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THERMODYNAMIC MODEL FOR PREDICTING INTERACTIONS OF GEOTHERMAL BRINES WITH HYDROTHERMAL ALUMINUM SILICATE MINERALS

Nancy Moller, Christomir Christov and John Weare

University of California San Diego
La Jolla, California, 92093
email: nweare@ucsd.edu

ABSTRACT

We report our continued progress on the development of a thermochemical model of aluminum silicate mineral solubilities in aqueous solutions containing H^+, Na^+, K^+, Al^{3+}, Cl^-, $Si(OH)_4$, $SiO(OH)_3^-$, OH^-, $Al(OH)^{2+}$, $Al(OH)_2^+$, $Al(OH)_3^0$, $Al(OH)_4^-$ as a function of pH to high salt concentrations ($I \leq 5$ *m*). Prior conference proceedings outlined our progress in developing an accurate model for the potassium free system to 100°C, and some preliminary results for that system to 300°C. In this article we report a fully developed model for the potassium free system to 300°C and preliminary results to 100°C for the full system. The model, which incorporates the Pitzer specific interaction equations (PITZER, 1987) accurately predicts fluid compositions for the low Al ($< 10^{-5}$ *m*) and $Si(OH)_4$ ($< 10^{-4}$ *m*) concentrations commonly encountered in the intermediate pH ranges typical of most natural fluids. With available solubility or free energy of reaction data, the solubility of complex Na and K hydrothermal aluminosilicate minerals can now be predicted as a function of solution composition and pH in this system to high temperature. Phase equilibrium diagrams illustrating the capabilities of this model are presented.

INTRODUCTION

Adequate fluid flow in a hydrothermal formation is essential to efficiently extract geothermal energy from the thermal energy of natural and enhanced formation fluids. While there are many other factors involved in the complex processes of the development or degradation of reservoir permeability, the dissolution and precipitation of minerals in the pore and fracture structure of a hydrothermal formation has a significant influence on the flow volume. Therefore, the ability to correctly predict the saturation conditions (supersaturation or undersaturation) of the reservoir fluids with respect to the mineralogy of the reservoir formation and potential replacement minerals is a critical first step in understanding and controlling permeability.

The saturation conditions of a hydrothermal fluid are a complex function of the concentration of all the solutes in the fluid phase, the temperature and the pressure on the system. Because the saturation chemistry is so sensitive to the composition of the hydrothermal fluid, it is not generally possible to extrapolate behavior from laboratory measurements on fluids with composition approximating those extracted from the reservoir. However, in our research program we have shown that we can develop a comprehensive model of saturation based on the Pitzer liquid density equation of state (EOS) for the highly complex solution interactions occuring in the system H^+, Na^+, K^+, Al^{3+}, Cl^-, $Si(OH)_4$, $SiO(OH)_3^-$, OH^-, $Al(OH)^{2+}$, $Al(OH)_2^+$, $Al(OH)_3^0$, $Al(OH)_4^-$, H_2O (in addition to Ca^{2+}, HSO_4^-, SO_4^{2-}, HCO_3^-, CO_3^{2-}, CO_2(aq), discussed elsewhere MOLLER, 1998 and references therein).

TABLE 1: MINERALS TO BE INCLUDED IN MODEL

Mineral	Composition
All Evaporite and Carbonate Minerals presently in TEQUIL*	
Al (III) minerals	
Aluminum chloride hexahydrate	$AlCl_3.6H_2O$(s)
Gibbsite	$Al(OH)_3$(s)
Boehmite	AlOOH(s)
Si (IV) minerals	
Quartz	SiO_2(s)
Chalcedony	SiO_2(s)
Crystobalite	SiO_2(s)
Amorphous silica	SiO_2(s)
Amorphous silica	$SiO_2.2H_2O$(s)
Al(III)-Si (IV) minerals	
Kaolinite	$Al_2Si_2O_5(OH)_4$ (s)
Dickite	$Al_2Si_2O_5(OH)_4$ (s)
Na(I)-Al(III)-Si (IV) minerals	
Low albite	$NaAlSi_3O_8$(s)
High albite	$NaAlSi_3O_8$(s)
K(I)-Al(III)-Si (IV) minerals	
Microcline	$KAlSi_3O_8$(s)
Sanidine	$KAlSi_3O_8$(s)
Sodium and potassium zeolites	
Analcime 1 (Si/Al = 2.0)	$NaAlSi_2O_6.H_20$(s)
Analcime 2 (Si/Al = 2.5)	$Na_{0.85}Al_{0.85}Si_{2.15}O_6.H_20$(s)
Na-clinoptilolite (Si/Al = 4.5)	$Na_{1.1}Al_{1.1}Si_{4.9}O_{12}.3.5H_20$(s)
K-clinoptilolite (Si/Al = 4.5)	$K_{1.1}Al_{1.1}Si_{4.9}O_{12}.2.7H_20$(s)

*see TEQUIL models on geotherm.ucsd.edu website.

