering reactions see Gerya & Perchuk, 1997; Gerya *et al.*, 2004). Such an approach is theoretically well developed for describing the hydrogen bonding in supercritical fluids (*e.g.*, Luck, 1980; Gupta *et al.*, 1992), and its potential applicability to any type of fluid has been demonstrated (Barelko *et al.*, 1994; Gerya & Perchuk, 1997). This approach is also in accord with the detailed Raman spectroscopic studies of Lindner (1970) and Kohl *et al.* (1991), who concluded on the basis of their data that water can be treated as a solution of liquid-like and gas-like types of $H_2O$ molecules. According to this formalism, the molar Gibbs free energy equation of pure $H_2O$, valid for a wide range of $P$-$T$ conditions, takes the form (see Gerya & Perchuk, 1997; Gerya *et al.*, 2004 for details of derivation)

$$G_{H_2O} = G_s + G_m, \qquad (4)$$

where

$$G_s = H_{298,1} - TS_{298,1} + V^\circ{}_s\Psi + RT[c_1\ln(1 - e_1) + c_2\ln(1 - e_2)] - (c_1 + c_2)[\Delta H_{s1}{}^o(1 - T/T_o)\ e_o/(1 - e_o) + \mathrm{R}T\ln(1 - e_o)], \qquad (5)$$

$$G_m = \mathrm{R}T[X_{Liq}\ln(X_{Liq}) + X_{Gas}\ln(X_{Gas})] + X_{Gas}\mathrm{R}T\ln(P + \phi\ X_{Liq}{}^2) - X_{Gas}\{\Delta H^\circ_{Liq\text{-}Gas} - T\Delta S^\circ_{Liq\text{-}Gas} + \Delta C_P{}^\circ_{Liq\text{-}Gas}[T - 298.15 - T\ln(T/298.15)]\} + \{W^H - TW^S + W^{Cp}[T - 298.15 - T\ln(T/298.15)]\}X_{Liq}X_{Gas}, \qquad (6)$$

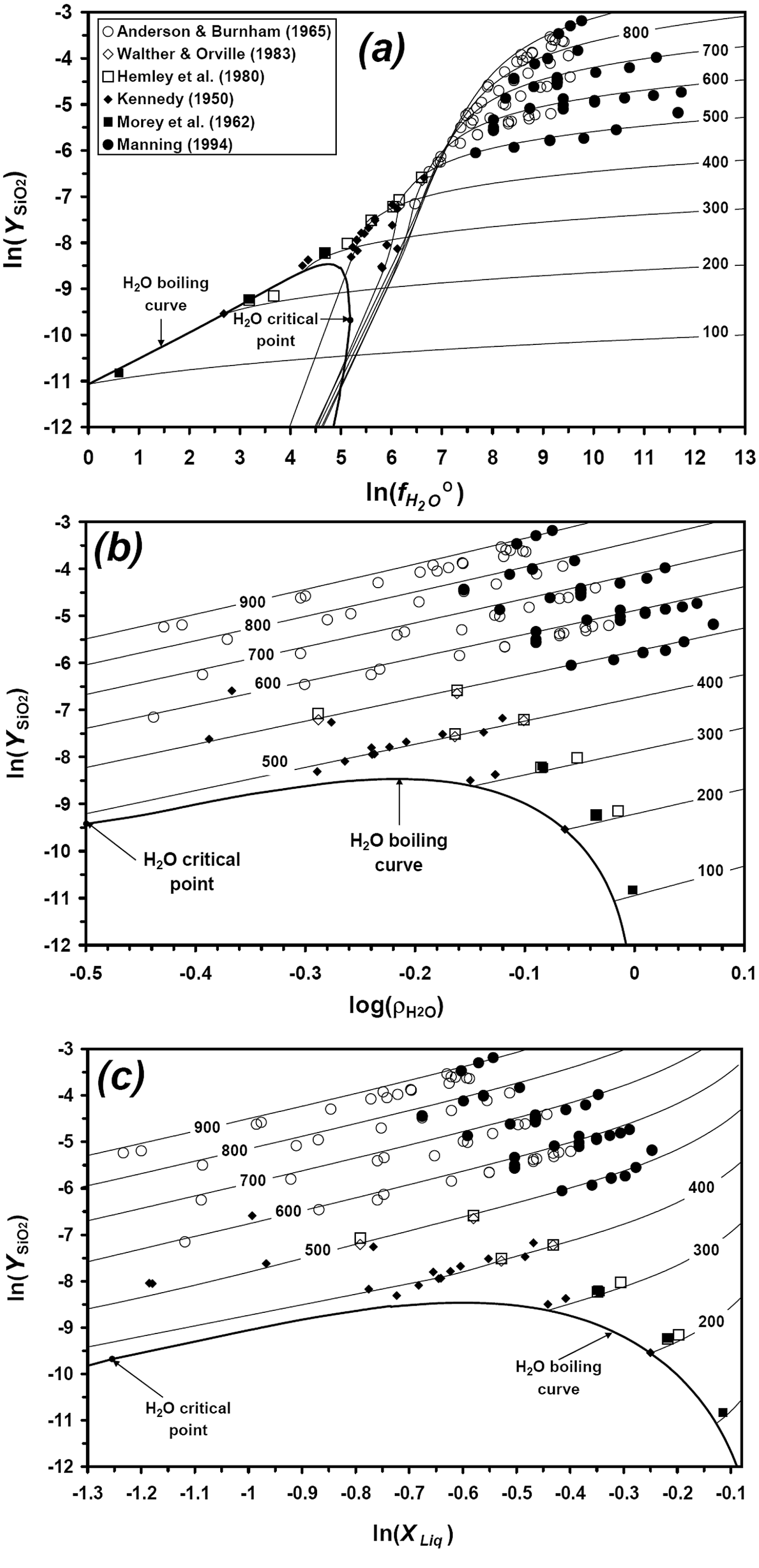

Fig. 1. Experimental data on the solubility of quartz in aqueous fluid $Y_{SiO_2} = SiO_2/(SiO_2 + H_2O)$ as a function of various thermodynamic parameters: (a) fugacity of pure $H_2O$, (b) density of pure $H_2O$, (c) mole fraction (thermodynamic probability) of "liquid-like" (associated, clustered) aqueous molecules ($X_{Liq}$) in pure $H_2O$, calculated according to equations (4)-(9). The different symbols represent experimental data from the literature sources indicated. The isotherms have been obtained from the empirical polynomial fit suggested by Manning (1994).

and $e_1 = \exp[-(\Delta H^\circ_{s1} + \Delta V^\circ_{s1}\Psi)/RT)]$, $e_2 = \exp[-\Delta H^\circ_{s1}/RT)]$, $e_o = \exp[-\Delta H^\circ_{s1}/R298.15)]$, $\Psi = 5/4(1+\phi)^{1/5}[(P+\phi)^{4/5} - (1+\phi)^{4/5}]$. $X_{Liq}$ and $X_{Gas}$ are the mole fractions (or more specifically the thermodynamic probabilities in this dynamic system) of molecules in "liquid-like" and "gas-like" states, respectively, and $X_{Liq} + X_{Gas} = 1$. $G_s$ is the standard molar Gibbs free energy of water in the pure "liquid-like" state ($X_{Liq} = 1$) and $G_m$ is that part of the

Gibbs free energy of $H_2O$ related to the association (clustering) of molecules. $\Delta H^{\circ}_{\text{Liq-Gas}} = -44839$ J, $\Delta S^{\circ}_{\text{Liq-Gas}} = -122.4$ J/K and $\Delta C_P{}^{\circ}_{\text{Liq-Gas}} = 21.5$ J/K are the differences in standard molar enthalpy, entropy and heat capacity of $H_2O$ in "liquid-like" and "gas-like" states at reference pressure ($P_o = 1$ bar) and temperature ($T_o = 298.15$ K). $W^{\text{H}} = -28793$ J, $W^{\text{S}} = -11.7$ J/K and $W^{\text{Cp}} = 5.1$ J/K are enthalpy, entropy and heat capacity Margules parameters for the interaction of "liquid-like" and "gas-like" water molecules at $P_{\text{o}}$ and $T_{\text{o}}$ $\phi = 6209$ bar is a parameter characterizing the attractive forces between all $H_2O$ molecules. $H_{298,1} = -286832$ J, $S_{298,1} = 65.2$ J/K are, respectively, the standard molar enthalpy of formation from the elements and the molar entropy of "liquid-like" water molecules at $P_{\text{o}}$ and $T_{\text{o}}$; $V^{\circ}_{\text{s}} = 1.714$ J/bar is the standard molar volume of "liquid-like" water molecules at $T = 0$ K and $P_{\text{o}}$; $c_1 = 7.236$, $c_2 = 0.315$, $\Delta H^{\circ}_{\text{s1}} = 4586$ J and $\Delta V^{\circ}_{\text{s1}} = 0.0431$ J/bar are empirical parameters for the vibrational part of the Gibbs potential.

