The free energy of formation of searlesite, NaBSi$_2$O$_5$(OH)$_2$, and its implications

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Abstract

The solubility of natural searlesite, NaBSi$_2$O$_5$(OH)$_2$, has been determined at temperatures between 25 and 100 °C at 1 atm using distilled water, 1-M NaCl, and various buffer solutions. The paths taken by different starting solutions to a steady state suggest that equilibrium was attained. When necessary, reciprocal time ($t^{-0.5}$) extrapolations of the activity products (Q) were used to estimate the equilibrium constant (K) of the dissolution reaction, thus permitting the calculation of the free energy of formation (ΔG_f^0) of searlesite. Log K values between 25 and 100 °C fit a linear equation, log K = 8.9502 − 2660.1/T (K); ΔG_f^0 of searlesite at 25 °C is −2897.1 ± 0.8 kJ/mol.

Activity diagrams (log $a_{H_3BO_3}$ vs. log a_{SiO_2}) for the system Na$_2$O-B$_2$O$_3$-SiO$_2$-H$_2$O at 25 °C, constructed using thermodynamic data, show that the searlesite stability field lies between the saturation limits of quartz and amorphous silica, flanked by fields for magadiite and borax at higher and lower log a_{SiO_2}, respectively. When log a_{Na^+}/a_{H^+} is fixed at 10.2 to approximate the compositions of many natural brines, the minimum value of log $a_{H_3BO_3}$ necessary for searlesite crystallization is −3. Supersaturation, however, is not a sufficient condition for the crystallization of natural searlesite. Thermodynamic calculations suggest that phillipsite may be altered by natural B-bearing brines to form searlesite and potassium feldspar at ambient temperatures. In nature the alteration reaction appears to be promoted under diagenetic conditions.

Introduction

In order to predict the fate and mobility of B in natural systems, a detailed knowledge of the thermodynamic properties of both the B-bearing aqueous and mineral species is required. Although the inorganic chemistry and thermodynamic properties of B in solution are relatively well understood, few thermochemical data are available for the borosilicate minerals. Even the relative stabilities of these minerals at surface conditions are unknown. Because of the lack of thermodynamic data, it is not possible to predict accurately the geochemical behavior of B in many natural processes.

Determination of thermodynamic data for borosilicate minerals has not been attempted because the two classical approaches for obtaining thermodynamic data for solid phases, calorimetric measurements and solubility studies, are difficult to apply to these minerals. Calorimetric studies are complicated by the inability to prepare or obtain pure compounds and by the large errors (in terms of log K) inherent in such measurements. Solubility studies are difficult and time consuming because of the very slow approach to equilibrium between the solid and the aqueous phase, but they appeared to be the better technique for obtaining at least an estimate of the thermochemical properties of the borosilicates. Therefore, an experimental investigation was initiated to determine the thermochemical properties of selected borosilicates using the solubility method.

Searlesite was selected for the first phase of this study because it was known to exist in alkaline lake evaporites and, therefore, was thought to have a higher solubility than other borosilicates. Searlesite is the only common authigenic silicate that is restricted to highly saline, nonmarine environments (Hay, 1966, p. 103). It occurs in sediments derived from alkaline lakes, which are common in the western United States, particularly in California (e.g., Searles Lake), and, consequently, it may be a component of some soils. Occurrences of authigenic searlesite have been reported by many authors. Large amounts of searlesite have been found associated with authigenic potassium feldspar and zeolites (phillipsite and analcite; Hay and Moiola, 1963) in the sediments of Searles Lake, California, at depths of 180–875 feet. Searlesite is also associated with potassium feldspar in the altered tuffs of Lake Tecopa (Sheppard and Gude, 1968). In Teels Marsh, Nevada, searlesite is present in mudstone and ash beds, along with authigenic zeolites (phillipsite and analcite; Taylor and Surdam, 1981). Searlesite is the most widespread and abundant B mineral in the Green River Formation in Wyoming and Utah; reedmergnerite (NaBSi$_3$O$_8$) occurs only in restricted areas (Milton and Eugster, 1959).

Thus, a solubility study of searlesite would not only provide an estimate of the free energy of formation of searlesite, but it would also have direct application to some alkaline lake and soil environments. Furthermore, B is in tetrahedral coordination in searlesite (Ghose and

TABLE 1. Molar stability constants (log K) of some B species at 25–100 °C

Reaction*	25 °C	50 °C	75 °C	100 °C
1	9.24	8.96	8.88	8.84
2	8.92	8.85	8.83	8.84
3	20.13	19.60	19.24	18.97
4	21.04	20.05	19.37	18.92
5	0.24	0.25	0.26**	0.27**

* Reactions and references: $1 = B(OH)_4^- + H^+ = H_3BO_3^0 + H_2O$ (Mesmer et al., 1972), $2 = 2B(OH)_4^- + H^+ = B_2O(OH)_5^- + 2H_2O$ (Mesmer et al., 1972), $3 = 3B(OH)_4^- + 2H^+ = B_3O_3(OH)_4^- + 5H_2O$ (Mesmer et al., 1972), $4 = 4B(OH)_4^- + 2H^+ = B_4O_5(OH)_4^{2-} + 7H_2O$ (Mesmer et al., 1972), $5 = B(OH)_4^- + Na^+ = NaB(OH)_4^0$ (Owen and King, 1943).
** Extrapolated from data at lower temperatures.

TABLE 2. Analytical data (EPMA) for searlesite from Boron, California, and its ideal composition (wt%)

Oxide	EPMA*	Ideal
Na_2O	13.12	15.19
FeO	0.02	0.00
K_2O	0.01	0.00
SiO_2	56.50	58.91
CaO	0.11	0.00
Al_2O_3	0.15	0.00
TiO_2	0.01	0.00
MgO	0.01	0.00
MnO	0.02	0.00
B_2O_3**	—	17.06
H_2O**	—	8.83
Total	74.96	100.00

* Average of six point analyses.
** B_2O_3 and H_2O cannot be analyzed by EPMA.

Wan, 1976), as it is in most borosilicates, with the important exception of tourmaline. Thus, determination of the free energy formation of searlesite should permit the approximation of free energies of other borosilicates using one of the published estimation methods (e.g., Chermak and Rimstidt, 1989).

SOLUTION CHEMISTRY OF B

The solution chemistry of inorganic B has been extensively studied for many years (e.g., Owen and King, 1943; Mesmer et al., 1972). The distribution of various B species in solution is a function of temperature, pH, and the total concentration of B. The stability constants of some important B polyanions and complexes at temperatures from 25 to 100 °C are listed in Table 1. The data of Mesmer et al. (1972), Owen and King (1943), and Reardon (1976) were selected in this study because they include the values of the equilibrium constant (K) at temperatures above 25 °C.