This system contains most of the solutes commonly encountered in high concentration in hydrothermal solutions. The saturation level of minerals whose composition are within this system can be predicted with high accuracy provided free energy data defining their stability are available. Table 1 lists the hydrothermal aluminosilicate minerals for which we have found sufficient data to include them in the model.

METHODOLOGY

The temperatures of the hydrothermal systems accessed by present day and projected geothermal systems are well below the critical point of pure water. In this situation the fluids are nearly incompressible and the largest variation in the solution free energy comes from changes in solute composition and temperature. A very accurate representation of the compositional behavior of incompressible aqueous solution phase is given by the free energy equations introduced by Pitzer (PITZER, 1987; HARVIE, 1984). In the model discussed here an ideal mixture or mixing equation of state is used for the vapor phase and the solid phases are assumed to be pure. These equations have been presented in several publications. They are included below for reference. Detailed explanations of these expressions can be found in the earlier references (PITZER, 1987; HARVIE, 1984).

As is usual in aqueous solution theory, the thermodynamics of the system are summarized in the chemical potentials of individual species, μ_i. The μ_i are given in terms of the activity of species i, γ_i via the Eq. (1),

$$\mu_i = \mu_i^o + RT \ln \gamma_i m_i \qquad (1)$$

γ_i is given by an equation of state (PITZER, 1987). Chemical equilibrium between reservoir rocks and the solution phase is determined by a chemical potential balance equation determined by the stiochiometry of the reaction. For example, the formation or dissolution of K-spar is given by the mass balance expression,

$$KAlSi_3O_8(s) + 8H_2O = Al(OH)_4^-(aq) + K^+(aq) + 3H_4SiO_4^0 , \qquad (2)$$

which leads to the chemical potential balance equation,

$$\Delta^0 G_f^{K-spar}(T) = \mu_{Al(OH)_4^-} + \mu_{K^+} + 3\mu_{H_4SiO_4^o} - 8\mu_{H_2O}. \qquad (3)$$

If the chemical potential sum on the right hand side of Eq. (3) does not equal the free energy of formation on the right hand side, the solid K-spar dissolves or precipitates until balance is obtained. This balance relation can also be replaced by a free energy minimization problem (HARVIE, 1987).

In the model we are developing, our (HARVIE, 1980; HARVIE, 1984; WEARE, 1987) implementation of the Pitzer activity expressions for the aqueous solution phase is used.

$$\begin{aligned}
\ln \gamma_M &= z_M^2 F + \sum_a m_a (2B_{Ma} + ZC_{Ma}) + \\
&\sum_c m_c (2\Phi_{Mc} + \sum_a m_a \psi_{Mca}) + \\
&\sum_a \sum_{a<a'} m_a m_{a'} \psi_{Maa'} + |z_M| \sum_c \sum_a m_c m_a C_{ca} \\
&+ \sum_n m_n (2\lambda_{nM}) + \sum_n \sum_a m_n m_a \zeta_{naM} \qquad (4) \\
F &= -A^\phi \{ I^{.5} / (1 + 1.2 I^{.5}) + \\
&(2/1.2) \ln(1 + 1.2 I^{.5}) \} \\
&+ \sum_c \sum_a m_c m_a B'_{ca} + \sum_c \sum_{c'<c} m_c m_{c'} \Phi'_{cc'} \\
&+ \sum_a \sum_{a'<a} m_a m_{a'} \Phi'_{a,a'} \qquad (5) \\
B_{ma} &= \beta^0_{Ma} + \beta^1_{Ma} g(\alpha, I^{.5}) + \beta^2_{Ma} g(12 I^{.5}), \\
g(x) &= 2(1 - (1+x)e^{-x}) / x^2 , \\
\Phi_{ij} &= \Theta_{ij} + {}^E\Theta_{ij}(I), \; Z = \sum_i |z_i| m_i \qquad (6)
\end{aligned}$$