By using the Gibbs-Duhem relation, chemical potentials of "liquid-like" ($\mu_{\text{Liq}}$) and "gas-like" ($\mu_{\text{Gas}}$) molecules can be calculated from equations (4)-(6) as follows

$$\mu_{\text{Liq}} = G_{\text{s}} + \text{R}T\ln(X_{\text{Liq}}) + 2\text{R}TX_{\text{Liq}}X_{\text{Gas}}{}^2\phi/(P + \phi X_{\text{Liq}}{}^2) + \{W^{\text{H}} - TW^{\text{S}} + W^{\text{Cp}}[T - 298.15 - T\ln(T/298.15)]\}X_{\text{Gas}}{}^2, \tag{7}$$

$$\mu_{\text{Gas}} = G_{\text{s}} + \text{R}T\ln(X_{\text{Gas}}) + \text{R}T\ln(P + \phi X_{\text{Liq}}{}^2) - 2\text{R}TX_{\text{Liq}}{}^2X_{\text{Gas}}\phi/(P + \phi X_{\text{Liq}}{}^2) - \{\Delta H^{\circ}_{\text{Liq-Gas}} - T\Delta S^{\circ}_{\text{Liq-Gas}} + \Delta C_P{}^{\circ}_{\text{Liq-Gas}}[T - 298.15 - T\ln(T/298.15)]\} + \{W^{\text{H}} - TW^{\text{S}} + W^{\text{Cp}}[T - 298.15 - T\ln(T/298.15)]\}X_{\text{Liq}}{}^2. \tag{8}$$

The equilibrium values for $X_{\text{Liq}}$ and $X_{\text{Gas}}$ in a pure $H_2O$ fluid at given pressure and temperature can then be calculated according to the standard relation

$$G_{\text{m}} = min,\ i.e.,\ \mu_{\text{Liq}} = \mu_{\text{Gas}}. \tag{9}$$

*The software for calculating the equilibrium values of $X_{Liq}$ according to equation (9) is available by request from the corresponding author.*

Furthermore, it is well-known (*e.g.*, Applin, 1987; Dove & Rimstidt, 1994; Zotov & Keppler, 2000, 2002) that dissolved silica can occur in the form of various types of species. Although $(SiO_2)\bullet(H_2O)_2$-monomers dominate in the fluid at low silica concentrations in equilibrium with quartz at 25°C and 1 bar (*e.g.*, Walther & Helgeson, 1977; Cary *et al.*, 1982; Applin, 1987), $(SiO_2)_2\bullet(H_2O)_3$-dimers and possibly higher polymers become important at higher silica concentrations, particularly with increasing pressure and temperature (*e.g.*, Zotov & Keppler, 2000, 2002; Newton & Manning, 2002, 2003). In the following, therefore, we propose that $H_2O$-$SiO_2$-fluids can be treated as a mixture of "liquid-like" $(H_2O)_L$ and "gas-like" $(H_2O)_G$ water molecules with $(SiO_2)\bullet(H_2O)_2$-monomers and all higher $(SiO_2)_n\bullet(H_2O)_{n+1}$-polymers ($2 \leq n \leq \infty$), such that

$$X_{\text{L}} + X_{\text{G}} + X_1 + \sum_{\text{n}=2}^{\infty} X_{\text{n}} = 1, \tag{10}$$

where $X_{\text{L}}$ and $X_{\text{G}}$ are the mole fractions of "liquid-like" $(H_2O)_L$ and "gas-like" $(H_2O)_G$ molecules, respectively, $X_1$ is the mole fraction of $(SiO_2)\bullet(H_2O)_2$-monomers, and $X_{\text{n}}$ is the mole fraction of silica polymers with dimension of $n \geq 2$.

On the basis of the above we can describe *both* the solubility *and* the speciation of silica in an aqueous fluid by the following two types of reactions:

a) the monomer-forming standard reaction:

$$SiO_2(s) + 2(H_2O)_L = (SiO_2)\bullet(H_2O)_2. \tag{11}$$

b) the polymer-forming chain reaction:

$$(SiO_2)_{n-1}\bullet(H_2O)_n + (SiO_2)\bullet(H_2O)_2 = (SiO_2)_n\bullet(H_2O)_{n+1} + (H_2O)_L, \tag{12}$$

where $2 \leq n \leq \infty$. The equilibrium conditions for these two reactions can be written as

$$\Delta G^{\circ}_{(\text{mono}),\text{r},P,T} + RT\ln(K_{(\text{mono})}) = 0, \tag{13}$$

$$\Delta G^{\circ}_{(\text{poly}),\text{r},P,T} + RT\ln(K_{(\text{poly})}) = 0, \tag{14}$$

where $K_{(\text{mono})} = a_1/(a_{\text{L}})^2$ and $K_{(\text{poly})} = a_{\text{n}}a_{\text{L}}/(a_{\text{n-1}}a_1)$ are the equilibrium constants of reactions (11) and (12), respectively; $a_{\text{L}}$ is the activity of "liquid-like" water molecules $(H_2O)_L$; $a_1$ is the activity of silica monomers and $a_{\text{n}}$ as well as $a_{\text{n-1}}$ are the activities of silica polymers with dimensions of n and n-1 respectively. $\Delta G^{\circ}_{(\text{mono}),\text{r},P,T}$ and $\Delta G^{\circ}_{(\text{poly}),\text{r},P,T}$ are the standard Gibbs free energy changes of reactions (11) and (12) as functions of $P$ and $T$, respectively.

In order to obtain analytical expressions for silica solubility we first assume that $\Delta G^{\circ}_{(\text{poly}),\text{r},P,T}$ is independent of n. According to equations (7) and (8), the activity of "liquid-like" water molecules differs from the mole fraction and varies with pressure and temperature. For the following derivations we therefore assume that the activities of the silica species are also different from their mole fractions and vary with pressure and temperature in such a way that the *ratios of the activity coefficients* (but not the *absolute values* of these coefficients) for the equilibrium constants of reactions (11) and (12) are always equal to one

$$\gamma_1/(\gamma_{\text{L}})^2 = 1, \tag{15}$$

$$\gamma_{\text{n}}\gamma_{\text{L}}/(\gamma_{\text{n-1}}\gamma_1) = 1, \tag{16}$$

where $\gamma_i = a_i/X_i \neq 1$.

