Thermochemical data for merlinoite: 2. Free energies of formation at 298.15 K of six synthetic samples having various Si/Al and Na/(Na + K) ratios and application to saline, alkaline lakes

Rona J. Donahoe

Department of Geology, Box 870338, The University of Alabama, Tuscaloosa, Alabama 35487-0338, U.S.A.

J. G. Liou

Department of Geology and Geophysics, Stanford University, Stanford, California 94305, U.S.A.

Bruce S. Hemingway

U.S. Geological Survey, National Center, M.S. 959, Reston, Virginia 22092, U.S.A.

Abstract

The standard Gibbs free energies of formation, $\Delta G^0_{f,298}$, for six synthetic merlinoite samples having various Si/Al and Na/(Na + K) ratios were calculated from previously determined entropies and enthalpies of formation:

Merlinoite composition	$\Delta G^0_{f,298}$ (kJ/mol)
$(Na_{0.81}K_{0.19}AlSi_{1.94}O_{5.88} \cdot 2.13H_2O)$	-3325.8 ± 5.4
$(K_{0.80}Na_{0.20}AlSi_{1.94}O_{5.88} \cdot 1.81H_2O)$	-3272.2 ± 5.5
$(KAlSi_{1.94}O_{5.88} \cdot 1.69H_2O)$	-3241.4 ± 5.5
$(Na_{0.81}K_{0.19}AlSi_{1.81}O_{5.62} \cdot 2.18H_2O)$	-3225.3 ± 5.2
$(K_{0.91}Na_{0.09}AlSi_{1.81}O_{5.62} \cdot 1.79H_2O)$	-3144.6 ± 5.3
$(KAlSi_{1.81}O_{5.62} \cdot 1.69H_2O)$	-3123.3 ± 5.2

The standard Gibbs free energies of formation have been corrected for configurational-entropy contributions.

The data obtained in this study are used to investigate some authigenic mineral reactions typical of saline, alkaline lakes. An activity diagram showing stability fields for analcime, potassian feldspar, merlinoite, and phillipsite was constructed and applied to the vertical mineral-zonation pattern from phillipsite through merlinoite to potassian feldspar observed at Searles Lake, California. Comparison of the activity diagram with available analyses of saline, alkaline pore waters from Searles Lake indicates that nonequilibrium growth and dissolution reactions may be necessary to explain the formation of the observed vertical diagenetic mineral trend.

Introduction

Zeolites are one of the most common groups of authigenic silicate minerals in sedimentary rocks; therefore, accurate thermochemical data for zeolites are necessary in order to understand solution-mineral equilibria in a number of important geochemical systems. Many natural zeolites exhibit extensive solid solution with respect to exchangeable cations, water content, and/or framework Si/Al ratios (see Breck, 1974, p. 133–180). Because relatively small changes in the composition of a zeolite can lead to significant variation in its thermochemical properties (e.g., Johnson et al., 1982, 1983), it is desirable to make calorimetric measurements for several different compositions in a solid-solution series in order to develop mixing equations that can be used to extend these properties to natural zeolite occurrences.

Merlinoite has been discovered at only five localities (Gottardi and Galli, 1985). However, merlinoite typically occurs in close association with phillipsite (Passaglia et al., 1977; Donahoe et al., 1984) and is similar to phillipsite structurally (Breck, 1974; Sherman, 1977). Understanding the thermochemical controls on merlinoite formation will lead to a better understanding of phillipsite crystallization. In addition, merlinoite is readily synthesized in pure samples having different Si/Al ratios and is thus more readily used in calorimetric studies than phillipsite.

Only two natural merlinoites have been analyzed chemically (Khomyakov et al., 1981; Passaglia et al., 1977); therefore, the full extent of Na-K and Si-Al mixing is not known. We can, however, put minimum boundaries on Na-K and Si-Al mixing based on these natural compositions. The exchangeable cations of the merlinoite

TABLE 1. Thermodynamic properties at 298.15 K and 1 bar of synthetic merlinoite samples

Sample	Formula weight (g)	ΔC_P^0	$(H_T^0 - H_0^0)/T$	$(G_T^0 - H_0^0)/T$	S_{298}^0*	$\Delta H_{f,298}^0$	$\Delta G_{f,298}^0$*
		[J/(mol·K)]				(kJ/mol)	
P-9(NaK)	239.967	305.5	154.4	128.0	328.8 ± 15.3	−3591.2 ± 2.9	−3325.8 ± 5.4
P-9(KNa)	244.028	278.0	148.3	128.3	324.4 ± 15.8	−3519.0 ± 2.9	−3272.2 ± 5.5
P-9(K)	245.088	265.1	145.4	128.9	320.7 ± 15.3	−3481.8 ± 3.0	−3241.4 ± 5.5
P-8(NaK)	233.057	301.5	150.4	124.2	319.2 ± 14.7	−3488.3 ± 2.8	−3225.3 ± 5.2
P-8(KNa)	237.629	253.1	138.0	122.5	305.9 ± 15.0	−3387.3 ± 2.8	−3144.6 ± 5.3
P-8(K)	237.277	247.5	136.8	122.9	304.3 ± 14.7	−3359.9 ± 2.8	−3123.3 ± 5.2