At a total B concentration less than 0.1 M, $H_3BO_3^0$ and $B(OH)_4^-$ are the only significant species in solution; they equilibrate according to the reaction

$$B(OH)_4^- + H^+ = H_3BO_3^0 + H_2O. \qquad (1)$$

At 25 °C, log K_1 for this reaction is 9.24 (Mesmer et al., 1972), and, thus the activities of $H_3BO_3^0$ and $B(OH)_4^-$ will be equal when pH = 9.24 ($a_{H_2O} = 1$). At lower pH values, $H_3BO_3^0$ is the major species in solution, whereas at higher pH values, $B(OH)_4^-$ predominates.

EXPERIMENTAL AND ANALYTICAL PROCEDURES

Starting materials: Solids

Searlesite from Boron, California, which was used in this investigation, occurs as veinlets, crusts, and clusters of radiating crystals in assemblages with colemanite, $Ca[B_3O_4(OH)_3]\cdot H_2O$, ulexite, $NaCa[B_5O_6(OH)_6]\cdot 5H_2O$, authigenic feldspar, and zeolites in the altered Saddle Back Basalt (Morgan and Erd, 1969; Wise and Kleck, 1988).

The separation of searlesite from the matrix was accomplished by crushing in a diamond mortar and hand-picking under a binocular microscope. Searlesite was also extracted using an isodynamic (magnetic) separator after

pulverizing the remaining material to a finer grain size. The small percentage of ulexite, found in the concentrate, was removed using gravity (heavy liquid) methods. The crystals were then ground under distilled H_2O to less than 50 μm and centrifuge-washed with distilled H_2O. The grain size fraction less than 0.2 μm was discarded and the remainder was dried at 60 °C.

Searlesite was used in the experiments without any further treatment. Due to the limited supply available, some material used in the earlier experiments was reused in the later experiments. Searlesite was characterized by X-ray powder diffractometry and optical microscopy, as well as by electron microprobe (EPMA) analysis (Table 2). Inasmuch as insignificant amounts of nonessential elements were observed, the ideal formula has been used throughout this study. Other solid starting materials used in this study without pretreatment include amorphous (fumed colloidal) silica (ROC/RIC, Sun Valley, California) and gibbsite (Kittrick, 1966b).

Starting materials: Solutions

Various starting solutions, including distilled H_2O, carbonate-bicarbonate buffer solution, borax buffer solution, and 1-M NaCl solution, were used in order to measure the solubility of searlesite over a range of chemical conditions. The carbonate-bicarbonate buffer solution and borax buffer solutions fix the pH at values between 8 and 10, depending on the proportions of their components (Perrin, 1974, p. 147–149). The pH of the distilled H_2O starting solution increases during the first one or two months; in experiments of longer duration the solution is self-buffering at a pH of about 9.2.

As the behavior of the buffer solutions at elevated temperatures is not known, they were used only in experiments at 25 °C. At higher temperatures, all experiments were carried out using distilled H_2O or 1-M NaCl solutions. Supersaturation with respect to searlesite was attained by adding various amounts of silica (200–1000 ppm), B (80–6000 ppm), and Na (500–23000 ppm) to the starting solutions, in the form of sodium metasilicate, boric acid, and NaCl, respectively.

Laboratory procedures

Experiments at 25 °C were carried out in tightly closed polyethylene bottles containing 80–150 mL of various solutions and 0.5–2 g of mineral powders. The bottles were sealed using commercial Teflon (PTFE) thread sealant and subjected to continuous shaking for up to 2 yr. Solutions were sampled for analysis at regular intervals. Similar experiments were carried out at 50 °C in a H_2O bath and at 75 °C in an oven, without shaking.

At 100 °C, experiments were carried out in Teflon-lined, Al or stainless-steel pressure vessels that were heated in ovens for up to four months and then quenched to room temperature in about 5 min using cold H_2O (Sass et al., 1987; Aja, 1989). The 20-mL Teflon liners usually contained 12–15 mL solution and 0.5–2 g of mineral powder.

Solution samples were filtered through 0.1-μm micro filters within 5 min after quenching; pH was measured immediately after filtration. For experiments at temperatures higher than 25 °C, solutions were diluted for analysis immediately after filtration and pH measurement to prevent precipitation. SiO_2 and B concentrations were determined within 5 h, whereas Na was analyzed within 24 h of the termination of an experiment. Solid materials were centrifuge-washed using distilled H_2O and dried at 60 °C for examination by X-ray diffractometry and optical microscopy.

Analytical methods

Quantitative analysis of B was accomplished using the azomethine-H method (John et al., 1975). Some solution samples were also analyzed using specific-ion electrode techniques; the results of the two methods are in close accord (Yang, 1990, p. 26). Silica was analyzed using the molybdosilicate method (Skougstad et al., 1979). Spectrophotometric measurements for both B and silica were carried out using a Bausch and Lomb Spectronic 88 spectrophotometer; the precision of the analyses is within 5%.

Na concentrations were determined by atomic absorption spectrophotometry; the precision of these analyses is estimated to be ±10%. Solution pH was measured at room temperature with a precision of ±0.05 pH units. The overall error in the free energy of formation of searlesite due to analytical uncertainties is estimated to be ±0.8 kJ/mol.

CALCULATIONS AND EXTRAPOLATIONS

Calculation of activity coefficients

Activity coefficients and pH at elevated temperatures were calculated using the program Solveq (Reed, 1981) by adding stability data for the B species (Table 1) to the data base. The stability constants of $NaB(OH)_4^0$ at 75 and 100 °C were extrapolated from lower temperatures because experimental data are not available at these temperatures. The concentrations of B and Na solutions are not very high (≤ 1 M), and, therefore, the error caused by extrapolation to higher temperatures should be small.

Reciprocal time extrapolation

Dissolution of minerals in aqueous solutions is often a slow process. Solubility measurements are therefore difficult for many minerals, especially silicates, which tend to be less soluble than carbonates and borates.

To circumvent this problem, Garrels et al. (1960) devised an empirical method for measuring the solubilities of carbonate minerals using free-drift dissolution rate data and reciprocal time extrapolations. Using this method, quantities such as pH or log activities of aqueous species are plotted as a function of the reciprocal square root of time ($t^{-0.5}$). As the reaction time increases ($t^{-0.5}$ decreases), the data array approaches linearity. The equilibrium values of activities are obtained by extrapolating the linear portion of the array to infinite time ($t^{-0.5} = 0$).

Because of the slow rate of the searlesite dissolution reaction at relatively low temperatures, equilibrium could not be reached in a reasonable time. Therefore, the reciprocal time extrapolation method was used to obtain the solubility constants (log K) of searlesite at 25, 50, and 75 °C. At 100 °C, the duration of experiments was sufficient to bring the dissolution reaction to equilibrium, and, therefore, reciprocal time extrapolation was not necessary.

Reciprocal time extrapolation has been criticized because it is not necessarily valid in all cases (Lafon, 1978). Although it is true that the method is purely empirical, it has been used successfully in many cases (e.g., Bricker, 1965; Plummer and Mackenzie, 1974; Walter and Morse, 1984) and is widely accepted. It has become one of the principal methods for determining the stabilities of biogenic magnesian calcites (Bischoff et al., 1987). Furthermore, Kittrick (1966a) and Routson and Kittrick (1971) successfully used this approach to determine the free energy of formation of kaolinite and illite, respectively. In this study, extrapolations of experiments carried out under various chemical conditions resulted in nearly identical log K values, suggesting that this method may be appropriate for the searlesite dissolution reaction.