The chemical potentials for all species in $H_2O$-$SiO_2$ fluids can then be formulated according to reactions (11), (12) and equations (7), (8) as follows

$(H_2O)_G$ - standard state: $X_{\text{G}} = 1, X_{\text{Gas}} = 1, X_{\text{Liq}} = 0$

$$\mu[(H_2O)_G] = \text{R}T\ln(X_{\text{G}}) + G_{\text{s}} + \text{R}T\ln(P + \phi X_{\text{Liq}}{}^2) - 2\text{R}TX_{\text{Liq}}{}^2X_{\text{Gas}}\phi/(P + \phi X_{\text{Liq}}{}^2) - \{\Delta H^{\circ}_{\text{Liq-Gas}} - T\Delta S^{\circ}_{\text{Liq-Gas}} + \Delta C_P{}^{\circ}_{\text{Liq-Gas}}[T - 298.15 - T\ln(T/298.15)]\} + \{W^{\text{H}} - TW^{\text{S}} + W^{\text{Cp}}[T - 298.15 - T\ln(T/298.15)]\}X_{\text{Liq}}{}^2. \tag{17}$$

$(H_2O)_L$ – standard state: $X_{\text{L}} = 1, X_{\text{Liq}} = 1, X_{\text{Gas}} = 0$

$$\mu[(H_2O)_L] = \text{R}T\ln(X_{\text{L}}) + G_{\text{s}} + 2\text{R}TX_{\text{Liq}}X_{\text{Gas}}{}^2\phi/(P + \phi X_{\text{Liq}}{}^2) + \{W^{\text{H}} - TW^{\text{S}} + W^{\text{Cp}}[T - 298.15 - T\ln(T/298.15)]\}X_{\text{Gas}}{}^2, \tag{18}$$

$(SiO_2)\bullet(H_2O)_2$ – standard state: $X_1 = 1, X_{\text{Liq}} = 1, X_{\text{Gas}} = 0$

$$\mu[(SiO_2)\bullet(H_2O)_2] = \mathrm{R}T\ln(X_1) + \Delta G^{o}_{(mono),r,P,T} + G^{o}_{Qtz} + 2G_s + 4\mathrm{R}TX_{Liq}X_{Gas}{}^2\phi/(P + \phi\, X_{Liq}{}^2) + 2\{W^{H} - TW^{S} + W^{Cp}[T - 298.15 - T\ln(T/298.15)]\}X_{Gas}{}^2, \quad (19)$$

$(SiO_2)_n\bullet(H_2O)_{n+1}$ – standard state: $X_n = 1$, $X_{Liq} = 1$, $X_{Gas} = 0$

$$\mu[(SiO_2)_n\bullet(H_2O)_{n+1}] = \mathrm{R}T\ln(X_n) + \mathrm{n}\Delta G^{\circ}_{(mono),r,P,T} + (\mathrm{n} - 1)\Delta G^{\circ}_{(poly),r,P,T} + \mathrm{n}G^{\circ}_{Qtz} + (\mathrm{n} + 1)G_s + (\mathrm{n} + 1)2\mathrm{R}TX_{Liq}X_{Gas}{}^2\phi/(P + \phi\, X_{Liq}{}^2) + (\mathrm{n} + 1)\{W^{H} - TW^{S} + W^{Cp}[T - 298.15 - T\ln(T/298.15)]\}X_{Gas}{}^2, \quad (20)$$

where $G^{\circ}_{Qtz}$ is the standard molar Gibbs free energy of quartz (*e.g.*, Holland & Powell, 1998; Gerya *et al.*, 1998, 2004); $X_{Liq}$ and $X_{Gas}$ are, respectively, equilibrium mole fractions (thermodynamic probabilities) of "liquid-like" and "gas-like" water molecules calculated for *pure* $H_2O$ fluid at given pressure and temperature according to equations (7)-(9). The presence of $X_{Liq}$- and $X_{Gas}$-dependent terms in equations (19), (20) means that, according to our model, the thermodynamic properties of silica species strongly depend on the degree of association of molecules in the aqueous fluid. These $X_{Liq}$- and $X_{Gas}$-dependent terms are similar to those of "liquid-like" rather than "gas-like" water molecules (*cf.*, equations (17)-(20)).

For the following derivations we assume that the presence of silica species affects the *absolute values* but does not change the *ratio between* the mole fractions of "liquid-like" and "gas-like" water molecules in $SiO_2$-$H_2O$-fluids. This *ratio* then always corresponds to the conditions of equilibrium in a pure water fluid at the same pressure and temperature

$$X_L/X_G = X_{Liq}/X_{Gas}. \quad (21)$$

The following analytical expressions can then be obtained for the concentrations of different fluid species

$$K_{(mono)} = \exp(-\,\Delta G^{\circ}_{(mono),r,P,T}/RT), \quad (22)$$

$$K_{(poly)} = \exp(-\,\Delta G^{\circ}_{(poly),r,P,T}/RT). \quad (23)$$

$$X_L = \{[4X_{Liq}K_{(mono)}(X_{Liq} - K_{(poly)}) + (1 + X_{Liq}K_{(mono)}K_{(poly)})^2]^{0.5} - (1 + X_{Liq}K_{(mono)}K_{(poly)})\}/[2K_{(mono)}(X_{Liq} - K_{(poly)})], \quad (24)$$

$$X_1 = K_{(mono)}(X_L)^2, \quad (25)$$

$$X_n = X_1(K_{(poly)}X_1/X_L)^{n-1}, \quad (26)$$

$$X_G = X_{Gas}X_L/X_{Liq}, \quad (27)$$

The bulk concentration of dissolved silica in the fluid, $Y_{SiO_2} = SiO_2/(SiO_2+H_2O)$, and the relative proportion of dissolved silica in monomers $Y_{SiO_2(mono)} = SiO_{2(mono)}/\ SiO_{2(total)}$ as well as in higher polymers $Y_{SiO_2(n\text{-}poly)} = SiO_{2(n\text{-}poly)}/\ SiO_{2(total)}$ can then be calculated according to

$$Y_{SiO_2} = (\sum_{i=1}^{\infty} X_i i)/[\sum_{i=1}^{\infty} X_i\,(2i + 1) + X_L + X_G] = (1 - X_L - X_G)^2/[2(1 - X_L - X_G)^2 + X_1], \quad (28)$$

$$Y_{SiO_2(mono)} = X_1/(\sum_{i=1}^{\infty} X_i i) = (X_1)^2/(1 - X_L - X_G)^2, \quad (29)$$

$$Y_{SiO_2(n\text{-}poly)} = \mathrm{n}X_n/(\sum_{i=1}^{\infty} X_i i) = \mathrm{n}X_1X_n/(1 - X_L - X_G)^2. \quad (30)$$

To derive equations (28)-(30) we have used equation (26), the condition $\sum_{i=1}^{\infty} X_i + X_L + X_G = 1$ (*cf.*, equation (10)) and the standard mathematical relations $\sum_{i=1}^{\infty} Z^{i-1} = 1/(1 - Z)$ and $\sum_{i=1}^{\infty} Z^{i-1}i = 1/(1 - Z)^2$, where $0 < Z < 1$ in order to obtain

$\sum_{i=1}^{\infty} X_i = X_1/(1 - K_{(poly)}X_1/X_L) = 1 - X_L - X_G$, $\sum_{i=1}^{\infty} X_i i = X_1/(1 - K_{(poly)}X_1/X_L)^2 = (1 - X_L - X_G)^2/X_1$.

## Application to available experimental data

Our test calculations for the $H_2O$-$SiO_2$ system in a wide region of pressure (1-20,000 bar) and temperature (25-1300°C) have shown that the standard molar Gibbs free energy change for reactions (11) and (12) can be represented well by the following, relatively simple standard formulae

$$\Delta G^{\circ}_{(mono),r,P,T} = \Delta H^{\circ}_{(mono),r} - T\Delta S^{\circ}_{(mono),r} + \Delta Cp^{\circ}_{(mono),r}[T - T_o - T\ln(T/T_o)] + \Delta V^{\circ}_{(mono),r}(P - P_o), \quad (31)$$

$$\Delta G^{\circ}_{(poly),r,P,T} = \Delta H^{\circ}_{(poly),r} - T\Delta S^{\circ}_{(poly),r} + \Delta V^{\circ}_{(poly)r}(P - P_o), \quad (32)$$

where $T_o = 298.15$ K and $P_o = 1$ bar are standard pressure and temperature, respectively; $\Delta H^{\circ}_r$, $\Delta S^{\circ}_r$, $\Delta Cp^{\circ}_r$ and $\Delta V^{\circ}_r$ are, respectively, standard molar enthalpy, entropy, isobaric heat capacity and volume changes at $T_o$ and $P_o$ in reactions (11) and (12).

