TRANSPORT AND DEPOSITION OF THE NON-SULPHIDE VEIN MINERALS. VI. QUARTZ

F. GORDON SMITH
University of Toronto, Toronto, Canada

ABSTRACT

Data on solubility of quartz in water are shown to obey equations of the type

$$\log S\%_V = \frac{-a}{T} + 2,$$

where $S\%_V$ is weight percent SiO_2 in solution at constant volume, a is a constant depending on specific volume, and T is the absolute temperature. The approximate solubility of quartz in near-neutral hydrothermal solutions in depth along a steep geothermal gradient is calculated.

Introduction

The solubility of quartz in aqueous solutions has received considerable study, but in natural hydrothermal solutions under temperature-pressure conditions deep within the crust, the quantitative relations are still obscure. This is an attempt to use the existing data to calculate the approximate solubility of quartz, with the understanding that the effect of many natural variables will remain unknown.

The principal variables are temperature and pressure, but components other than SiO_2 and H_2O must be considered in exact treatments. The concentration of free alkaline ions especially is important, because in strongly alkaline solutions the solubility of quartz may be several orders of magnitude greater than it is in water alone. Geological data and inference allow a certain amount of restriction of this problem. We are considering vein-forming solutions, which, from fluid inclusion evidence, are reasonably well established to be aqueous solutions of sodium chloride and other salts, neutral or slightly alkaline (Smith, 1953). Therefore ionic species stable only in strongly acid and strongly alkaline solutions can be neglected. The approximate treatment here adopted consists of showing the solubility of quartz in solutions with no free acid or alkali, and then considering the effect of a small amount of free alkali.

The published data on solubility of quartz in water at elevated temperatures and pressures, principally by Kennedy (1950) and Morey & Hesselgesser (1951) provide some of the information required. However, the temperature-pressure range of the reliable data does not enclose the geothermobaric zone of interest. Consequently, it is first necessary to derive a method of extrapolation into the desired temperature-pressure range.

A thermodynamic treatment of the problem by Mosebach (1957) was published recently. It was assumed that the differential heat of solution of quartz in water is a constant, whereas in the following treatment it is a variable.

Thermodynamics of Solubility Equilibria

A rigorous treatment of solubility equilibria (such as by Harned & Owen, 1943) involves concepts of equality of chemical potential of reactants and products, and their activity, but equations showing relations at equilibrium can be simplified to the older conventional form in which only concentrations appear, if the solutions are dilute. This applies to both homogeneous and heterogeneous equilibria.

The equilibrium constant of any reversible process varies with pressure and temperature independently due to reactants and products having different volumes and heat contents. The numerical relations are as follows (see Harned & Owen, 1943):

$$\left|\frac{\partial \ln K}{\partial P}\right|_T = \frac{-\Delta V}{RT}, \text{ and}$$

$$\left|\frac{\partial \ln K}{\partial T}\right|_P = \frac{\Delta H}{RT^2},$$

where K is the equilibrium constant, and ΔV and ΔH are the net volume and heat content changes in the process. Taking these as constants for the moment, the integrated forms are as follows, substituting $(\Delta E+P\Delta V)$ for ΔH:

$$\ln K_T = \frac{-P\Delta V}{RT}+c_1, \text{ and}$$

$$\ln K_P = \frac{-\Delta E-P\Delta V}{RT}+c_2,$$

where c_1 and c_2 are different constants of integration. If this equilibrium constant is made monovariant in T by the restriction that V is constant, the volume change (ΔV) is zero, the $P\Delta V$ term cancels, and therefore

$$\ln K_V = \frac{-\Delta E}{RT}+c_3. \tag{1}$$

In the case of saturated solutions, for K in equation (1) we may write S, the concentration of solute in the solution in heterogeneous equilibrium with the solid solute:

$$\ln S_V = \frac{-\Delta E}{RT}+c_4, \tag{2}$$

or in general terms,

$$\log S_V = \frac{-a}{T} + c. \tag{3}$$

With reference to solubility of quartz in water, equation (3) states that the logarithm of the solubility of quartz is equal numerically to a constant minus a value consisting of an energy term divided by the absolute temperature at which the solution takes place, provided that the tentative assumption is correct, *i.e.*, the internal energy change due to solution of quartz is constant when the volume remains constant. The validity of the assumption can be tested by the solubility data in the literature: the logarithm of the solubility of quartz in water, plotted against the reciprocal of the absolute temperature should be a set of straight lines, one for each specific volume.