* Values corrected for configurational-entropy contributions.

found in Russia by Khomyakov et al. (1981) are K and Ba (K > Ba) and the Si/Al ratio is 1.67; the unit-cell formula is $(K,Ba)_8Al_{12}Si_{20}O_{64} \cdot 20H_2O$. The merlinoite discovered in Italy and described by Passaglia et al. (1977) has exchangeable cations K and Ca (K > Ca) and a Si/Al ratio of 2.55; the unit-cell formula is $K_5Ca_2Al_9Si_{23}O_{64} \cdot 24H_2O$. The exchangeable cations of the merlinoite discovered at Searles Lake in California are K and Na (K > Na), as determined by semiquantitative energy-dispersive spectral analysis (see Donahoe et al., 1984; unit-cell composition undetermined). It is likely that the Searles Lake merlinoite, which occurs in a rhyolitic tuff layer, has a higher Si/Al ratio than the Italian merlinoite, which occurs in the vugs of a mafic volcanic rock. The synthetic equivalent of merlinoite, zeolite W, is reported by Breck (1974) to have Si/Al ratios from 1.15 to 2.45 (typical Si/Al is given as 1.80). The range in the Si/Al ratio of natural merlinoite is therefore at least 1.67 to 2.56, and possibly larger.

From the natural merlinoite occurrences, it is apparent that significant variation in the exchangeable-cation composition is possible. The merlinoite structure can accommodate K, Na, Ba, and Ca in exchangeable-cation sites. Merlinoite synthesized from aluminosilicate solutions with equal Na and K concentration in this study selectively incorporates K in its structure relative to Na (see Donahoe et al., 1984). Solution-synthesis experiments have shown that aqueous K is necessary for merlinoite crystallization. However, although pure-Na merlinoite cannot be synthesized directly from appropriate solutions, previously synthesized potassian and potassian-sodian merlinoites can be cation-exchanged to the Na endmember without any reconstructive change in the aluminosilicate framework (Donahoe, unpublished data).

In the preceding paper (Donahoe et al., 1990), calorimetric low-temperature heat capacities and heats of solution and derived entropies and enthalpies of formation at 298.15 K were presented for six synthetic merlinoites having various Si/Al and Na/(Na + K) ratios. This paper presents the derived thermodynamic properties for these samples and applies the results to a natural system.

SYNTHETIC MERLINOITES

Two 40-g samples of potassian-sodian merlinoite having Si/Al ratios of 1.81 and 1.94 were synthesized at 80 °C from clear solutions. The synthesis method is described in Donahoe et al. (1984). Two splits from each sample were ion-exchanged in saturated NaCl and KCl solutions to obtain sodian-potassian and pure-K compositions, respectively, for each Si/Al ratio. The resulting six merlinoite samples have Si/Al ratios of either 1.81 or 1.94 and Na/(Na + K) ratios ranging from 0 to 0.81. The ion-exchange procedure, chemical analyses, and unit-cell parameters for the samples are in Donahoe et al. (1990).

THERMODYNAMIC FUNCTIONS

The thermodynamic properties of the six synthetic merlinoite samples at 298.15 K are in Table 1. The experimental apparatus used to obtain the low-temperature heat capacities and heats of solution and the procedures used to derive values of the enthalpy function, the Gibbs energy function, S_{298}^0, and $\Delta H_{f,298}^0$ for these samples are described in Donahoe et al. (1990). The molecular weights used in the calculations were based on the 1975 atomic weights (Commission on Atomic Weights, 1976). Values of ΔS_{298}^0 for the merlinoite samples were calculated from experimentally measured values of $S_{298}^0 - S_0^0$, corrected for configurational entropy contributions, and standard entropies for Si, Al, K, Na, O_2, and H_2 taken from Robie et al. (1979). The free energies of formation from the elements, ΔG_f^0, at 298.15 K were calculated from

$$\Delta G_{f,298}^0 = \Delta H_{f,298}^0 - 298.15\Delta S_{f,298}^0.$$

Because the enthalpies of solution measured for the P-8 samples are believed to represent maximum values (Donahoe et al., 1990), the calculated free energies of formation for these merlinoites, particularly P-8(NaK), should also be viewed as maxima.