In the case where additional $SiO_2$-buffering mineral assemblages are equilibrated with aqueous fluid (*e.g.*, Zhang & Frantz, 2000; Newton & Manning, 2003), the Gibbs free energy change of the monomer-forming reaction (11) can be obtained as follows:

$$\Delta G^{\circ}_{(mono),r,P,T} = \Delta G^{o}_{(Buffer\text{-}Quartz),P,T} + \Delta H^{\circ}_{(mono),r} - T\Delta S^{\circ}_{(mono),r} + \Delta Cp^{\circ}_{(mono),r}[T - T_o - T\ln(T/T_o)] + \Delta V^{\circ}_{(mono),r}(P - P_o), \quad (33)$$

where $\Delta G^{o}_{(Buffer\text{-}Quartz),P,T}$ is the difference between the standard molar Gibbs free energies of the given $SiO_2$-buffering mineral assemblage and quartz in J/mol, which is a function of $P$ and $T$ (Newton & Manning, 2003). For calculating $\Delta G^{o}_{(Buffer\text{-}Quartz)P,T}$ we used the internally consistent thermodynamic database of Holland & Powell (1998). As shown by Zhang & Frantz (2000) and Newton & Manning (2003), experimental data on silica solubility in the presence of various $SiO_2$-buffering mineral assemblages allow accurate modeling of silica speciation at elevated pressure and temperature.

In order to quantify the seven parameters in equations (31) and (32), we have used a set of 439 experimental data points (Table 2) retrieved from the literature on the bulk silica solubility in the presence of quartz (Anderson & Burnham, 1965; Walther & Orville, 1983; Hemley *et al.*, 1980; Kennedy, 1950; Morey *et al.*, 1962; Manning, 1994;

Table 2. Experimental data used for the calibration of equations (31)-(33).

| **References** | **$SiO_2$-buffer** | **No of data points** | ***P*, kbar** | ***T*, °C** | $Y_{SiO_2}$ | **Statistical weight for each data point** | **Mean square error $\sigma(Y_{SiO_2})$, %** | **$\Delta Y_{SiO_2}$,%** | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | **min** | **max** |
| Anderson & Burnham (1965) | quartz | 52 | 1-9.85 | 596-900 | 0.0008-0.03 | 1 | 12 (16)* | -6 (-3)* | +35 (+41)* |
| Walther & Orville (1983) | quartz | 13 | 1-2 | 350-550 | 0.0004-0.002 | 1 | 6 (8) | -12 (-15) | +9 (+16) |
| Hemley *et al.*, 1980; | quartz | 14 | 1-2 | 200-500 | 0.0001-0.001 | 1 | 7 (9) | -14 (-14 | +3 (+4) |
| Kennedy (1950) | quartz | 87 | 0.01-1.75 | 182-610 | 0.00005-0.001 | 1 | 13 (11) | -11 (-42) | +38 (+12) |
| Morey *et al.* (1962) | quartz | 28 | 1.01 | 45-300 | 0.000006-0.0003 | 1 | 24 (19) | -37 (-31) | -3 (-6) |
| Manning (1994), exp. | quartz | 51 | 5-20 | 500-900 | 0.002-0.04 | 1 | 8 (10) | -17 (-21) | +17 (+22) |
| Manning (1994), calc. | quartz | 91 | 0.001-20 | 25-900 | 0.000002-0.04 | 3 | 9 | -16 | +14 |
| Watson & Wark (1997) | quartz | 3 | 10 | 570-810 | 0.005-0.02 | 1 | 14 (17) | +7 (+15) | +18 (+18) |
| Newton & Manning (2002) | quartz, enstatite-forsterite, | 22 | 1-14 | 700-900 | 0.0005-0.05 | 1 | 8 (5) | -14 (-13) | +15 (0) |
| Newton & Manning (2003) | quartz, enstatite-forsterite, kyanite-corundum forsterite-rutile-geikielite | 6 | 12 | 800 | 0.001-0.02 | 1 | 10 | -9 | +22 |
| Woodland & Walther (1987) | quartz | 53 | 0.95-2.71 | 345-500 | 0.0004-0.002 | 1 | 7 (9) | -20 (-19) | +11 (+18) |
| Walther & Woodland (1993) | quartz | 15 | 1.5-2 | 400-600 | 0.0009-0.002 | 1 | 13 (13) | -19 (-19) | +17 (+24) |
| Hemley *et al.* (1977a,b) | talc-chrysotile-water, talc-forsterite-water, talc-antigorite-water, talc-anthophyllite-water, talc-enstatite-water, anthophyllite-forsterite-water | 75 | 1-2 | 200-715 | 0.00001-0.001 | 1 | 22 | (-32) | +70 |
| Hemley *et al.* (1977b) | enstatite-forsterite | 7 | 1 | 680-720 | 0.00047-0.00053 | 1 | 10 (9) | -14 (-16) | +15 (+4) |
| Zhang & Frantz (2000), exp. | enstatite-forsterite | 6 | 10-20 | 900-1200 | 0.006-0.04 | 1 | 34 (62) | +16 (0) | +52 (+103) |
| Zhang & Frantz (2000), calc. | enstatite-forsterite | 7 | 10 | 700-1300 | 0.002-0.09 | 1 | 31 (60) | -2 (-19) | +51 (+103) |
| Dove & Rimstidt (1994) | quartz | 1 | 0.001 | 25 | 0.000002 | 10,000 | 0 (-9) | - | - |

* values in brackets are calculated on the basis of the polynomial fits of Manning (1994) and Newton & Manning (2002)

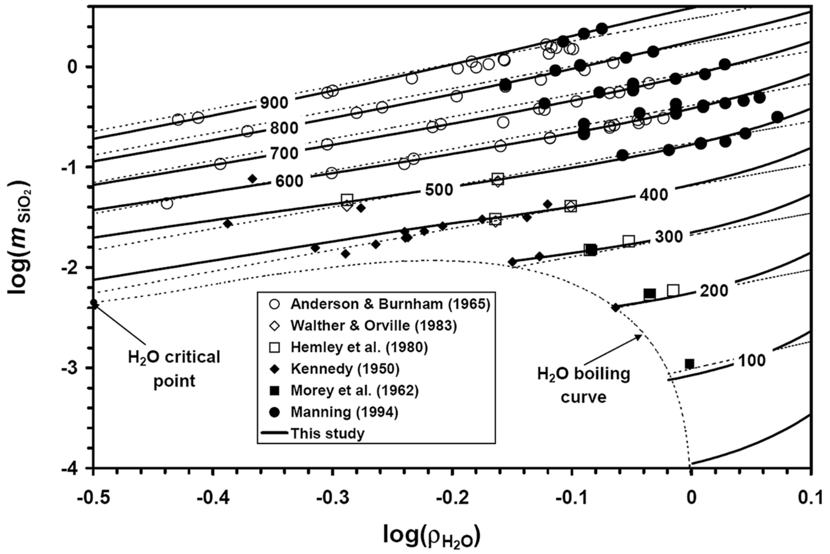

Fig. 2. Results of modeling bulk molality of dissolved silica in aqueous fluid in the presence of quartz based on equations (21)-(30) (solid lines). The different symbols represent experimental data from the sources indicated. Dashed lines are calculations on the basis of the empirical equation suggested by Manning (1994).

Walther & Woodland, 1993; Woodland & Walther, 1987; Watson & Wark, 1997; Newton & Manning, 2002) and other $SiO_2$-buffering mineral assemblages (Zhang & Frantz, 2000; Newton & Manning, 2002, 2003; Hemley *et al.*, 1977a,b), as well as silica diffusion (Applin, 1987) and NMR data (Cary *et al.*, 1982) at 25°C and 1 bar for estimating both the bulk mole fraction of silica and the fraction of silica in monomeric form. *In situ* measurements of Raman spectra for $H_2O$-$SiO_2$ fluids coexisting with quartz (Zotov & Keppler, 2000; 2002) provide qualitative constraints in that the relative amount of silica in polymeric form must increase with an isochoric increase of temperature for $T$ = 600-900°C and $P$ = 5.6-14 kbar.

As discussed further below, it was not possible to integrate the numerical results of Zotov & Keppler (2002), who derived quantitative data on the mole fractions of silica monomers and dimers from *in situ* Raman spectra of aqueous fluid equilibrated with quartz at pressure from 5.6-14 kbar and temperatures from 700 to 900°C. These results have been excluded from our database for two reasons: (i) our calculations show that these data are in large part inconsistent with the other studies considered here, requiring a much more pronounced dependence of silica speciation on the density of the fluid at a given temperature, and (ii) it was not possible to resolve the discrepancies in the paper by Zotov & Keppler (2002) between the formalism presented in their equations (9) and (10) and the derived data on monomer and dimer quantities presented in their Table 2.