The ionization constant of water can be treated in an analogous way. This leads to the possibility that two equations of the type of (3) could be combined to give

$$\log S = a \log K + b, \tag{4a}$$

where a and b are constants. If this relation is established, not only could the solubility of quartz in water be calculated to temperatures and pressures beyond the present limits of the established data, but the ionization constant of water similarly could be calculated.

An interesting extension of this method is the possibility of calculating the ionization constant of H_2S in water solution from the ionization constant of H_2O, since they may be related as derived above, *i.e.*

$$\log K\ (H_2S) = a \log K(H_2O) + b \tag{4b}$$

where a is the ratio of the two internal energies of ionization, and b is a constant.

The Solubility of Quartz in Water

In order to plot log S against $1/T$, a number of interpolation plots of the original data of Kennedy (1950) were made. First, solubility in percent was plotted against temperature and isobaric curves were drawn (first smoothing). Then the temperatures on each isobar corresponding to specific volumes were marked, and iso-volume curves were drawn through these points (second smoothing). The solubility and temperature values at intersections of isobars and iso-volume lines were tabulated. The first set was changed to logarithms of solubility and the second, to reciprocals of absolute temperature. These data were plotted and iso-volume lines were drawn (third smoothing). At this stage it was seen that the best fit was obtained with a set of straight lines which converged to meet near 100% solubility at infinite temperature. Therefore all of the set of iso-volume lines were made to pass through this point and to best fit the plotted points (fourth smoothing). The divergence of the set of lines was made internally consistent by plotting solubility at one temperature against the cube root of the specific volume. This gives only roughly a straight line, but the best curve was constructed empirically and the set of iso-volume lines were adjusted slightly (fifth smoothing). The result is shown in Fig. 1. It is quite clear that the solubility of silica in water can be expressed in the form

$$\log S\%_V = \frac{-a}{T} + 2\,, \tag{5}$$

where a is a constant which is a complex function of specific volume. Also, it is evident that the extrapolation of the iso-volume lines, especially to higher solubility values, is reasonably certain.

It should be noted that virtually all of Kennedy's (1950) data on solubility of silica in water are related in the above way, which has a thermodynamic rationale. This indicates that true solubility was measured and not colloidal dispersion as has been contended (Frederickson & Cox, 1954). Morey & Hesselgesser (1951—2 papers) and Khitarov (1956) give solubility data which substantiate Kennedy's measurements. Mosebach (1957) discussed this point quite thoroughly.

The value of a in equation (5) was derived empirically as explained above for each of several specific volumes (Table 1). Perhaps it might be possible to derive a relation between a and the specific volume, taking the structure of the solution into consideration, but this was not attempted. An empirical relation, giving a between $V = 1$ and 3 to within 2% is

$$a = 2700 - 1220\,V.$$

It should be noted that equation (5), with the suitable value of a, applies only to the range of temperature and pressure wherein there is no vapor phase and the specific volume of water is between 0.90 and 4.0. Even approaching the boiling curve there is some departure, notably above the critical volume (note curve for $V = 4.0$ in Fig. 1).

We can evaluate ΔE, the molar differential internal energy of solution

TABLE 1. $\log S\%_V = \frac{-a}{T} + 2$

V	0.90	0.95	1.00	1.05	1.1	1.2	1.3	1.4	1.6	1.8	2.0	2.5	4.0
a	1320	1400	1475	1540	1600	1700	1760	1820	1910	1990	2060	2200	2480