The calculated free energies of formation for the merlinoite samples are plotted as a function of Si/Al ratio and mole fraction of Na in Figure 1a and 1b, respectively. The free energy of formation becomes more negative with increasing Si/Al ratio and with increasing Na content. In a separate study (Donahoe, in preparation), differential thermal analysis and Guinier-Lenne X-ray diffraction techniques confirmed that the thermal stability of merlinoite increases with both increasing Si and Na contents. Increasing thermal stability with increasing Si content has been noted for other zeolite structures (see, for example, Breck, 1974, p. 507–519; McDaniel and Maher, 1976).
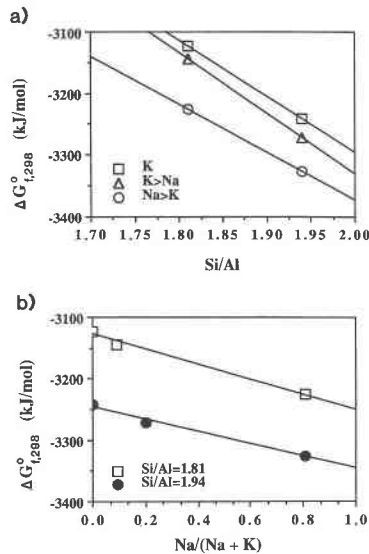
Fig. 1.   Merlinoite free energies of formation as a function of (a) Si/Al ratio and (b) Na/(Na + K) ratio. Lines do not accurately represent compositional dependence.
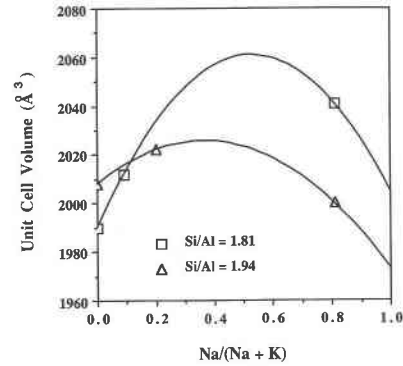

Fig. 2.   Molar volumes of synthetic merlinoite samples as a function of Na/(Na + K) ratio. Curves do not accurately represent compositional dependence.

The increase in merlinoite thermal stability with increasing Na content results from the higher water content of these samples. The adsorption of water onto the surface of merlinoite decreases the surficial energy of the crystal and thus lowers the total free energy of the zeolite. The effect of water content on the stability of zeolite structures has also been observed for analcime (Johnson et al., 1982) and for zeolite NaX, a synthetic faujasite (Breck, 1974, p. 410).

With only two merlinoite Si/Al ratios and three different Na/(Na + K) ratios for each Si/Al ratio, it is impossible to determine the shapes of the free energy–composition curves. For example, the free energy–composition relationships could be approximated by nearly parallel straight lines or as concave-upward curves. As a result, the lines shown on Figure 1 should not be taken as accurate representations of the free energy–composition relationship. Some constraints on mixing can be determined by plots of unit-cell volume vs. Na/(Na + K) ratio (Fig. 2). These plots reveal an excess volume of mixing; therefore, these merlinoite solid solutions cannot be ideal.

Structurally and compositionally, zeolites are most similar to feldspars. This is particularly true for phillipsite and merlinoite, which, like the feldspars, contain the "double crankshaft" linkage of tetrahedra as a basic structural component (Smith and Rinaldi, 1962; Galli et al., 1979). By comparison with the enthalpy and entropy of Na-K mixing in the alkali feldspars (Waldbaum and Robie, 1971; Hovis and Waldbaum, 1977; Thompson and Hovis, 1979), it is probable that free energy–composition relationships for cation mixing in merlinoite are nonideal. In order to develop accurate mixing curves for the thermodynamic properties of merlinoite, more data are needed. This calorimetric study will be extended to

include at least two additional merlinoite Si/Al ratios and two more Na/(Na + K) compositions for each Si/Al ratio.

COMPARISON OF CALCULATED FREE ENERGIES WITH ESTIMATED VALUES

Many investigators have developed methods by which the Gibbs free energy of formation can be estimated for minerals (e.g., Slaughter, 1966; Karpov and Kashik, 1968; Tardy and Garrels, 1974, 1976, 1977; Chen, 1975; Nriagu, 1975; Mattigod and Sposito, 1978; Sposito, 1986; La Iglesia and Aznar, 1986; Chermak and Rimstidt, 1989). Many of the methods are limited because they are applicable to only one group of silicates. However, the estimation techniques of Karpov and Kashik (1968), Chen (1975), and more recently, Chermak and Rimstidt (1989) are applicable to all silicates.