For the calculation of thermodynamic parameters we used a *non-linear* least square method in order to minimize the relative error of reproducing the bulk silica concentration, which is defined as

$\Delta Y_{SiO_2}$ (%) = 100[$Y_{SiO_2}$(calculated) –
$Y_{SiO_2}$(experimental)]/$Y_{SiO_2}$(experimental).

We have used a uniform statistical weight of 1 for all experimental data points (Table 2), thus making no attempt to gauge the relative quality of the various data subsets in their accuracy and precision (see discussion by Manning, 1994). However, because of the very irregular distribution of data points in pressure and temperature, we found it necessary to balance our database by adding 91 points interpolated from the polynomial equation of Manning (1994) within the P-T range of experiments used for the calibration of this equation. These "synthetic" points were regularly distributed with pressure (1 kbar steps) along 9 isotherms (100 to 900°C, with 100°C steps). A higher statistical weight of 3 was assigned to these data points. In order to insure an exact reproduction of the concentration and the speciation of silica at the reference conditions of $T_o$ = 25°C and $P_o$ = 1 bar (Morey *et al.*, 1962; Applin, 1987; Dove & Rimstidt, 1994; Cary *et al.*, 1982) we assigned a very high statistical weight of 10,000 to the single data point representing these conditions. The resulting values for the thermodynamic parameters of equations (31) and (32) are

$\Delta H^{\circ}_{(mono),r} = 24014 \pm 1781$ J,
$\Delta S^{\circ}_{(mono),r} = -28.10 \pm 4.23$ J/K,
$\Delta V^{\circ}_{(mono),r} = -0.2354 \pm 0.0749$ J/bar,
$\Delta Cp^{\circ}_{(mono),r} = 31.96 \pm 6.45$ J/K,
$\Delta H^{\circ}_{(poly),r} = -21059 \pm 3589$ J,
$\Delta S^{\circ}_{(poly),r} = 9.66 \pm 11.66$ J/K,
$\Delta V^{\circ}_{(poly),r} = 0.3161 \pm 0.1798$ J/bar.

Table 2 and Fig. 2, 3 show that the data set is fitted well by the above parameters. The mean square error in reproducing 439 data points on bulk silica solubility is 14.2 % relative. No systematic variations of calculated errors with temperature, pressure, bulk silica concentration and $X_{Liq}$ have been found (Fig. 3). In quartz-buffered systems relatively large deviations (> 20 %) are indicated for the experimental data of Morey *et al.* (1962) and Kennedy (1950) at pressures below 1 kbar and temperatures below 200°C. Our test calculations show that these data are in part inconsistent with the bulk silica concentrations at the reference conditions of $T_o$ = 25°C and $P_o$ = 1 bar (Dove & Rimstidt, 1994), requiring either notably higher (Morey *et al.*, 1962) or lower (Kennedy, 1550) values. These discrepancies can in part be explained by the problems of reaching equilib-

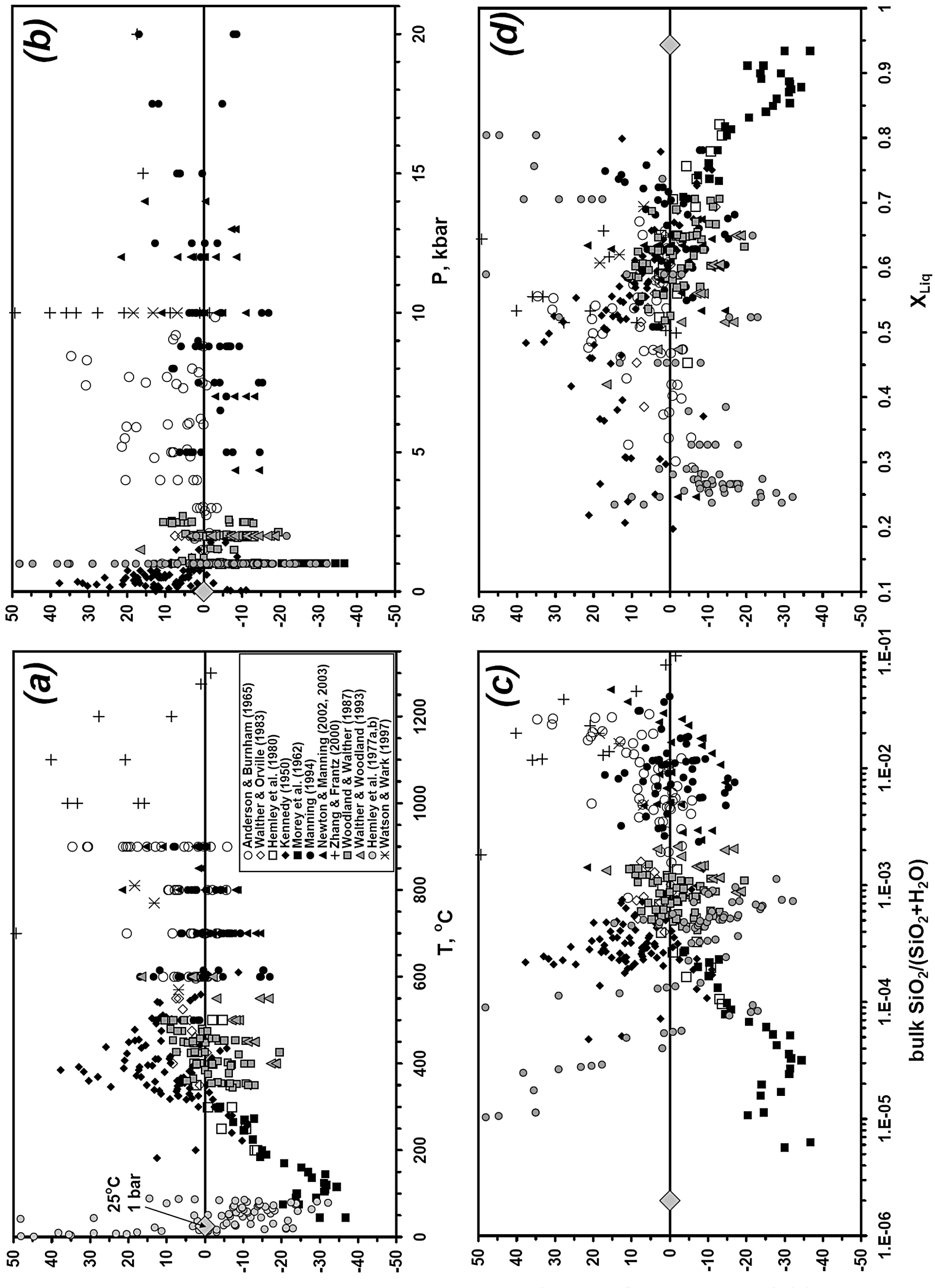

Fig. 3. Distribution of relative error $\Delta Y_{SiO_2}$ (%) = $100[Y_{SiO_2}$(calculated)-$Y_{SiO_2}$(experimental)]/$Y_{SiO_2}$(experimental) of reproducing experimental data with temperature (a), pressure (b), bulk silica concentration (c) and degree of association ($X_{Liq}$) of pure water fluid (d). The different symbols represent experimental data from the sources indicated.