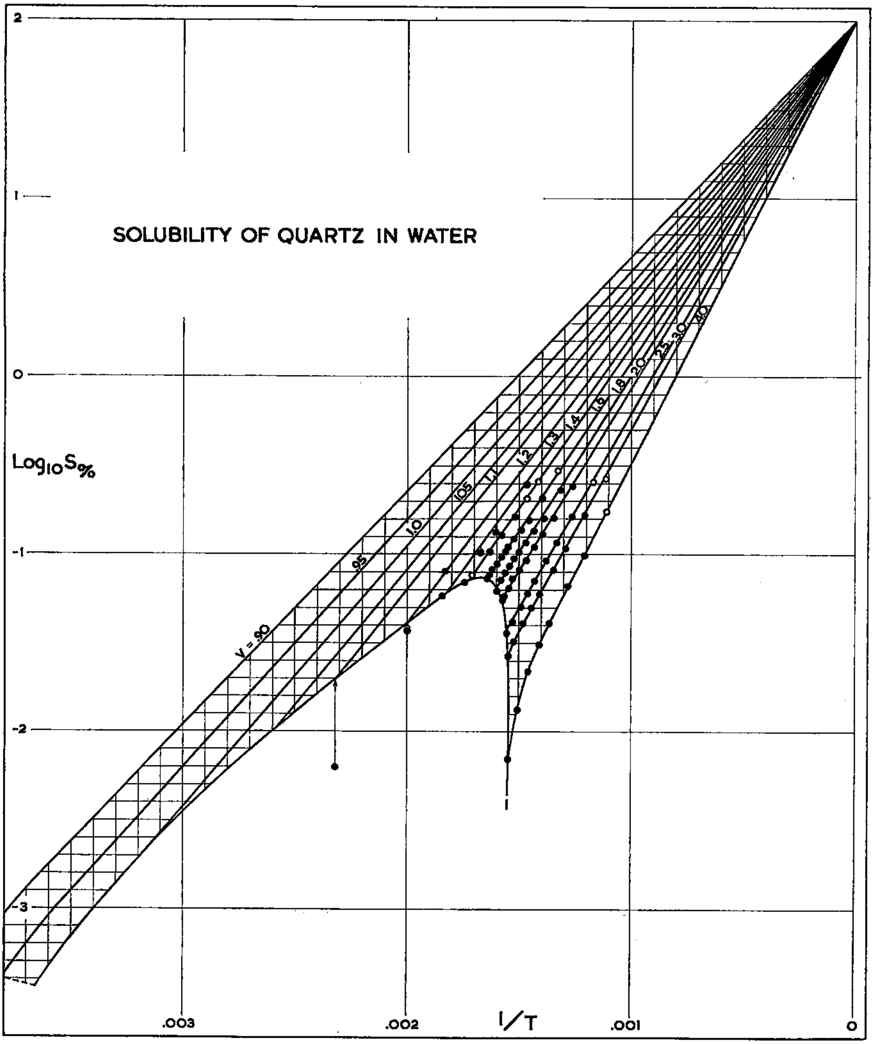

FIG. 1. Kennedy's (1950) data on solubility of quartz in water, plotted as logarithm of weight percentage of SiO_2 in solution *versus* the reciprocal of absolute temperature, at the indicated specific volumes. Filled circles represent good interpolations and short range extrapolations from Kennedy's prime data and open circles represent uncertain interpolations and extrapolations.

of quartz in water from the empirical values of a. This will be less than the molar differential enthalpy of solution by a small undetermined amount. If the concentration unit of solubility, S, is the mole fraction of SiO_2 in solution,

$$\ln S_V = \frac{-\Delta E}{RT}. \qquad (6)$$

In dilute solution, the mole fraction can be converted to weight fraction by the factor M.W.SiO_2/M.W.H_2O. Converting to common logarithms and weight percent, equation (6) becomes

$$\log S\%_V = \frac{-\Delta E}{2.303\,RT}+2.523. \qquad (7)$$

Empirically, it was found that

$$\log S\%_V = \frac{-a}{T}+2. \qquad (5)$$

Equating (7) and (5),

$$\Delta E = 2.303\times 1.986\,(a+0.523\,T) \qquad (8)$$

The values of ΔE, calculated from values of a from Table 1, along the vapor-pressure curve, are shown in Table 2. These enclose the average value (9.47 kcal./mole) obtained by Mosebach (1957).

Relation (5) was used to calculate the solubility of quartz in water to low temperatures. This showed disagreement with Kennedy's (1950) lowest temperature results, but these must be in error, since any reasonable extrapolation of his orthobaric data gives negative solubility below about 149°C. The calculated solubility of quartz at 25°C from equation (6) is 0.00114% (11.4 p.p.m.). Recent critical reviews of the solubility of silica indicate a value of about 10 times this for the amorphous form (Krauskopf, 1956). However, the greater solubility of amorphous silica is reasonable (Kennedy, 1950).

TABLE 2. DIFFERENTIAL INTERNAL ENERGY OF SOLUTION OF QUARTZ IN WATER UNDER VAPOR PRESSURE

$$\Delta E = 4.574\,a + 2.39\,T$$

V	1.00	1.05	1.1	1.2	1.3	1.3	1.6	1.8	2.0	2.5	3.0
T	273	381	431	498	542	573	608	625	635	643	646
ΔE (k cal.)	7.40	7.96	8.35	8.97	9.35	9.70	10.20	10.60	10.94	10.60	12.02

Effect of Alkalinity

Alexander, Heston & Iler (1954) showed that the solubility of amorphous silica in water is independent of *p*H from a value of 1 to 9 at 25°C, and above a value of about 9, the increase in solubility with *p*H is due to ionization of silicic acid. Roller & Ervin (1940) give $10^{-9.8}$ as the first ionization constant of this acid.