This expression is symmetric for cations and anions. The *B* coefficients describe the ionic strength dependence of binary solutions. When either the cation or anion for an electrolyte is univalent, we set α equal to 2.0 and omit the $\beta^{(2)}$ term. For 2-2 or higher valence pairs, α = 1.4. In addition the $\beta^{(2)}$ term accounts for the increased tendency of these higher charged species to associate in solution. When strong ion association is present the ion pair species must be added to the species list (HARVIE, 1984). Examples for the complicated Al system include the monomeric hydrolysis species, $Al(OH)^{2+}$, $Al(OH)_2^+$, $Al(OH)_3^o$ and $Al(OH)_4^-$ species. The ionic strength dependence of the ternary mixing coefficients is found in the Φ terms, which account for mixing between two ions of like charges. In Φ_{ij}, Θ_{ij} is the only adjustable parameter. The ionic strength dependent ${}^E\Theta_{ij}(I)$ term accounts for electrostatic unsymmetric mixing effects that depend only on the charges of ions i and j and the total ionic strength. The terms with λ and ζ account for neutral species interactions with anions and cations (FELMY, 1986). In this model the third virial coefficients, *C*, and the ψ terms, are independent of ionic strength.

All these parameters are adjusted to fit the available data in binary and ternary systems using a non-linear least squares method (HARVIE, 1987). Note that only binary and ternary data are required to evaluate all the parameters in the Pitzer equations described here no matter how many components are in the solution. Eq's. 4-6, therefore, provide a means to extrapolate data from ternary and lower systems to systems of higher order. We (CHRISTOV, 2004 ab; HARVIE, 1984) have shown that these equations can provide solubility predictions for a range of ionic strengths that include most of the compositions found in nature. Temperature dependence (MOLLER, 1988; GREENBERG, 1989; CHRISTOV, 2004ab) of the solution parameters is built into the model by adjusting selected constants in the following equation,

parameter (T) = $a_1 + a_2T + a_3(T^2) + a_4(T^3) + a_5/T + a_6 \ln T + a_7(1/(T-263)) + a_8(1/(680-T))$. (7)

To constrain our parameter evaluation as much as possible in our modeling program we include all measurements available in our data base. This, for example, means that data for very low and high pH values not usually encountered in natural waters are used to evaluate the parameters in the aqueous Al system. Due to the strong hydrolysis in this system, the Al^{3+} ion dominates the solute Al compositions only at low pH. This is the region where measured thermodynamic properties are most sensitive to Al^{3+} parameters (e.g. $\beta^{0,1}_{Al,Cl}$ and $\Theta_{Al,H}$ in Eq's. 4-6). This focus on including all the data not only generalizes the model to treat very low and high pH hydrothermal brines but also allows the evaluation of parameters in composition regions where they make the largest and most independent contribution. Thereby, the reliability of the model is increased.

RECENT MODEL IMPROVEMENTS

A higher temperature model (T<300°C) for the H^+, Na^+, Al^{3+}, Cl^-, OH^-, $Al(OH)^{2+}$, $Al(OH)_2^+$, $Al(OH)_3^0$, $Al(OH)_4^-$ system

In the previous conference proceedings, we presented a model for this system, 0°-120°C. This model was constrained by all the data available for this temperature range. Results for a preliminary model for higher temperatures were also given. Here, we present results of recent efforts to better define the high temperature behavior of this system to 300°C.

The solubility of Al minerals in water is relatively high in very low and very high pH solutions. However, in the near neutral range the low solubility of Al containing minerals (gibbsite, boehmite, kaolinite, etc., Table 1) constrains the concentration of Al in most natural waters to levels below 10^{-5} m. At these almost trace levels, the kind of experiments that provide free energy data for the various solute species (e.g., $Al(OH)^{2+}$, $Al(OH)_2^+$, $Al(OH)_3^0$, $Al(OH)_4^-$) is limited to solubility measurements in various background medium. Fortunately, due to the great importance of this system to the prediction of rock-water interactions there have been a number of efforts to carefully measure solubilities for temperatures up to 300°C (e.g., CASTET, 1993; PALMER, 2001; BOURCIER, 1993; BENEZETH, 2001; KUYUNKO, 1983 and references therein).

Using these data, we have parameterized a model to 300°C. The agreement of the model over the composition and temperature range of the data is very good as shown in Figs. 1-3 below.