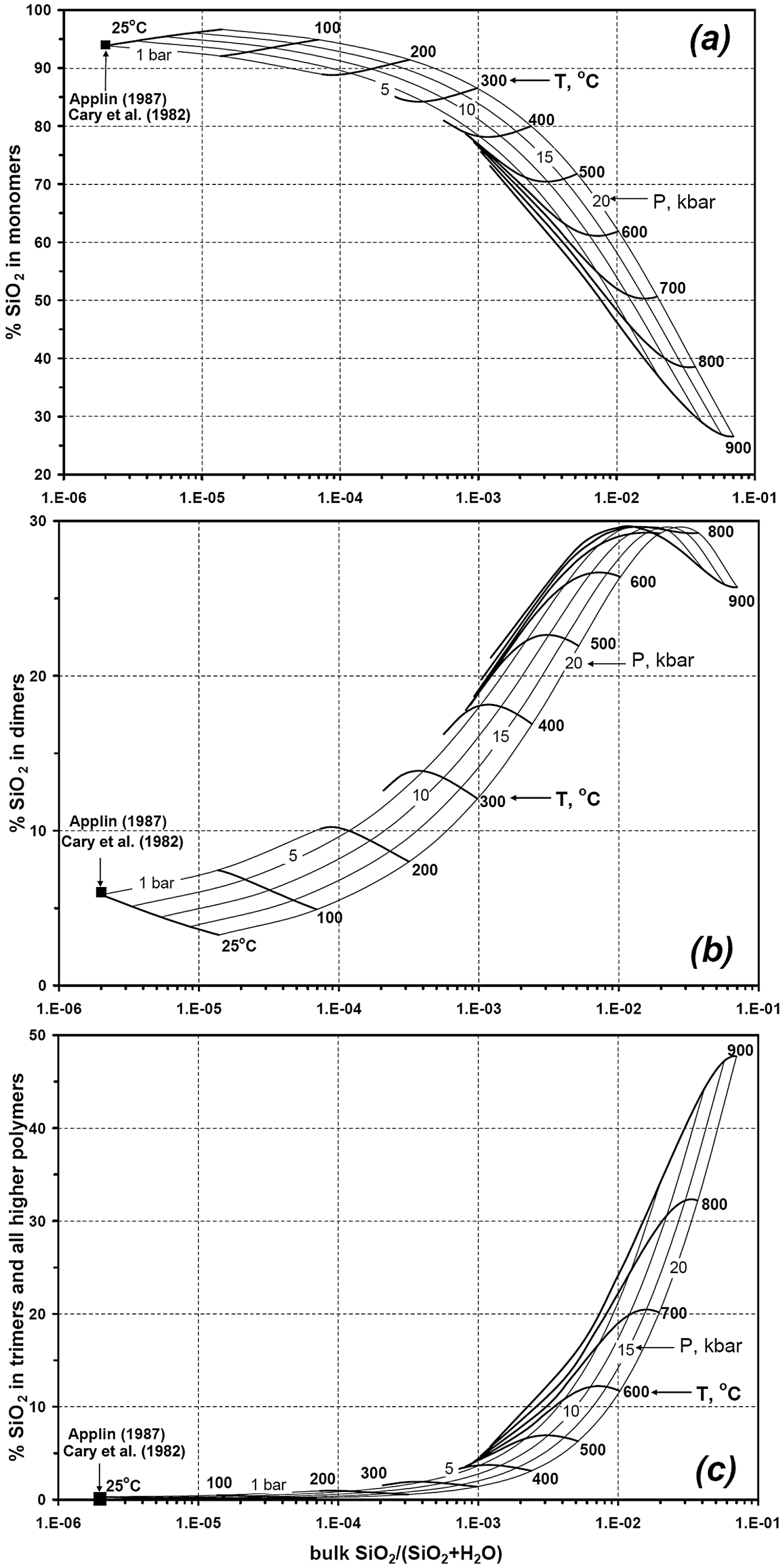

Fig. 4. Relative concentration of silica in monomers (a), dimers (b) and higher silica polymers (c) dissolved in aqueous fluid in the presence of quartz at $P = 0.001$-20 kbar and $T$ = 25-90°C. Calculations are based on equations (21)-(30). Thin grey lines are isobars. Black lines are isotherms. The solid square represents the experimental data of Cary *et al.* (1982) and Applin (1987) at 25°C and 1 bar.

rium at low temperatures (*e.g.*, Walther & Helgeson, 1977). Indeed, the overall accuracy of reproducing these experiments is comparable (Table 2) with the polynomial equation suggested by Manning (1994). Larger errors were detected in silica-undersaturated systems (Table 2, Fig. 3) for the experimental data of Hemley *et al.* (1977a, b) and

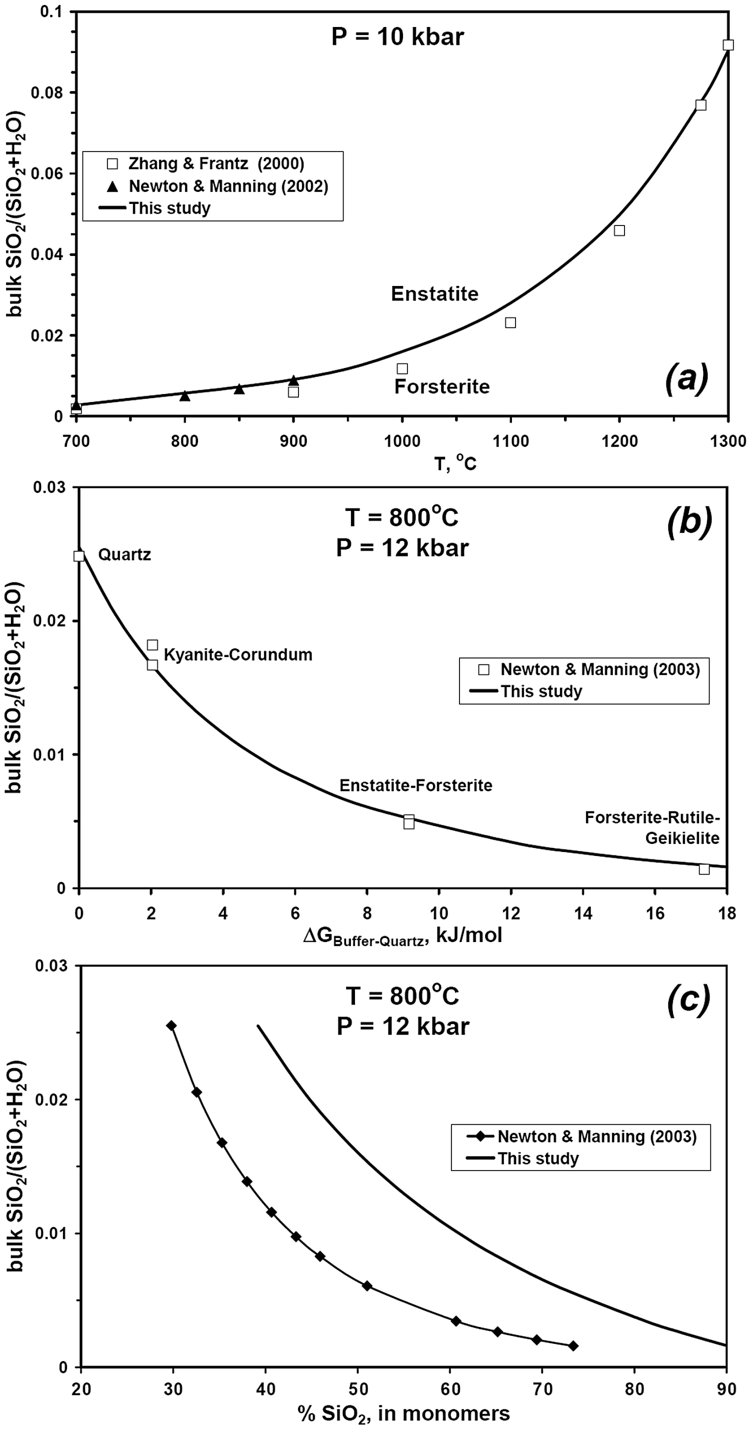

Fig. 5. Results of modeling bulk concentration (a), (b) and speciation (c) of dissolved silica in aqueous fluid in the presence of different buffering mineral assemblages. The symbols represent data from the sources indicated: (a) experimental data of Newton & Manning (2002) and empirical calibration of Zhang & Frantz (2000) based on original and published (Nakamura & Kushiro, 1974; Manning & Boettcher, 1994) experimental data, (b) experimental data of Newton & Manning (2003), (c) monomer-dimer speciation model of Newton & Manning (2003).