Calculation of free energy of formation (ΔG_f^0)

Free energies of formation were calculated using the standard-state convention of Helgeson et al. (1978), (ΔG_f^0 of elements defined as zero only at 298.15 K and 1 bar) because the most recent thermodynamic data for aqueous species (Tanger and Helgeson, 1988; Shock et al., 1989) are based on this convention. The free energies of formation of the aqueous species used in this study are listed in Table 3.

The searlesite dissolution reaction may be expressed as

$$NaBSi_2O_5(OH)_2 + H^+ = Na^+ + H_3BO_3^0 + 2SiO_{2,aq}. \quad (2)$$
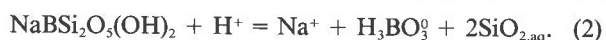
The equilibrium constant for this reaction, K_2, can be calculated using the equation

$$\log K_2 = \log a_{Na^+} + \log a_{H_3BO_3} + 2 \log a_{SiO_2} - \log a_{H^+} \quad (3)$$

where a is the activity of the chemical species when the reaction is in equilibrium. The free energy of reaction,

TABLE 3. The ΔG_f^0 (kJ/mol) values of the aqueous species at 25–100 °C

T (°C)	SiO_2^0	$H_3BO_3^0$	H_2O	Na^+
25	−833.41	−968.76	−237.19	−261.92
50	−834.88	−972.70	−238.99	−263.42
75	−836.26	−976.71	−240.57	−265.05
100	−837.64	−980.86	−243.09	−266.73
Ref.*	1	1	2	3

* References: 1 = Shock et al. (1989), 2 = Helgeson and Kirkham (1974), 3 = Tanger and Helgeson (1988).

TABLE 4. Average values of log K_2 for the searlesite dissolution reaction and the free energy of formation of searlesite at 25, 50, 75, and 100 °C

T (°C)	log K_2	ΔG_f^0 (kJ/mol)
25	0.05	−2897.1
50	0.69	−2901.5
75	1.32	−2905.3
100	1.83	−2909.7

ΔG_r^0, can be calculated from the log K_2 value using the relationship

$$\Delta G_r^0 = -2.303 \, RT \log K_2 \qquad (4)$$

where R is the gas constant and T is the temperature in kelvins. Since the ΔG_f^0 of the species in solution are known (Table 3), the $\Delta G_{f,\text{searlesite}}^0$ can be calculated by difference from the equation

$$\Delta G_{f,\text{searlesite}}^0 = \Delta G_{f,Na^+}^0 + \Delta G_{f,H_3BO_3}^0 + 2\Delta G_{f,SiO_2,aq}^0$$
$$- \Delta G_{f,H^+}^0 - \Delta G_r^0. \qquad (5)$$

EXPERIMENTAL RESULTS

Searlesite dissolution experiments were carried out at 25, 50, 75, and 100 °C. Experiments at higher temperatures were not successful because concentrations of Si and B in the final solutions were sufficient to cause the precipitation of a gel during the quench.

The analytical results are tabulated in Appendix 1[1] whereas the calculated activities of chemical species, log K, and the free energy of formation of searlesite, obtained in experiments from undersaturation, are listed in Table 4. The average values of log K and the free energy of formation of searlesite at 25, 50, 75, and 100 °C are given in Table 4.

The activity product, Q_2, for the searlesite dissolution reaction (Eq. 2) is given by the equation

$$\log Q_2 = \log a_{Na^+}/a_{H^+} + \log a_{H_3BO_3,aq} + 2 \log a_{SiO_2,aq} \qquad (6)$$

where a represents the activities of the chemical species in solution. As the dissolution reaction progresses, log Q_2 changes toward a limiting value. When the system reaches equilibrium, log Q_2 = log K_2, where K is the equilibrium constant.

A typical diagram showing a gradual increase in log Q_2 with the duration of the experiments is shown in Figure 1a. Because a plateau was not attained, reciprocal time extrapolation was used to estimate log Q_2 at infinite time as a measure of log K_2. Figure 1b shows the reciprocal time extrapolation procedure used in this study. As the experimental duration increases ($t^{-0.5}$ decreases), the relationship of log Q_2 vs. $t^{-0.5}$ approaches linearity; the ex-

trapolation of log Q_2 to infinite time ($t^{-0.5} = 0$) is taken as log K_2 of the reaction. Because log Q_2 tends to vary irregularly during the first two to three weeks of the experiments, linear regression was carried out using only the data points (three to six) representing the longest experimental durations.

Changes in the concentrations of chemical species in solution with the duration of experiments at 25 °C for a typical experiment (W66, Appendix 1) are illustrated in Figure 2. The dissolution of searlesite is clearly incongruent, inasmuch as the Si/B and Si/Na ratios are not stoichiometric, as required by Equation 2. During the first
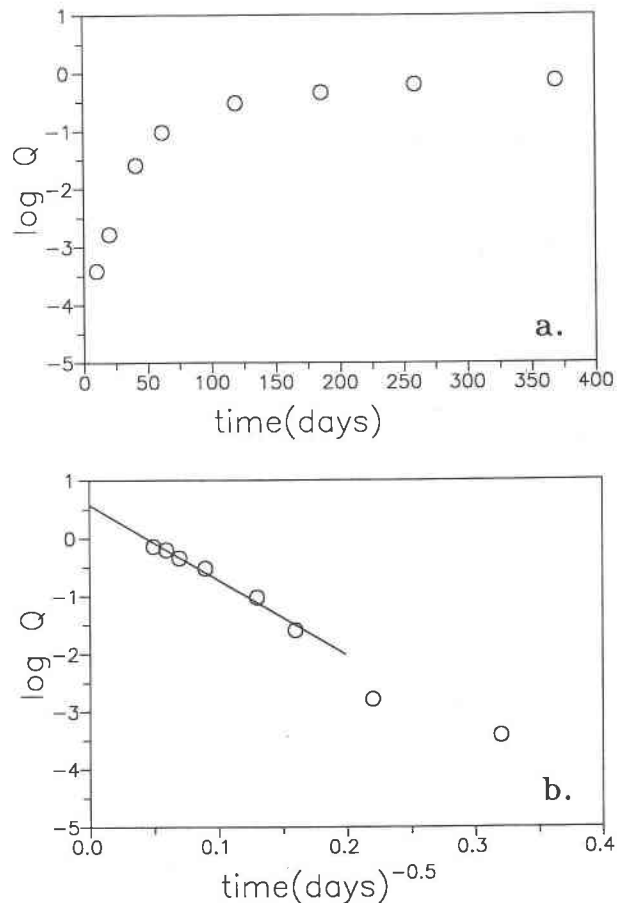

Fig. 1. (a) The variation of log Q_2 with experimental duration. (b) Reciprocal time extrapolation; log Q_2 vs. $t^{-0.5}$ (experiment W56, Appendix 1).