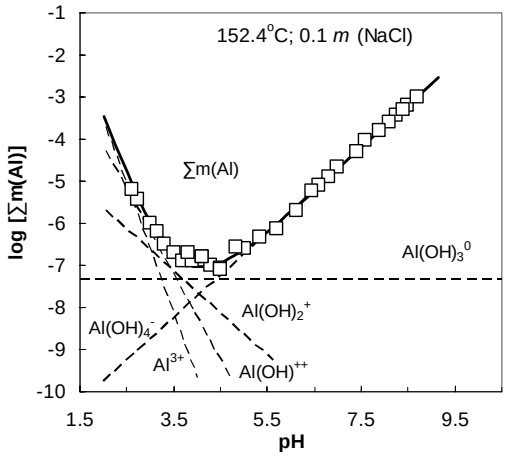

Figure 1: Model predictions of the solubility of boehmite (solid line) vs. the data of PALMER, 2001.

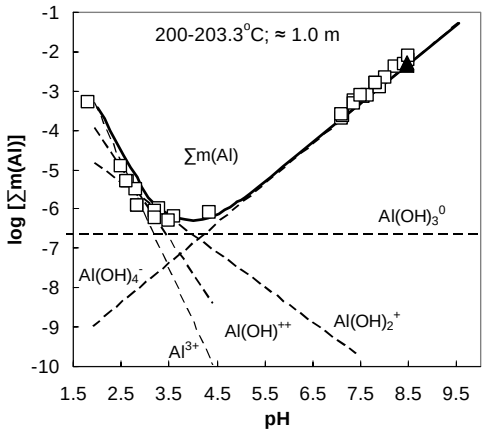

Figure 2: Model predictions of the solubility of boehmite (solid line) vs. the data of PALMER, 2001.

In Fig. 3. we have included all the available data for T≈ 250°C. Note the considerable scatter in the measurements. Generally the high pH solubility data are the most reliable. The process of simultaneously

fitting the data from all temperatures reduces the uncertainty of the parameterization.

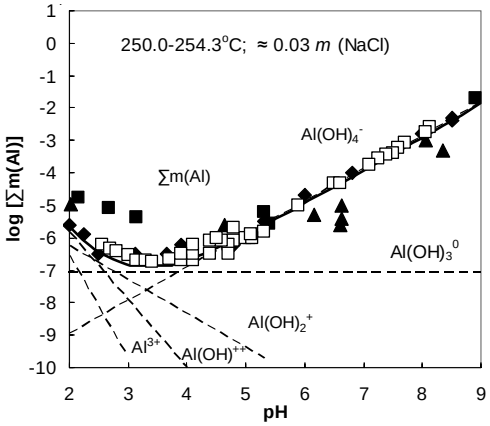

Figure 3: Model predictions of the solubility of boehmite vs. pH (solid line) vs. experimental data. Open squares: BENEZETH, 2001; filled squares: Kuyunko, 1983; filled diamonds: CASTET, 1993; filled triangles: BOURCIER, 1993.

Addition of K^+ to aluminum solution model

A significant advantage of using the Pitzer equation of state approach defined by Eq's. 4-6, is that many of the parameters required for a very complex system can be (are best) established in much simpler systems for which there are more precise data. Our evaluation of the parameters for the potassium containing system Na^+, K^+, Al^{3+}, Cl^-, OH^-, $Al(OH)^{2+}$, $Al(OH)_2^+$, $Al(OH)_3^0$, $Al(OH)_4^-$ illustrates this. Low pH solubility data for $AlCl_3$ in KCl solutions were used to evaluate the Al-K interactions (e.g., $\theta_{Al,K}$). The agreement of model predictions with these acid side data is illustrated in Fig. 4.

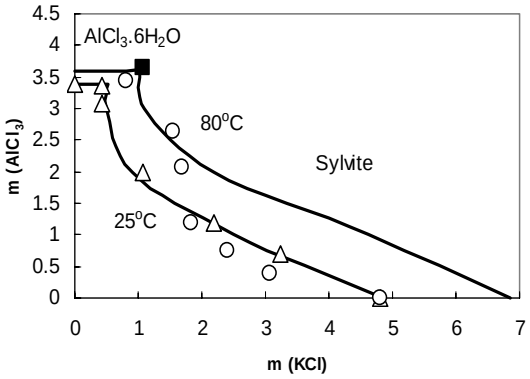

Figure 4: The predicted solubility (solid lines) of $AlCl_3.6H_2O$ as a function of KCl concentration. Data, circles: MALQUORI, 1928 (see Linke, 1965); triangles: PATEL 1966 (see Linke, 1965).