Karpov and Kashik (1968) used multiple linear regression to estimate the compositional contribution of 36 different oxides to the total free energy of silicate minerals. Chen (1975) pointed out that for some minerals there are rather large discrepancies between measured values of ΔG_f^0 and those predicted by this technique and attributed the discrepancies to the failure to account for structural contributions to free energy. Chen (1975) proposed a composition- and structure-dependent method based on an exponential function that describes the progressive decrease of free-energy values obtained when the composition of a mineral is built by summing simple oxides as opposed to complex silicates and oxides. Neither of these techniques has been widely used because they are mathematically cumbersome. Like Karpov and Kashik (1968), Chermak and Rimstidt (1989) have proposed a technique that models the free energy of minerals as sums of polyhedral-unit contributions determined by multiple linear regression. The technique considers hydroxide as well as oxide components and therefore accounts for some structural contributions. The polyhedral contribution of the various components need only be summed in a mineral's stoichiometric proportions to obtain the free energy of formation.

A ΔG_f^0 estimation method for zeolite minerals was de-

TABLE 2. Comparison of free-energy data calculated for the synthetic merlinoite samples

| Sample | Measured ΔG_f^0 (kJ/mol)* | Estimated ΔG_f^0 (kJ/mol)† | |
		Chermak and Rimstidt (1989)	La Iglesia and Aznar (1986)
P-9(NaK)	−3325.8	−3324.4 (0.04)	−3307.9 (0.54)
	(−3312.0)	(0.37)	(0.12)
P-9(KNa)	−3272.2	−3263.0 (0.28)	−3249.8 (0.69)
	(−3257.9)	(0.16)	(0.25)
P-9(K)	−3241.4	−3239.2 (0.07)	−3227.3 (0.43)
	(−3227.6)	(0.36)	(0.01)
P-8(NaK)	−3225.3	−3225.4 (0.003)	−3208.4 (0.52)
	(−3212.0)	(0.42)	(0.11)
P-8(KNa)	−3144.6	−3150.0 (0.17)	−3137.0 (0.24)
	(−3131.1)	(0.60)	(0.19)
P-8(K)	−3123.3	−3128.2 (0.16)	−3116.0 (0.23)
	(−3110.0)	(0.59)	(0.19)

* Free-energy values in parentheses are those calculated by using uncorrected calorimetric third-law entropies.
† Percent deviation between estimated and measured values are given in parentheses.

veloped by La Iglesia and Aznar (1986). Like other summation techniques, this method assumes that ΔG_f^0 is only a function of composition. Because the oxide data are refined for a single mineral group, however, structural contributions to the standard free energy of formation may be small (Tardy and Garrels, 1974). La Iglesia and Aznar used zeolite solubility and cation-exchange data in the development of their estimation method because there are few zeolite ΔG_f^0 values determined by calorimetry or phase equilibria.

Table 2 compares merlinoite free-energy values estimated by the techniques of Chermak and Rimstidt (1989) and La Iglesia and Aznar (1986) with those determined in this study, giving the percent deviation between the estimated and calculated values. With one exception [P-9(KNa)], the correlation between the measured and estimated values of Chermak and Rimstidt is better for free-energy values corrected for configurational contributions. This is expected because at least 93% of the data used to develop the model were either determined by phase-equilibrium reversals or by calorimetry with magnetic or other configurational corrections (John Chermak, personal communication, 1989). Free-energy values estimated by using the method of La Iglesia and Aznar (1986) show lower deviations when compared with free-energy values calculated from measured entropies. Similar trends are seen using free-energy data for natrolite measured by Johnson et al. (1983). The percent deviation between the estimated and calorimetric free energy for natrolite increases from 0.03% to 0.08% for La Iglesia and Aznar's method and decreases from 0.54% to 0.49% for Chermak and Rimstidt's method when configurational-entropy corrections are made.

IMPLICATIONS OF THE THERMODYNAMIC DATA

Saline, alkaline nonmarine zeolite deposits form in closed hydrologic systems as the result of reactions between volcanic glass and connate formation water (Hay,

1966). The high pH and salinity of saline, alkaline brines makes this type of depositional environment ideal for zeolite formation.