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[1] A copy of Appendix 1 may be ordered as Document AM-92-511 from the Business Office, Mineralogical Society of America, 1130 Seventeenth Street NW, Suite 330, Washington, DC 20036, U.S.A. Please remit $5.00 in advance for the microfiche.
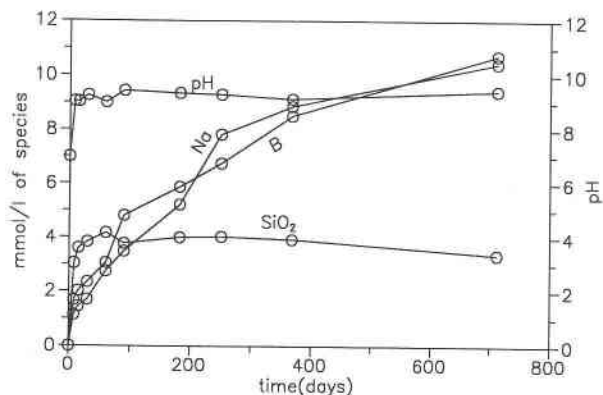
Fig. 2. The variations of SiO_2, B, Na, and H^+ concentrations in solution during searlesite dissolution (experiment W66, Appendix 1).

several weeks, the concentrations of SiO_2, B, and Na increase proportionally according to Equation 2. Later, the concentration of SiO_2 becomes fixed at about 3.5 mmol/L while the concentrations of Na and B continue to increase. Extrapolation to infinite time, using the procedure as described above, gives a $-\log SiO_2 M$ of 2.61, which is close to the theoretical saturation limit of amorphous silica (2.67, Walther and Helgeson, 1977). Since searlesite is the only crystalline product observed by means of X-ray diffractometry and optical microscopy, amorphous silica is presumed to have precipitated. The B/Na ratio remains stoichiometric after equalization for up to 2 yr, providing no evidence for the precipitation of B- or Na-bearing species.

At the outset of the experiments, the rate at which silica is added to the solution exceeds its rate of precipitation, owing to the rapid dissolution of searlesite. Thus, solutions become supersaturated with respect to amorphous silica. During the course of the experiments, the rate of addition and subtraction of silica from solution equalizes as the rate of searlesite dissolution decreases.

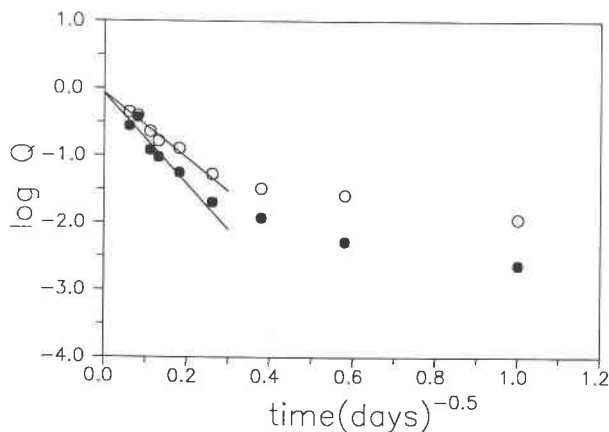Experiments with different proportions of solid and liq-

Fig. 3. The variation of $\log Q_2$ with reciprocal time ($t^{-0.5}$) for experiments W67 (open circles) and W68 (filled circles) (Appendix 1).
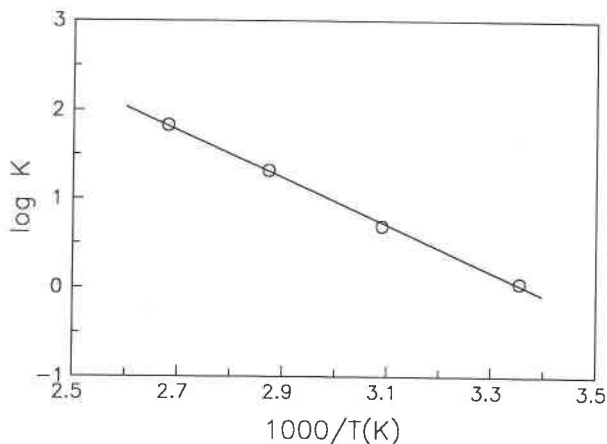

Fig. 4. The variation of $\log K_2$ with $1000/T$ (K) for the searlesite experiments. Linear regression equation, $\log K_2 = 8.9502 - 2660.1/T$(K) ($R = 0.99$). Symbol size is approximately equal to analytical error.

uid were carried out to test the attainment of equilibrium. If the $\log K_2$ values obtained from experiments with different solid/liquid ratios are similar, equilibrium is likely to have been achieved. The changes in $\log Q_2$ with time for two experiments with different solid/liquid ratios are shown in Figure 3. A linear extrapolation of the $\log Q_2$ values for each experiment gives very similar values of $\log K_2$. Thus, the solid/liquid ratio does not appear to influence the experimental results, provided that the experiments are of sufficient duration.

In Figure 4, the $\log K_2$ values at different temperatures are plotted against reciprocal temperature [$1000/T$(K)]. the relationship can be expressed by the equation $\log K_2 = 8.9502 - 2660.1/T$(K), with a correlation coefficient (R) of 0.99. The apparent linearity suggests that equilibrium was probably attained and that ΔH_r^0 for the dissolution of searlesite is approximately constant over the temperature range of this study.

The paths taken by different starting solutions in approaching equilibrium are shown on a diagram in Figure 5 of $\log a_{Na^+}/a_{H^+}$ vs. $\log a_{H_3BO_3}$ (arrows); $\log a_{SiO_2}$ is fixed at -3, the average value in these experiments. The solid triangles represent experiments from undersaturation, whereas the open triangles represent experiments from supersaturation. The paths of the solution compositions are indicated only for experiments from undersaturation, since the solution compositions in the experiments from assumed supersaturation remained unchanged during the course of the experiments. The straight line is the inferred equilibrium boundary between searlesite and solution; its slope is determined by the stoichiometry of the dissolution equation (Eq. 2), whereas its intercept is based on the experiments from undersaturation. The slope inferred from the experimental data conforms quite well to the slope calculated from Equation 2, again suggesting that equilibrium was attained.