As the pH is increased, the Al^{3+} ion reacts with waters of hydration forming hydrolysis species, $Al(OH)_4^{(3-n)+}$, finally arriving at the tetrahedrally coordinated $Al(OH)_4^-$ species at sufficiently high pH. The most important parameters for positively charged species (n<3) are the binary interactions with Cl^- (e.g., $\beta^{0,1}_{Al(OH)_2^+,Cl^-}$; see Eq's. 4-6). These parameters were established in the better determined Na system and, consistent with the Pitzer mixing approach, are accepted for the K system which has few data.

The negatively charged $Al(OH)_4^-$ ion is expected to interact strongly with the positive K^+ ion. Fortunately, there is enough data (WESOLOWSKI, 1992) to evaluate the important binary parameters (e.g. $\beta^{0,1}_{Al(OH)_4^-,K^+}$; see Eq's. 4-6). The agreement of the parameterized model with the available data is illustrated in Fig. 4.

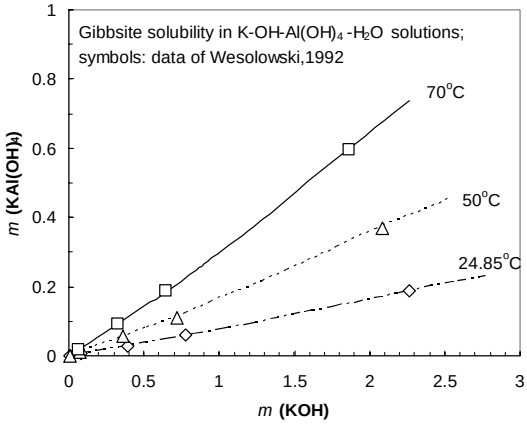

Figure 5: Gibbsite solubility (solid lines) in K solutions for various temperatures. Data of WESOLOWSKI (1992).

PREDICTION OF MINERAL SOLUBILITIES

With the parameterization of the solution model, the free energies (chemical potentials, see Eq's. 1-6) of the solute species are available. Given the standard free energies of formation of the solid phases, as in Eq. (3), as a function of temperature, the saturation status of hydrothermal brines within the H^+, Na^+, K^+, Al^{3+}, Cl^-, $Si(OH)_4$, $SiO(OH)_3^-$, OH^-, $Al(OH)^{2+}$, $Al(OH)_2^+$, $Al(OH)_3^0$, $Al(OH)_4^-$, H_2O system with respect to minerals in this system (see Table 1) may be predicted. The sources for the mineral free energies are compiled in Table 2.

This model was developed for use in predicting the saturation status of hydrothermal brines having many compositional degrees of freedom with respect reservoir rocks. However, to illustrate the capabilities of the model we present below solubility diagrams for some ternary and quaternary systems.

TABLE 2	
Mineral:	Data used in parameterization
Al (III) minerals	
$AlCl_3.6H_2O$	LINKE, 1965
$Al(OH)_3$	WESOLOWSKI, 1992 PALMER, 1992 WESOLOWSKI, 1994
AlOOH	CASTET, 1993; DIAKONOV, 1996; BENEZETH 2001; PALMER., 2001
Si (IV) minerals	
Quartz SiO_2	HEMLEY, 1980; GUNARSSON, 2000
Chalcedony: SiO_2	ARNORSSON, 1982
Crystobalite: SiO_2	GUNARSSON, 2000
Amorphous: SiO_2	GUNARSSON 2000
Amorphous: $SiO_2.2H_2O$	CHEN,1982
Al(III)-Si (IV) minerals	
Kaolinite $Al_2Si_2O_5(OH)_4$	DEVIDAL, 1996
Dickite: $Al_2Si_2O_5(OH)_4$	ZOTOV, 1998; FIALIPS, 2003
Na(I)-Al(III)-Si (IV) minerals	
Low $NaAlSi_3O_8$	ARNORSSON, 1999
High $NaAlSi_3O_8$	ARNORSSON, 1999
K(I)-Al(III)-Si (IV) minerals	
Microcline $KAlSi_3O_8$	ARNORSSON 1999
Sanidine: $KAlSi_3O_8$	ARNORSSON, 1999
Sodium and potassium zeolites	
$NaAlSi_2O_6.H_20$	WILKIN, 1998
$Na_{0.85}Al_{0.85}Si_{2.15}O_6.H_20(s)$	WILKIN, 1998
$Na_{1.1}Al_{1.1}Si_{4.9}O_{12}.3.5H_20$	WILKIN, 1998
$K_{1.1}Al_{1.1}Si_{4.9}O_{12}.2.7H_20$	WILKIN, 1998

Ternary Systems

Fig. 6 shows the stability fields of the minerals, sanidine and high albite, in aqueous solutions at 100° predicted by the model. The composition of the solution phase is distributed according to the complex speciation scheme included in the model. However the total composition of any solution on this diagram may be written in terms of the compositions of the minerals as shown.