We can expect an increase of the ionization constant of silicic acid with temperature, but the magnitude of the increase is not established. However, it is sufficient for the development of a theory of formation of hydrothermal vein deposits that the solubility of quartz as measured in pure water can be taken as independent of acidity-alkalinity over the most probable range of hydrothermal solutions, but if there is a substantial amount of free alkali present the solubility may be many times greater than the minimum.

The effect of neutral salts such as sodium chloride on the solubility of quartz in water appears to be negligible (Krauskopf, 1956).

Solubility of Quartz in Hydrosaline Solutions along a Steep Geothermobar

The quartz iso-volume solubility lines (Fig. 1) are not suitable for showing solubility as a function of temperature and pressure. Therefore, from the iso-volume lines, the temperature of integral log $S\%$ values were recorded, and replotted on an isometric phase diagram of water derived from Kennedy's (1950) data (Smith, 1953). Curves were drawn through the iso-solubility points (sixth smoothing), and are shown in Fig. 2. Also shown are (1) a few iso-volume lines of water from data by Kennedy (1950), (2) the quartz inversion curve from data by Yoder (1950), (3) the "boiling" curve of granite (Smith, 1948) and (4) a steep geothermal gradient starting at 50°C per kilometer but lessening in depth so that a temperature of 700°C is reached at 20 kilometers. The quartz iso-solubility lines represent metastability at temperatures higher than the inversion temperature, and hydrous solutions may have no stable occurrence in the earth at temperatures higher than the granite "boiling" curve.

The final operation was to plot the solubility of quartz in water as a function of depth (temperature and pressure) along the chosen geothermobar (Fig. 3). Also shown in this figure is the temperature of filling of aqueous fluid inclusions in quartz crystallized in water solutions under the selected geothermobaric conditions.

The curves of Fig. 3 show that, in near-neutral water solutions at elevated temperatures and pressures deep within the crust of the earth, quartz has a limited, but substantial solubility. Water solutions saturated with quartz and rising from depth will deposit the mineral at any one place in an amount which will be a small but not insignificant fraction of the amount of water that passes past that place. However, the curves show that the solubility of quartz in water drops off exponentially with decrease of depth in the earth.

The reliance that can be placed on the calculated values of quartz solubility in water within the crust depends upon assessment of all of