Efforts to approach equilibrium from assumed supersaturation were not successful; the concentrations of the chemical species in solution did not change appreciably
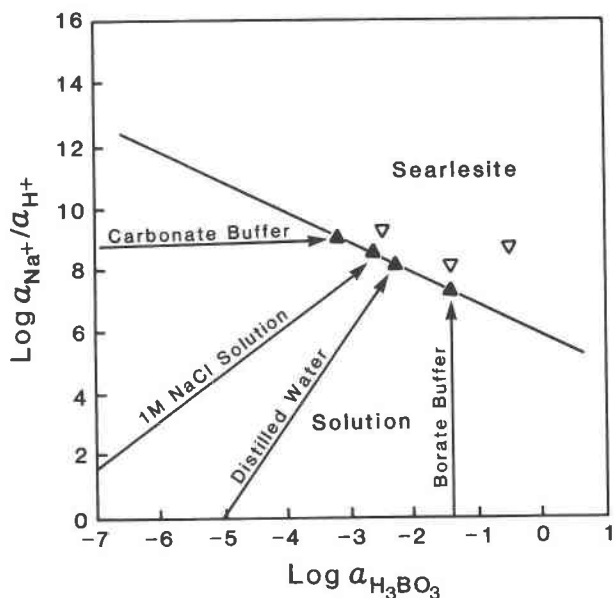
Fig. 5. The paths taken by solution compositions during searlesite experiments at 25 °C. Filled triangles represent average values obtained in experiments from undersaturation, and the open triangles represent experiments from supersaturation.

Fig. 6. Variation of log Q with experimental time for experiments W79 (filled triangles) and W80 (open triangles) (Appendix 1).

during the course of these experiments. The variations of log Q_2 with the duration of experiments from undersaturation (W79, Appendix 1) and from supersaturation (W80, Appendix 1) are shown in Figure 6. Log Q_2 in the experiment from supersaturation is essentially unchanged with time.

Furthermore, evaporation of searlesite-seeded, dilute solutions at 25 °C up to very high concentrations (11200 ppm Na, 1870 ppm B, and 380 ppm silica, pH = 9.56) resulted in the precipitation of borax and a silicious gel. The failure of searlesite to crystallize from solution may be due to a reaction between $B_4O_7^{-2}$ and $SiO_{2,aq}$, which formed a relatively stable gel (see Iler, 1979, p. 190) rather than a crystalline material.

PHASE RELATIONS IN THE SYSTEM Na_2O-B_2O_3-SiO_2-H_2O

Stability relationships

There are five minerals in the system Na_2O-B_2O_3-SiO_2-H_2O that are important to this study: searlesite [$NaBSi_2O_5(OH)_2$], reedmergnerite ($NaBSi_3O_8$), borax ($Na_2B_4O_7 \cdot 10H_2O$), kernite ($Na_2B_4O_7 \cdot 4H_2O$), and magadiite ([$NaSi_7O_{13}(OH)_3 \cdot 4H_2O$]. Borax and magadiite precipitate at the Earth's surface (Sonnenfield, 1984; Jones et al., 1977), whereas the crystallization of searlesite and reedmergnerite appear to require diagenetic conditions (Hay and Guldman, 1987). Borax is stable up to about 60 °C; at higher temperatures it dehydrates to form kernite ($Na_2B_4O_7 \cdot 4H_2O$) or tincalconite ($Na_2B_4O_7 \cdot 5H_2O$), the latter being metastable with respect to the former (Bassett, 1976).

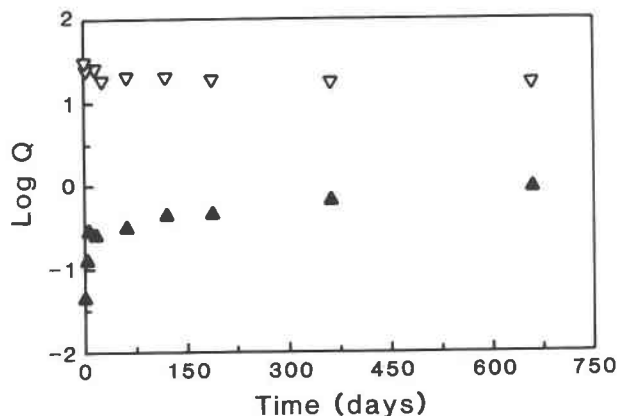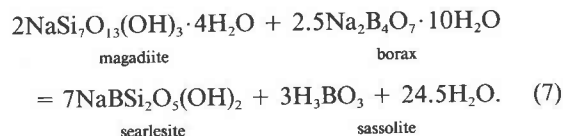Although searlesite and reedmergnerite are both sodium borosilicates, searlesite is a OH-bearing sheet struc-

ture (Ghose and Wan, 1976), and reedmergnerite is isostructural with albite (Clark and Appleman, 1960). The stability relations of these two minerals are of great interest because they determine the fate of B in solution under a wide range of geochemical conditions. Unfortunately, data for reedmergnerite are not available in the literature, and therefore its stability relationships are unknown.

Searlesite is frequently found in nature, although the occurrence of reedmergnerite is rare. Searlesite is present in alkaline lake evaporites at Searles Lake (Hay and Guldman, 1987), Teels Marsh (Smith and Drever, 1976), and Lake Tecopa (Sheppard and Gude, 1968), whereas reedmergnerite is found in significant amounts only in the Green River Formation in Utah, where it occurs with abundant searlesite (Milton and Eugster, 1959).

Like searlesite, magadiite [$NaSi_7O_{13}(OH)_3 \cdot 4H_2O$] is an important mineral in soils and sediments in certain highly alkaline environments (McAtee et al., 1968). Thus, stability relationships of magadiite in the system Na_2O-B_2O_3-SiO_2-H_2O are of considerable interest.

With free-energies-of-formation values of -5513.7 kJ/mol for borax (Felmy and Weare, 1986), -7373 kJ/mol for magadiite (calculated from Bricker, 1969), -968.8 kJ/mol for sassolite (Wagman et al., 1982), and -2897.1 kJ/mol for searlesite (Table 4), it can be shown that magadiite and borax are metastable with respect to searlesite and should react according to the equation

$$2NaSi_7O_{13}(OH)_3 \cdot 4H_2O + 2.5Na_2B_4O_7 \cdot 10H_2O$$
$$\underset{\text{magadiite}}{} \qquad \underset{\text{borax}}{}$$

$$= 7NaBSi_2O_5(OH)_2 + 3H_3BO_3 + 24.5H_2O. \quad (7)$$
$$\underset{\text{searlesite}}{} \qquad \underset{\text{sassolite}}{}$$

The free energy of reaction (ΔG_r^0) equals -486.8 kJ/mol and, therefore, the reaction should proceed to the right. As expected, the assemblage magadiite + borax has not been reported in nature. However, the assemblage searlesite + sassolite has not been reported either, presumably due to the high solubility of sassolite.
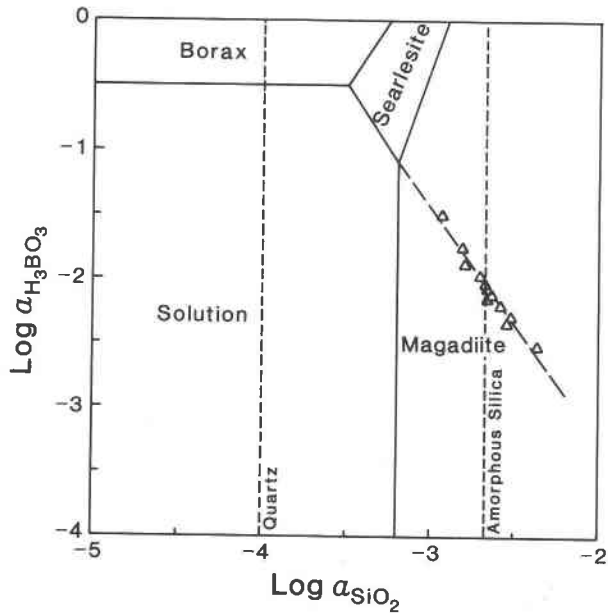
Fig. 7. Stability relations of some phases in the system Na_2O-B_2O_3-SiO_2-H_2O at 25 °C as functions of log $a_{H_3BO_3}$ and log a_{SiO_2}, with the value of log a_{Na^+}/a_{H^+} fixed at 7.5. The borax-searlesite and searlesite-magadiite boundaries are drawn assuming that Na is conserved in the reactions. Triangles = searlesite experiments at 25 °C (Appendix 1); dashed lines = quartz and amorphous silica saturation limits (Walther and Helgeson, 1977).