In geothermal applications, the stabilities of mineral phases in highly concentrated salt solutions are often required. Fig. 7 illustrates the effect of dissolved salt concentration on plagioclase mineral coexistence. The initial concentrations of the solution before the addition of excess solids are given on the axes.

The flow of an NaCl rich brine through a formation of coexisting high-albite and sanadine will convert the sanadine to albite, substantially changing the concentration of K in the solution phase. However as illustrated in Fig.7 the total solubility of solid mineral is still small. For example, in the example illustrated in Fig. 7 it was assumed excess solid phase (sanidine and high-albite) were equilibrated with 1000gm of water containing x moles of dissolved NaCl. For x=1. in equilibrating the system .015 moles of K were transferred to the solution. However, the total Al in solution remained at $\approx 1.7x10^{-5}$. Since the volumes of minerals are different this replacement process could affect the pore volumes in the reservoir.

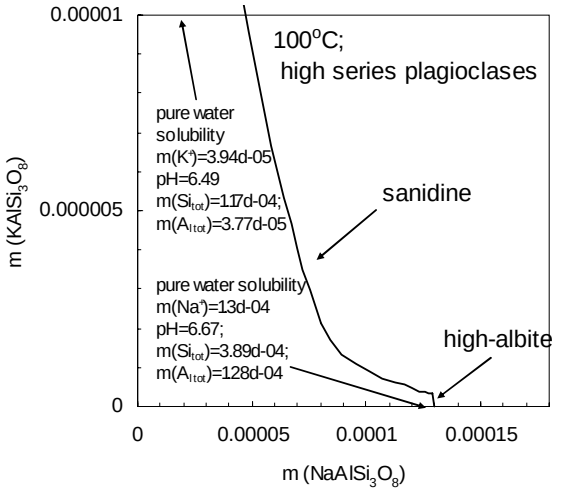

Figure 6: Solubility in the sandine/high albite ternary.

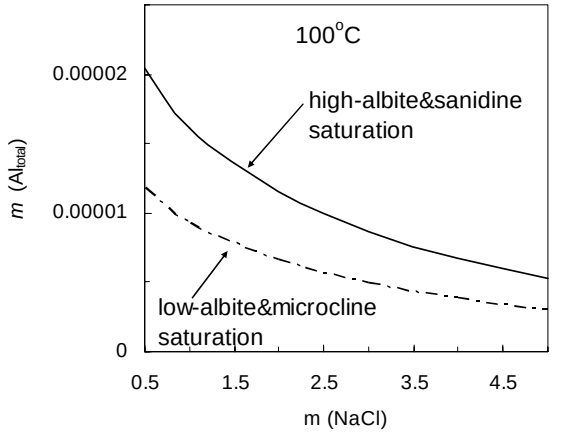

Figure 7: Total Al concentration at coexistence in the plagioclase series.

Quaternary systems

As a further illustration of the capabilities of the model we show in Fig. 8 the quaternary solubility diagram for the system SiO_2, low-albite, microcline, H_2O. Note the dominance of the SiO_2 concentration in most of the diagram.

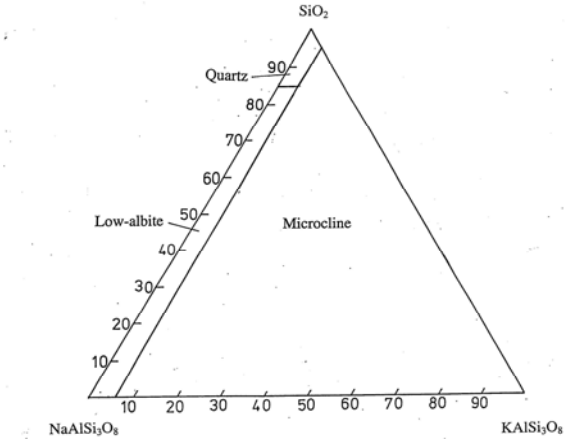

Figure 8: Solubility of minerals in the low-albite, microcline, quartz, H_2O. T=100°C.

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