Zhang & Frantz (2000). This may be related to the relatively large experimental uncertainties (Zhang & Frantz, 2000; Newton & Manning, 2002) and to possible errors incurred during the calculation of $\Delta G^{o}_{(\text{Buffer-Quartz})P,T}$ for $SiO_2$-buffering reactions involving water at low pressure and temperature (Hemley *et al.*, 1977a, b) in combination with the database of Holland & Powell (1998). Obviously, at $T$ = 25°C and $P$ = 1 bar, the highly weighted reference data on the concentration of silica in the presence of quartz (Dove & Rimstidt, 1994) and on the distribution of silica between $(SiO_2)\bullet(H_2O)_2$-monomers and $(SiO_2)_2\bullet(H_2O)_3$-dimers (Cary *et al.*, 1982; Applin, 1987) are accurately reproduced with a relative error of less then 0.2 % (Table 2, Fig. 3, 4a). Figure 2 shows that the results of our thermodynamic modeling coincide well with the *empirical* approximation suggested by Manning (1994) for the bulk solubility of silica in water in the presence of quartz. Table 2 also compares our numerical values (Table 2) with those obtained from the empirical equations of Manning (1994) for the quartz-buffered system and of Manning & Newton

(2002) for the enstatite-forsterite-buffered system. For the 358 compared experimental data points (Table 2) our model yields a mean square error of 13.4 % versus 16.5 % for the equations of Manning (1994) and Manning & Newton (2002).

As noted above, our model was constrained to accurately reproduce experimental data on silica partitioning between monomers and larger clusters at 25°C and 1 bar (Cary *et al.*, 1982; Applin, 1987). The silica species at these conditions (Fig. 4) are represented by $(SiO_2)\bullet(H_2O)_2$-monomers (94 % of total dissolved silica) and $(SiO_2)_2\bullet(H_2O)_3$-dimers (6 % of total dissolved silica) with a negligible amount of higher polymers (< 0.3 % of total dissolved silica). Cary *et al.* (1982) detected the presence of $(SiO_2)_2\bullet(H_2O)_3$-dimers by NMR in solutions containing 1.6 mM $SiO_2$ at a pH of 7.2, and estimated their concentration to be about 6 % of the total dissolved silica. No additional polymerized forms were detected, which is consistent with our calculations for higher polymers (Fig. 4c). However, the lack of such accurate experimental data for speciation over a wider range of pressures and temperatures (*e.g.*, Watson & Wark, 1997) leads to the relatively large uncertainties in $\Delta S°_{(poly),r}$ and $\Delta V°_{(poly),r}$, *i.e.*, for chain reaction (12). It should be noted that reaction (12) can also be used for the calculation of silica speciation at an arbitrary bulk concentration of dissolved silica, $Y_{SiO_2} = SiO_2/(SiO_2 + H_2O)$. Equations characterizing speciation then become

$$X_1 = X_{Liq}X_{SS}(1 - X_{SS})/[X_{SS}K_{(poly)} + (1 - X_{SS})X_{Liq}], \quad (34)$$

$$X_L = X_{Liq}(1 - X_{SS}), \quad (35)$$

$$X_{SS} = \{[4X_{Liq}Y_{SiO_2}(K_{(poly)} - X_{Liq})(1 - 2Y_{SiO_2}) + (X_{Liq})^2(1 - Y_{SiO_2})^2]^{0.5} - X_{Liq}(1 - Y_{SiO_2})\}/ [2(K_{(poly)} - X_{Liq})(1 - 2Y_{SiO_2})], \quad (36)$$

where $X_{SS} = X_1 + \sum_{n=2}^{\infty} X_n$ is the sum of the mole fractions of all dissolved silica species (*i.e.*, $X_{SS} + X_L + X_G = 1$). Other quantities are as given in equations (21)-(27).

Figure 4 shows $SiO_2$ speciation in the presence of quartz as a function of pressure, temperature and bulk silica content, as predicted from our model calculations. It is seen that the relative amount of silica in the form of monomers is most strongly dependent on bulk silica concentration, and generally decreases with increasing $SiO_2$ content of the solution (Fig. 4a). Significant amounts of dissolved silica (10-30 %) in dimeric form are calculated for temperatures > 300°C (Fig. 4b). The relative proportion of dimeric silica shows a maximum (Fig. 4b) at $Y_{SiO_2} \approx 0.01$. At higher $Y_{SiO_2}$, trimers and higher polymers become important (Fig. 4c), consuming 10 to 50 % of the dissolved silica at temperatures > 500°C. Because increasing temperature leads to higher bulk silica, there is also a similar correlation with temperature. The dependence on pressure is least pronounced, as can be expected from the competing effects of reactions (11) and (12). $(H_2O)_L$ is consumed during the monomer-forming reaction (11) and liberated during the polymer-forming reaction (12), therefore dictating opposite signs of $\Delta V°_r$ of the reactions. Increasing pressure should lead to increased bulk silica solubility (due to reaction (11), $\Delta V°_{(mono),r} < 0$) and therefore increasing polymerization on the one hand (Fig. 4a), whereas increasing pressure should also favor depolymerization according to reaction (12) ($\Delta V°_{(poly),r} > 0$) on the other.

Figure 5 shows silica solubility and speciation in aqueous fluid coexisting with different $SiO_2$-buffering mineral assemblages. It is seen that our model accurately reproduces the available experimental data (Zhang & Frantz, 2000; Newton & Manning, 2003) on bulk silica solubility (Fig. 5a,b). The calculated distribution of silica between monomers and higher polymers as a function of bulk $SiO_2/(SiO_2 + H_2O)$ at constant pressure and temperature (Fig. 5c) is very similar to the results of Newton & Manning (2003), which are based on a somewhat simpler monomer-dimer model. At constant pressure and temperature the amount of monomeric silica decreases non-linearly with decreasing bulk silica solubility.

## Discussion

The semi-empirical thermodynamic formalism developed in this paper allows accurate reproduction of existing data on silica concentration and silica speciation in aqueous fluid coexisting with quartz and other silica-buffering assemblages up to 20 kbar and 1300°C. In comparison to Manning's (1994) polynomial fit, our approach also predicts the speciation of silica in the aqueous fluid without increasing the number of empirical parameters in the model. In addition, our chain-reaction model allows an excellent data fit with full consideration of all silica polymers (Fig. 4) rather than only monomers and dimers (*cf.*, Newton & Manning, 2003). Figure 6 shows the positions of isopleths of bulk silica concentration calculated for both silica-saturated (Fig. 6a) and the silica-undersaturated enstatite-forsterite-buffered (Fig. 6b) systems at elevated temperature and pressure. It is seen that our results are in general compatible with the polynomial equations suggested by Manning (1994) and Newton & Manning (2002), with the largest discrepancies found in the high-temperature (> 900°C), high-$Y_{SiO_2}$ (> 0.05) region. It should be emphasized here that our present model has been developed for a bulk silica concentration ($Y_{SiO_2}$) in the fluid of less than 0.1 (Table 2). Therefore, this model may require modification (*e.g.*, by incorporating terms for non-ideality of the aqueous solution) in order to account properly for the thermodynamics of silica-rich hydrous solutions (*e.g.*, Shen & Keppler, 1997; Audetat & Keppler, 2004) in proximity to the second critical point in the $H_2O$-$SiO_2$ system.

Our model predicts basic similarities between the thermodynamic properties of dissolved silica species and those of associated, clustered, “liquid-like” water molecules (*e.g.*, equations (18)-(20)). This is consistent with the conclusions of Bockris (1949) and Walther & Orville (1983), who suggested that hydrous monomeric silica species _ $Si(OH)_4$ _ are associated with two more water dipoles to form an aqueous silica complex _ $Si(OH)_4\bullet 2H_2O$ _ by hydrogen bonding. This mechanism of association of molecules is in fact identical to the association (clustering) of molecules of pure water (*e.g.*, Luck, 1980; Gorbaty & Kalinichev, 1995)