Fig. 8. Stability relations of some phases in the system Na_2O-B_2O_3-SiO_2-H_2O, as functions of log $a_{H_3BO_3}$ and log a_{SiO_2}, with the value of log a_{Na^+}/a_{H^+} fixed at 10.2. The borax-searlesite and searlesite-magadiite boundaries are drawn assuming that Na is conserved. Analytical data for some natural brines are also shown on the diagram. Data sources: Searles Lake (filled circles), Smith (1979); Owens Lake (open triangles), Friedman et al. (1976); Lake Magadi (open squares), Jones et al. (1977); Teels Marsh (open circles), Taylor and Surdam (1981). See text for details.

The system Na_2O-B_2O_3-SiO_2-H_2O

Stability relationships in the system Na_2O-B_2O_3-SiO_2-H_2O are shown in Figure 7; log a_{Na^+}/a_{H^+} is fixed at 7.5, an average value for the searlesite dissolution experiments (Appendix 1). The borax-searlesite and searlesite-magadiite boundaries are drawn with the assumption that Na is conserved in the reactions. The quartz and amorphous silica saturation limits (Walther and Helgeson, 1977) are shown by dashed lines.

Under the conditions specified for Figure 7, the searlesite stability field is located entirely between the saturation limits of quartz and amorphous silica, and above log $a_{H_3BO_3}$ values of about -1. Borax is stable at log $a_{H_3BO_3}$ values higher than -0.5, whereas magadiite is stable at log a_{SiO_2} values higher than -3.2.

The data obtained from searlesite solubility experiments from undersaturation at 25 °C (Appendix 1) are shown in Figure 7 as triangles. Because the purpose of this diagram is to evaluate the stability of searlesite, the B activities for the experimental data have been adjusted in the diagram based on the searlesite dissolution reaction (Eq. 6) and the assumption that log a_{Na^+}/a_{H^+} = 7.5. Adjustment is necessary because log a_{Na^+}/a_{H^+} is fixed at 7.5 in Figure 7, but log a_{Na^+}/a_{H^+} for each experimental solution is not necessarily 7.5. If the log a_{Na^+}/a_{H^+} of an experimental solution is not 7.5, the difference has been added to or subtracted from the log $a_{H_3BO_3}$ value, in order to keep the log Q_2 of the solution unchanged. The ad-

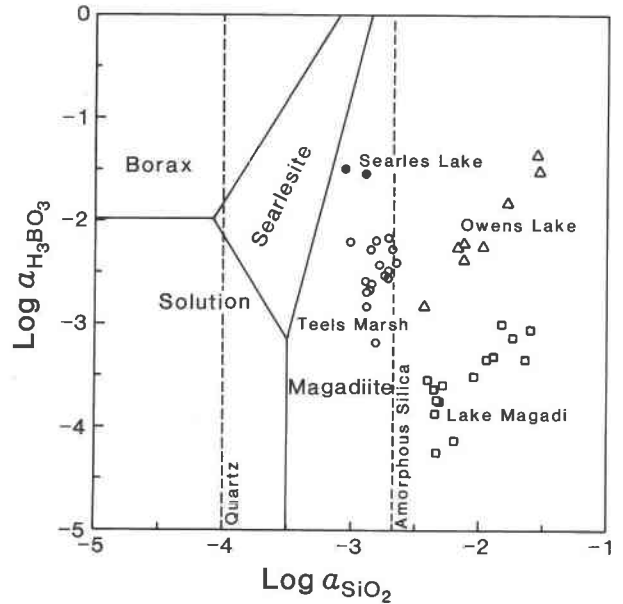justed results of the searlesite dissolution experiments lie along the metastable extension of the searlesite-solution boundary in the stability field of magadiite (Fig. 7).

Natural brines in the system Na_2O-B_2O_3-SiO_2-H_2O

In order to evaluate the stability of the minerals in Figure 7 in natural brines, a phase diagram for the system Na_2O-B_2O_3-SiO_2-H_2O has been constructed (Fig. 8) with log a_{Na^+}/a_{H^+} fixed at 10.2, the average value for the natural brines (Searles Lake, Teels Marsh, Owens Lake, and Lake Magadi) shown on the diagram. The borax-searlesite and searlesite-magadiite boundaries are drawn with the assumption that Na is conserved in the reactions involving these mineral pairs. At the higher log a_{Na^+}/a_{H^+} of Figure 8, the stability fields of the solid phases are enlarged and the stability field of solution is reduced as compared with Figure 7. Because of the high concentrations of dissolved solids in the natural brines (Fig. 8), the activities of the chemical species in solution were calculated using the Pitzer equations (Pitzer, 1975), following the procedure of Felmy and Weare (1986). Inasmuch as the purpose of this diagram is to evaluate the degree of saturation of these brines with respect to searlesite, log $a_{H_3BO_3}$ values of the brines have been adjusted in the light of Reaction 6 and the assumption that log a_{Na^+}/a_{H^+} equals 10.2; a similar adjustment was made for Figure 7.

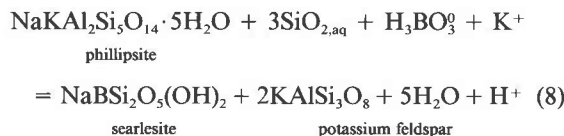Brines from all four of the lakes are supersaturated with

respect to searlesite as well as magadiite. Searles Lake brines and some of the Owens Lake brines are also supersaturated with respect to borax. Although searlesite has been observed in the sediments of Searles Lake and Teels Marsh, it has not been reported at Owens Lake or at Lake Magadi. Thus, supersaturation is not a sufficient condition for searlesite precipitation in nature.

Precipitation of searlesite in nature

Precipitation of borates and borosilicates is known to be an extremely slow process in nature (Sonnenfield, 1984, p. 221), despite high B concentrations in solution. Experimental evaporation of sea water produced only a gel, which yielded anhydrous boracite $[Mg_3Cl(B_7O_{13})]$ upon dehydration (Valyashko et al., 1969).