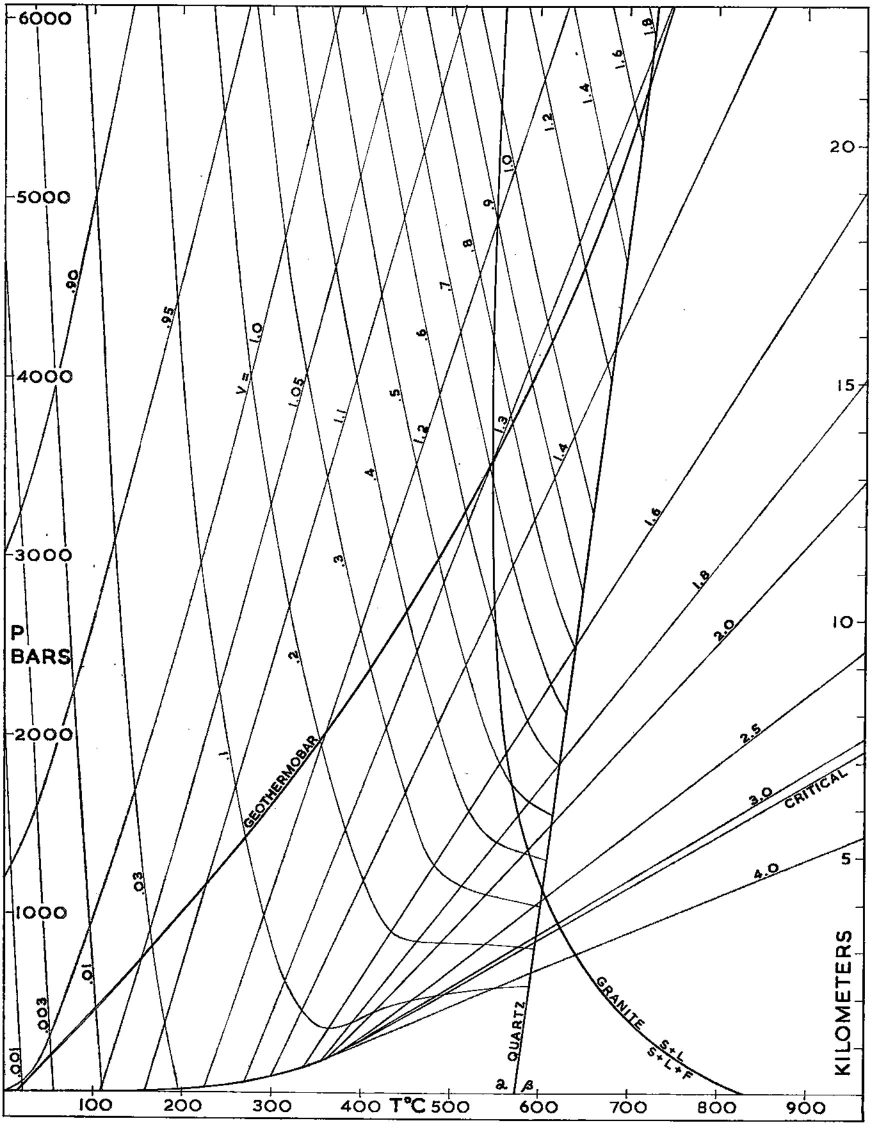

FIG. 2. Solubility of quartz in water shown as isosolubility lines *versus* temperature and pressure. Also shown are a few iso-volume lines of water (Kennedy, 1950), the inversion curve of quartz (Yoder, 1950), the "boiling" curve of granite (Smith, 1948), and a possible geothermobar with a steep temperature gradient near the surface and flatter in depth. The intersections of the selected geothermobar with the other curves give some of the data plotted in Fig. 3.