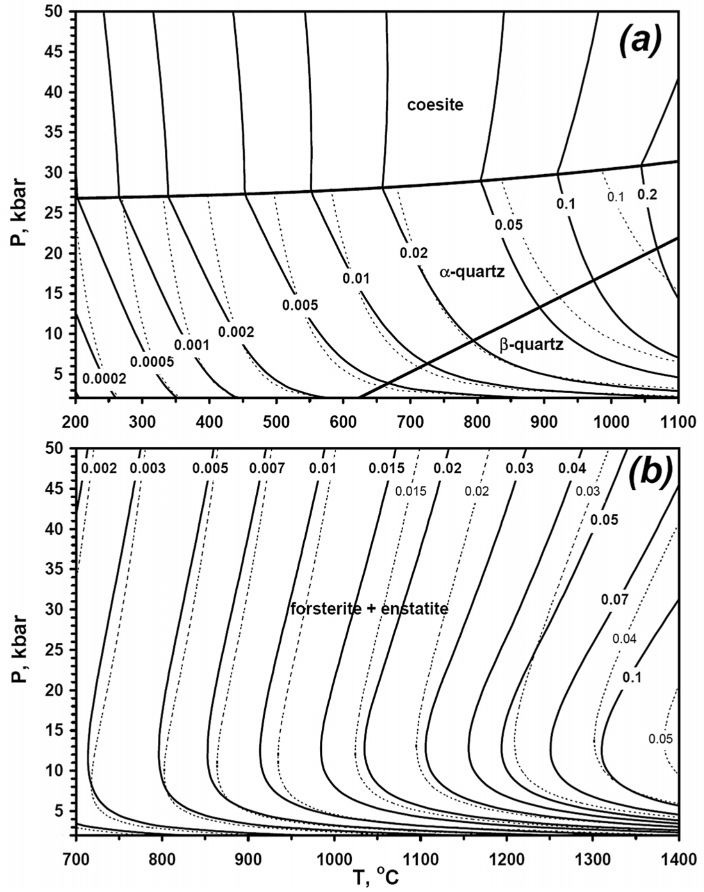

Fig. 6. Isopleths of bulk silica concentration (solid lines) calculated according to equations (21)-(27) and (31)-(33) for silica-saturated (a) and silica-undersaturated enstatite-forsterite buffered (b) system at elevated temperature and pressure. Dashed lines show isopleths calculated with the equations suggested by Manning (1994) and Newton & Manning (2002). Phase boundaries in (a) are calculated from the database of Holland & Powell (1998). Melting relations in the presence of water are not shown.

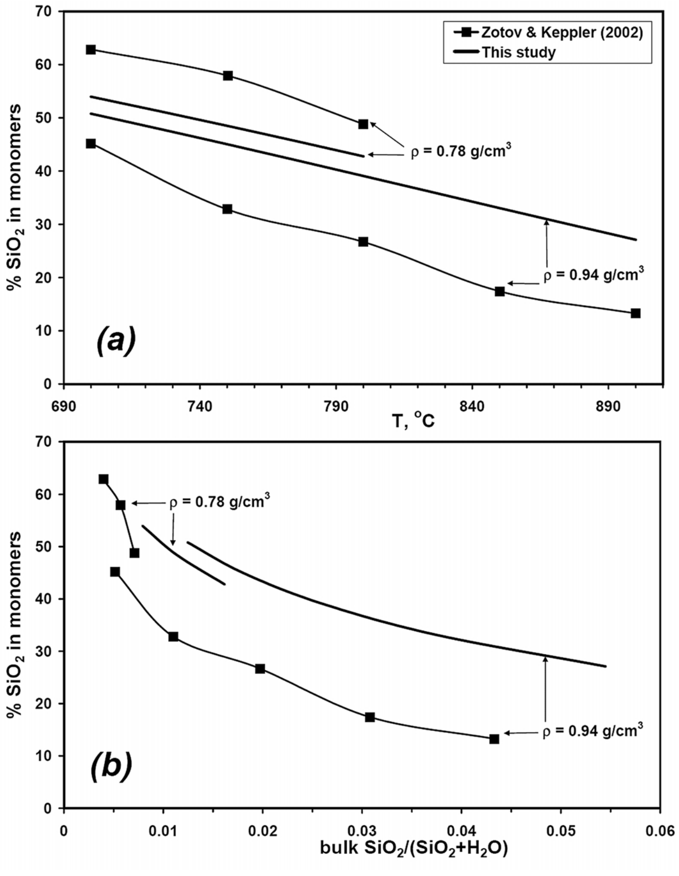

Fig. 7. Results of modeling silica speciation in aqueous fluid in the presence of quartz along the two isochores presented by Zotov & Keppler (2002): ρ = 0.78 g/cm³, $P$ = 5.6-6.8 kbar and ρ = 0.94 g/cm³, $P$ = 10.6-14.0 kbar. The solid squares represent the results of Zotov & Keppler (2002) based on the interpretation of *in situ* Raman spectra. (a) dependence of silica speciation on temperature, (b) dependence of silica speciation on bulk silica content.

and is directly accounted for by equations (4)-(6) (for a discussion see Gerya & Perchuk, 1997; Gerya *et al.*, 2004). The formation of similar complexes with dimers and higher polymers can also be expected, thus supporting our thermodynamic formalism.

An important unresolved question is the discrepancy between the results obtained from our data set, which is based mainly on direct solubility measurements, and data obtained from Raman spectra (Zotov & Keppler, 2000, 2002). This is particularly evident in the pressure effect on silica polymerization. The positive $\Delta V^\circ_r$ of reaction (12) suggests that at constant temperature and bulk silica any increase in pressure (*i.e.*, in fluid density) should lead to a decrease in the degree of polymerization. This is also supported by the *ab initio* molecular dynamics simulations of Doltsinis *et al*. (2004), who calculated higher effective pressures for monomeric-dimeric systems in comparison with purely monomeric systems at $T = 900$ K and constant fluid density. In the presence of quartz, bulk silica content increases with pressure and the competing effects of reactions (11) and (12) should lead to only *small changes* in the degree of polymerization. Figure 7 indicates the trends predicted from our model. In contrast, the results of Zotov & Keppler (2002) suggest *strong increase* in the degree of polymerization with pressure (*i.e.*, fluid density) requiring a notably negative $\Delta V^\circ_r$ of polymer-forming reaction (12). Our test calculations show that no consistent set of thermodynamic parameters for reactions (11) and (12) can provide an accurate description of both the silica solubility measurements and the changes of degree of polymerization with fluid density calculated by Zotov & Keppler (2002).

We suggest that an explanation for the above discrepancies must be sought in (i) the possible problems of equilibration in the relatively short experiments in the diamond-anvil cell performed by Zotov & Keppler (2000, 2002), and (ii) the difficult task of quantifying the Raman spectra of aqueous silica solutions. The interpretation of Raman spectra is based mainly on theoretical spectra obtained using empirical interaction potentials (Catlow, 1980; Price & Parker, 1984) or on single molecule *ab initio* calculations, as in the case of Zotov & Keppler (2000, 2002). The problem with the latter is that they do not include crucial temperature- and pressure-dependent solvent effects. To test these environmental effects, we have initiated a series of both *ab initio* molecular dynamics (AIMD) simulations and static gas phase *ab initio* calculations (Doltsinis *et al*., 2004). Our results to date suggest that while the strong feature at *ca.* 780-800 cm$^{-1}$ can be ascribed to monomers with some confidence, there are still considerable uncertainties in interpreting other features of the Raman spectra in terms of monomers and/or dimers. Considering the low amounts of total silica involved, and the increasingly "floppy" nature of larger polymers leading to increasingly broadened spectral features, it appears that the recognition and identification of trimers and higher polymers can be problematical. If "hidden" trimers are present, then an interpretation based solely on monomer/dimer ratios will obviously be flawed. Thus, while the results of Zotov & Keppler (2000, 2002) represent a valiant first attempt to tackle the problem, and provide valuable qualitative data, direct comparisons with classical solubility results should not be overextended. We suggest that further Raman spectroscopic measurements on well-defined solutions with given bulk silica contents at different pressures and temperatures, rather than quartz-buffered solutions only, will be a valuable step toward a better understanding of such spectra.

The approach outlined in this paper has been successfully used to fit and describe experimental data on bulk spinel ($MgAl_2O_4$) solubility up to 30 kbar by Zakhartchouk *et al.* (2004), despite the lack of detailed information on the actual speciation of the dissolved spinel components in that system. Given additional independent data on the detailed structure of condensed phase water in the future (*e.g.*, Marx, 1999, and in press) and on solute speciation at various temperatures and pressures (see Doltsinis *et al*., 2004), the formalism described here can be used to provide an increasingly complete thermodynamic description of aqueous solutions at depths corresponding to the lower crust and upper mantle.

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