As an authigenic mineral, searlesite is almost always related to tuffaceous rocks and alkaline, saline lakes (Hay, 1966; Sheppard and Gude, 1968). It is usually found at depth in ancient playa deposits. Precipitation of searlesite under surface conditions in modern saline lakes is unknown, suggesting that searlesite usually crystallizes under diagenetic conditions. Studies of the sediments at Searles Lake by Hay and Guldman (1987), Teels Marsh by Taylor and Surdam (1981), and Lake Tecopa by Sheppard and Gude (1968) suggest that zeolite precursors, formed by the alteration of volcanic ash, may be necessary for the crystallization of searlesite. Searlesite often occurs in assemblages with authigenic potassium feldspar and zeolites (Hay and Moiola, 1963). In the Pleistocene and Recent sediments of Searles Lake, phillipsite forms 80–90% of some rhyolitic tuff horizons in the upper 110 feet; the association potassium feldspar–analcime–searlesite is dominant at depths greater than 230 feet (Hay, 1964). Furthermore, Sheppard and Gude (1968) provide textural evidence showing that potassium feldspar and searlesite replace phillipsite. Therefore, it appears that most of the authigenic searlesite reported in the literature formed by the alteration of zeolites when the activity of B was sufficiently high, as suggested by Hay and Guldman (1987).

This inference may be confirmed by consideration of the reaction for the alteration of phillipsite to searlesite. The phillipsite in saline lakes and soils is usually very low in alkaline-earth ions and has a SiO_2/R_2O_3 ratio near 5.0 (Hay, 1964). With the assumption that Al is conserved in the solid phases, the alteration reaction can be written as

$$NaKAl_2Si_5O_{14} \cdot 5H_2O + 3SiO_{2,aq} + H_3BO_3^0 + K^+$$
phillipsite

$$= NaBSi_2O_5(OH)_2 + 2KAlSi_3O_8 + 5H_2O + H^+ \quad (8)$$
searlesite   potassium feldspar

where

$$\log K_8 = -\log a_{H_3BO_3} - 3 \log a_{SiO_2} - \log(a_{K^+}/a_{H^+})$$
$$= -\Delta G_r^0/(2.303\,RT) \quad (9)$$

where $-\Delta G_r^0$ is the free energy of reaction of Equation 8,

R is the gas constant (8.314 J/k·mol) and T is the temperature in kelvins.

The log K_8 value for Equation 9 is 1.4 at 25 °C, based on the free energies of formation of the minerals and aqueous species in Equation 8. The free energy of formation of phillipsite (-7798 ± 27 kJ/mol) was calculated using the method of Chermak and Rimstidt (1989); its entropy and C_p^0 values were taken from the 1988 data base of SUPCRT (Tanger and Helgeson, 1988). Free energies of species other than searlesite are also from the 1988 data base of SUPCRT.

Calculations by Hay and Moiola (1963) have shown that log a_{K^+}/a_{H^+} and log a_{SiO_2} in the Searles Lake brine are about 9 and -4, respectively. Log $a_{H_3BO_3}$ for the same brine, calculated from the data of Smith (1979), is about -1.6 (Yang, 1990, p. 144–145). With these data, the calculated value of log Q_8 (1.4) is lower than log K_8 at 25 °C (3.87), indicating that the reaction should proceed toward the right and that searlesite + potassium feldspar is the stable assemblage. Thus, the crystallization of searlesite under surface conditions according to Equation 8 is thermodynamically favorable but kinetically unfavorable at ambient temperatures.

According to Smith (1979), the average temperature at the surface of Searles Lake is about 19 °C, while at a depth of 875 feet, the temperature is estimated to be 45 °C; searlesite and potassium feldspar appear at depths of 180 (about 26 °C) to 875 feet. Elevated temperatures at depth probably promoted the alteration of zeolites to form searlesite and potassium feldspar. Alteration of phillipsite to searlesite and potassium feldspar (Eq. 8) at Teels Marsh and Searles Lake buffers the activity of silica in brines at lower levels than those at Lake Magadi (Surdam and Sheppard, 1978), which are lower in B and have not precipitated searlesite. Crystallization of searlesite apparently leads to the formation of borax at Searles Lake, where it is a relatively common mineral. In the deeper tuff layers, including the searlesite-bearing levels, the activity of silica in solution is controlled by equilibrium with quartz (Hay, 1964). Thus, solution compositions probably lie in the stability field of borax (Fig. 8). At Owens Lake, most of the ash is unaltered (Sheppard and Gude, 1968), little phillipsite is present, and searlesite is absent despite the high B and silica contents of the brine (Fig. 8).

References cited

Aja, S.U. (1989) A hydrothermal study of illite stability relationships between 25° and 250 °C and $P_v = P_{H_2O}$, 191 p. Ph.D. thesis, Washington State University, Pullman, Washington.

Bassett, R.L. (1976) The geochemistry of boron in thermal waters, 290 p. Ph.D. thesis, Stanford University, Stanford, California.

Bischoff, W.D., Mackenzie, F.T., and Bishop, F.C. (1987) Stabilities of

synthetic magnesian calcites in aqueous solution: Comparison with biogenic materials. Geochimica et Cosmochimica Acta, 51, 1413–1423.

Bricker, O.P. (1965) Some stability relations in the system MnO_2-H_2O at 25 °C and 1 atmosphere total pressure. American Mineralogist, 50, 1296–1354.

——— (1969) Stability constants and Gibbs free energies of formation of magadiite and kenyaite. American Mineralogist, 54, 1026–1033.

Chermak, J.A., and Rimstidt, J.D. (1989) Estimating the thermodynamic properties (ΔG_f^0 and ΔH_f^0) of silicate minerals at 298 K from the sum of polyhedral contributions. American Mineralogist, 74, 1023–1031.

Clark, J.R., and Appleman, D.E. (1960) Crystal structure refinement of reedmergnerite, the boron analog of albite. Science, 132, 1837–1838.

Felmy, A.R., and Weare, J.H. (1986) The prediction of borate mineral equilibria in natural waters: Application to Searles Lake, California. Geochimica et Cosmochimica Acta, 50, 2771–2783.

Friedman, I., Smith, G.I., and Hardcastle, K.G. (1976) Studies of quaternary saline lakes—II. Isotopic and compositional changes during desiccation of the brines in Owens Lake, California, 1969–1971. Geochimica et Cosmochimica Acta, 40, 53–72.

Garrels, R.M., Thompson, M.E., and Siever, R. (1960) Stability of some carbonates at 25 °C and one atmosphere total pressure. American Journal of Science, 268, 439–453.

Ghose, S., and Wan, C. (1976) Structural chemistry of borosilicates, Part II: Searlesite, $NaBSi_2O_5(OH)_2$: Absolute configuration, hydrogen locations, and refinement of the structure. American Mineralogist, 61, 123–129.

Hay, R.L. (1964) Phillipsite of saline lakes and soils. American Mineralogist, 49, 1366–1387.

——— (1966) Zeolite and zeolitic reactions in sedimentary rocks. Geological Society of America Special Paper, 85, 130 p.