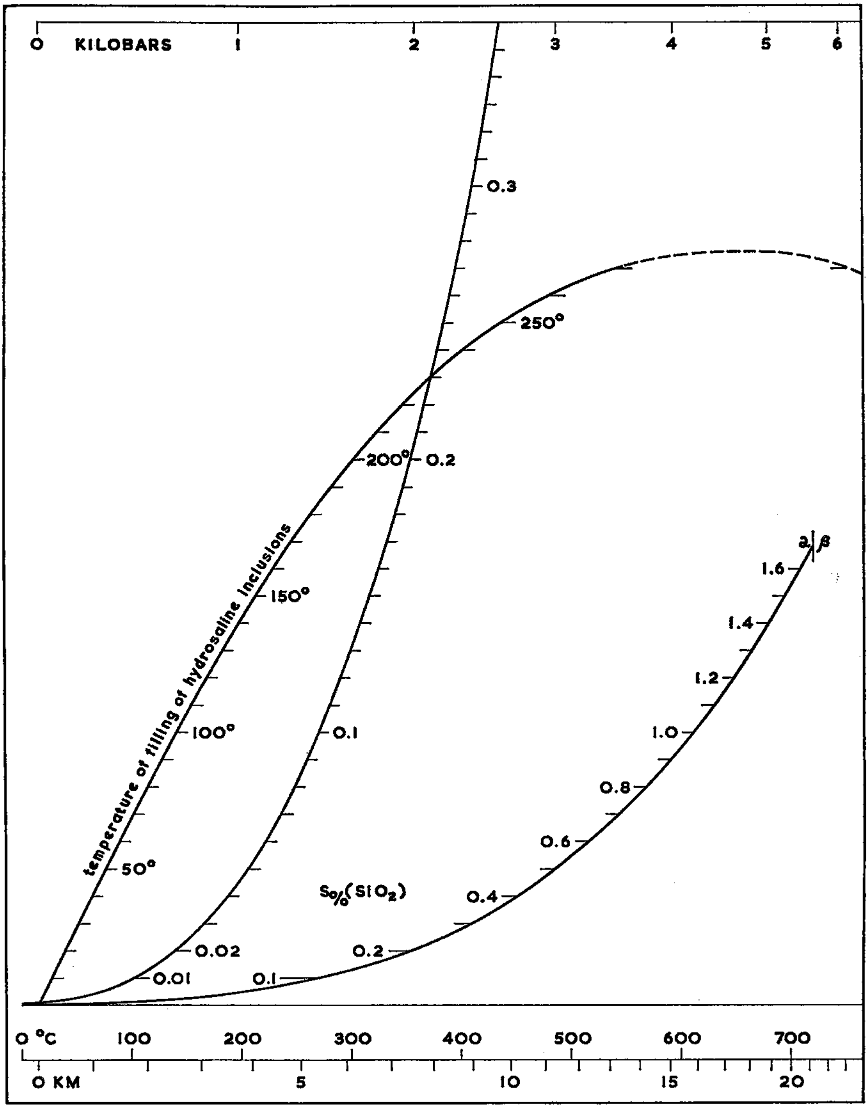

FIG. 3. Solubility of quartz in water along a selected high geothermobar. Also shown is the temperature of filling of aqueous inclusions by the liquid phase, when the mineral is formed at temperatures and pressures on the selected geothermobar.

the assumptions inherent in the methods of calculation. The geological variables such as (1) difference between the geothermobaric gradient in the solutions and in the host rocks, (2) distortion of the gradient near intrusives, (3) change of the gradient with time, (4) change of the gradient with rate of flow, and so on, will be of major importance. Equally important, too, may be large changes of alkalinity due to chemical processes within the solution, some of which are related to reaction with minerals of the wall-rocks. However, a full discussion of all the variables, their interdependences and relative quantitative importance is impossible at the present level of knowledge of the chemistry of natural aqueous solutions within the crust of the earth. Ultimately, perhaps, when much more is known about solubility of minerals in aqueous solutions, it may become possible to compare relative amounts of minerals deposited at the same time in veins and thereby to derive some facts about temperature, pressure, and composition of natural solutions.

The principal use of the quartz solubility values at the present time is for qualitative control in developing theories of vein formation. For example, it is unnecessary to postulate that vein-forming aqueous solutions are alkaline in order to account for transportation and deposition of quartz, because its solubility in neutral and acid solutions is both independent of alkalinity-acidity and large enough to be significant. The solubility values also can be used to derive qualitative and approximately quantitative relations between amount of mineral precipitate in veins and minimum solution requirements as functions of depth in the earth and other variables. A few specimen calculations which may be of interest are given below. If a natural aqueous solution under geothermobaric conditions is saturated with quartz at 500°C and contains about 0.5% silica by weight, a fall of temperature to 400°C precipitates about 50% of the soluble silica, to 300°C about 80%, and to 200°C about 90%. If quartz is deposited to fill a vein during a 10° drop in temperature near 500°C, then a minimum of 1.5 tons of solution flowed through the

TABLE 3. RELATIONS BETWEEN TEMPERATURE, PRESSURE, SOLUBILITY OF QUARTZ IN WATER, SPECIFIC VOLUME OF WATER, AND DEPTH ALONG A SELECTED HIGH GEOTHERMOBAR (50° C/Km at the surface)

t(°C)	P (Bars)	S% (SiO_2 Wt.%)	V (cc/gm)	Depth (Km)
15	1	0.000758	1.00	0.0
100	450	0.00912	1.01	1.7
200	1010	0.0479	1.08	3.8
300	1610	0.130	1.15	6.1
400	2300	0.279	1.23	8.7
500	3110	0.546	1.28	11.7
600	4070	0.942	1.31	15.4
700	5310	1.54	1.31	20.0

fissure for every pound of quartz deposited, but for similar conditions near 100°C, a minimum of 20 tons of solution. If a sedimentary rock, containing quartz, is metamorphosed at 500°C and loses 2% of its weight as a water solution saturated with silica, the real loss of silica (0.01% of the original rock) is small compared with apparent gain of silica (about 1% of the original rock) due to the loss of water, but a cubic kilometer of original rock so metamorphosed could provide the silica for about 250,000 tons of vein quartz.

Solubility of Other Slightly Soluble Oxides which Form Ionized Complexes

Since equations derived from thermodynamical relations give the experimental results for quartz solubility when the proper constants are used, it is suggested that the solubility of some other geologically important oxides might be derived by calculation from a small number of experimental determinations. For example, if the solubility of an oxide can be treated as above for silica, then by using the relation

$$\log S\% \text{ (oxide)} = c \log S\% \text{ (SiO}_2) - 2c + 2,$$

one solubility determination in the temperature-pressure range of the quartz solubility data, to determine c, and the use of Fig. 1 or Table 1 would allow calculation over the entire range of extrapolation of the quartz results.

Acknowledgments

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