Hay, R.L., and Guldman, S.G. (1987) Diagenetic alteration of silicic ash in Searles Lake, California. Clays and Clay Minerals, 35, 449–457.

Hay, R. L., and Moiola, R.J. (1963) Authigenic silicate minerals in Searles Lake, California, Sedimentology, 2, 312–332.

Helgeson, H.C., and Kirkham, D.H. (1974) Theoretical prediction of the thermodynamic behavior of aqueous electrolytes at high pressures and temperatures. I. Summary of the thermodynamic/electrostatic properties of the solvent. American Journal of Science, 274, 1089–1198.

Helgeson, H.C., Delany, J.M., Nesbitt, H.W., and Bird, D.K. (1973) Summary and critique of the thermodynamic properties of rock-forming minerals. American Journal of Science, 278A, 229 p.

Iler, R.K. (1979) The chemistry of silica, 230 p. Wiley, New York.

John, M.K., Chush, H.H., and Nenfeld, J.H. (1975) Application of improved azomethine-H method to the determination of boron in soils and plants. Analytical Letters, 8, 559–568.

Jones, F.B., Eugster, H.P., and Retting, S.L. (1977) Hydrochemistry of the Lake Magadi basin, Kenya. Geochimica et Cosmochimica Acta, 41, 53–72.

Kittrick, J.A. (1966a) Free energy of formation of kaolinite from solubility measurements. American Mineralogist, 51, 1457–1466.

——— (1966b) Free energy of formation of gibbsite and $Al(OH)_4^-$ from solubility measurements. Soil Science Society of America Proceedings, 30, 595–589.

Lafon, G.M. (1978) Equilibrium criteria for two-component solids reacting with fixed composition in an aqueous phase—Example: The magnesian calcites. American Journal of Science, 278, 1455–1488.

McAtee, J.L., House, R., and Eugster, H.P. (1968) Magadiite from Trinity County, California. American Mineralogist, 53, 2061–2069.

Mesmer, R.E., Base, C.F., Jr., and Sweeton, F.H. (1972) Acidity measurements at elevated temperatures. Inorganic Chemistry, 11, 537–543.

Milton, C., and Eugster, H.P. (1959) Mineral assemblages of the Green River Formation. In P.H. Abelson, Ed., Researches in geochemistry, vol. 1, p. 118–150. Wiley, New York.

Morgan, V., and Erd, R.D. (1969) Minerals of the Kramer Borate District, California. California Division of Mines Geology, Mineral Information Service 22, 143–153, 165–172.

Owen, B.B., and King, E.T. (1943) The effect of sodium chloride upon the ionization of boric acid at various temperatures. Journal of the American Chemical Society, 65, 1612–1620.

Perrin, D.D. (1974) Buffers for pH and metal ion control, 176 p. Wiley, New York.

Pitzer, K.S. (1975) Thermodynamics of electrolytes: 5. Effects of higher-order electrostatic terms. Journal of Solution Chemistry, 4, 249–265.

Plummer, L.N., and Mackenzie, F.T. (1974) Predicting mineral solubility from rate data: Application to the dissolution of magnesian calcites. American Journal of Science, 274, 61–83.

Reardon, E.T. (1976) Dissociation constants for alkali earth and sodium borate ion pairs from 10 ° to 50 °C. Chemical Geology, 18, 309–325.

Reed, M.H. (1981) Calculation of multicomponent chemical equilibria and reaction processes in systems involving minerals, gases and aqueous phases. Geochimica et Cosmochimica Acta, 46, 513–528.

Routson, R.A., and Kittrick, J.A. (1971) Illite solubility. Soil Science Society of America Proceedings, 35, 714–718.

Sass, B.M., Rosenberg, P.E., and Kittrick, J.A. (1987) The stability of illite/smectite during diagenesis: An experimental study. Geochimica et Cosmochimica Acta, 51, 2103–2115.

Sheppard, R.A., and Gude, A.J. (1968) Distribution and genesis of authigenic silicate mineral in tuffs of Pleistocene Lake Tecopa, Inyo County, California. U.S. Geological Survey Professional Paper 597, 38 p.

Shock, E.L., Helgeson, H.C., and Sverjensky, D.A. (1989) Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: Standard partial molal properties of inorganic neutral species. Geochimica et Cosmochimica Acta, 53, 2157–2183.

Skougstad, M.W., Fishman, M.J., Friedman, L.D., Erdman, D.E., and Duncan, S.S. (1979) Methods for determination of inorganic substances in water and fluvial sediments. In Techniques of water resource investigations of the United States Geological Survey, p. 495–496. U.S. Geological Survey, Washington, DC.

Smith, C.L., and Drever, J.I. (1976) Controls on the chemistry of springs at Teels Marsh, Mineral County, Nevada. Geochimica et Cosmochimica Acta, 40, 1081–1093.

Smith, G.I. (1979) Subsurface stratigraphy and geochemistry, Quaternary evaporites, Searles Lake, California. U.S. Geological Survey Professional Paper 1043, 130 p.

Sonnenfield, P. (1984) Brines and evaporites, 613 p. Academic Press, New York.

Surdam, R.C., and Sheppard, R.A. (1978) Zeolites in saline, alkaline-lake deposits. In L.B. Sand and F.A. Mumpton, Eds., Natural zeolites: Occurrence, properties, use, p. 145–174. Pergamon Press, New York.

Tanger, J.C., and Helgeson, H.C. (1988) Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: Revised equations of state for the standard partial molal properties of ions and electrolytes. American Journal of Science, 288, 19–98.

Taylor, M.W., and Surdam, R.C. (1981) Zeolite reactions in the tuffaceous sediments at Teels Marsh, Nevada. Clays and Clay Minerals, 29, 341–352.

Valyashko, M.G., Zherebstsova, I.K., and Lavrova, A.N. (1969) Behavior of some trace elements during the eutonic-(bischofite) stage of seawater concentration. Geochimiya, 5, 614–619.

Wagman, D.D., Evans, W.H., Parker, V.B., Schumm, R.H., Halow, I., Bailey, S.M., Churney, K.L., and Nuttall, R.L. (1982) The NBS tables of chemical thermodynamic properties: Selected values for inorganic and C1 and C2 organic substances in SI units. Journal of Physical Chemistry Reference Data, 11 (suppl. 2), 392 p.

Walter, L.M., and Morse, J.W. (1984) Magnesian calcite stabilities: A reevaluation. Geochimica et Cosmochimica Acta, 48, 1059–1069.

Walther, J.V., and Helgeson, H. (1977) Calculation of the thermodynamic properties of aqueous silica and the solubility of quartz and its polymorphs at high pressures and temperatures. American Journal of Science, 277, 1315–1351.

Wise, W.S., and Kleck, W.D. (1988) Sodic clay-zeolite assemblages in basalt at Boron, California. Clays and Clay Minerals, 36, 131–136.

Yang, W. (1990) Solubilities of selected borosilicate minerals between 25 °C and 250 °C and $P_v = P_{H_2O}$, 159 p. Ph.D. thesis, Washington State University, Pullman, Washington.