Saline, alkaline lake deposits typically exhibit lateral mineral zonation basinward from glass to alkalic, silicic zeolites to analcime to potassian feldspar (Hay, 1966; Sheppard and Gude, 1968). Vertical mineral zonation is usually also present. The lateral zonation is commonly used to distinguish saline, alkaline lake deposits from hydrothermal, burial metamorphic and open hydrologic systems, which only display vertical zonation (see Hay, 1977, for literature review). Mineral zonation in saline, alkaline lakes has been attributed to "equilibrium" fluid-mineral reactions caused by changing water chemistry (Hay, 1966; Surdam, 1977) and to kinetically controlled nonequilibrium growth and dissolution reactions (Dibble and Tiller, 1981).

Searles Lake is a dry, saline, alkaline lake in the Mojave Desert of southeastern California, whose 693 m of tuffaceous sediments are saturated by complex brines having pH of 9.1 to 9.9 (see Gale, 1914; Smith, 1979). A lateral mineral-zonation pattern is presumed to exist, but has not been confirmed because of the limited areal extent of sampling (Richard Hay, personal communication, 1986). Drill-core analysis has revealed a vertical zonation of phillipsite → phillipsite + merlinoite → potassian feldspar with increasing depth in the upper 291 m of sediment (Donahoe et al., 1984). Analcime and clinoptilolite are found in ash layers within the lower 53 m of the lacustrine stratigraphy (Hay and Guldman, 1987). The downward zonation from clinoptilolite to analcime in the lowermost tephra units probably represents progressive diagenesis in a lower-alkalinity environment than that of the phillipsite to potassian feldspar sequence (Hay and Guldman, 1987). Analcime also occurs in carbonate sediment layers below the merlinoite zone and above the potassian feldspar–bearing tuffs, but not in tuffaceous sediments. Hence, it is not clear if analcime is the result of conversion from alkalic, silicic zeolites or the result of a different pore-fluid chemistry within the carbonate units (Sandra Guldman, personal communication, 1983).

The vertical zonation of phillipsite through merlinoite to potassian feldspar observed at Searles Lake could have been caused by "equilibrium" fluid-mineral reactions of the type described by Surdam (1977). Synthesis experiments (Donahoe et al., 1984) suggest that increasing pH or increasing K concentration in the pore solutions with depth could cause fluid-mineral reactions that generate the observed mineral zonation pattern. To examine chemical equilibrium controls on zeolite-feldspar authigenesis, a stability diagram was constructed and applied to the Searles Lake system.

The boundaries of mineral zones in saline, alkaline lakes can be described in part by the following schematic reactions:
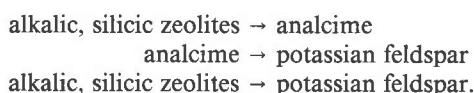
alkalic, silicic zeolites → analcime
analcime → potassian feldspar
alkalic, silicic zeolites → potassian feldspar.

TABLE 3. Saline, alkaline lake mineral reactions used to construct Fig. 3

Reaction	log K
(1) Analcime → potassian feldspar $NaAlSi_{2.125}O_{6.25} \cdot 1.04H_2O + K^+ + 0.4375H_4SiO_4$ $+ 0.4375H_3SiO_4^- + 0.4375H^+ \rightarrow KAlSi_3O_8 + Na^+ + 2.79H_2O$	9.625
(2) Analcime → phillipsite $NaAlSi_{2.125}O_{6.25} \cdot 1.04H_2O + 0.19K^+ + 1.46H_2O$ $\rightarrow Na_{0.81}K_{0.19}AlSi_{1.94}O_{5.88} \cdot 2.13H_2O + 0.0925H_4SiO_4$ $+ 0.0925H_3SiO_4^- + 0.19Na^+ + 0.0925H^+$	1.345
(3) Phillipsite → potassian feldspar $Na_{0.81}K_{0.19}AlSi_{1.94}O_{5.88} \cdot 2.13H_2O + 0.53H_4SiO_4 + 0.53H_3SiO_4^-$ $+ 0.53H^+ + 0.81K^+ \rightarrow KAlSi_3O_8 + 0.81Na^+ + 4.25H_2O$	8.279
(4) Merlinoite → phillipsite $K_{0.80}Na_{0.20}AlSi_{1.94}O_{5.88} \cdot 1.81H_2O + 0.61Na^+ + 0.32H_2O$ $\rightarrow Na_{0.81}K_{0.19}AlSi_{1.94}O_{5.88} \cdot 2.13H_2O + 0.61K^+$	1.690
(5) Merlinoite → potassian feldspar $K_{0.80}Na_{0.20}AlSi_{1.94}O_{5.88} \cdot 1.81H_2O + 0.20K^+ + 0.53H_4SiO_4$ $+ 0.53H_3SiO_4^- + 0.53H^+ \rightarrow KAlSi_3O_8 + 0.20Na^+$ $+ 3.93H_2O$	6.589

Fig. 3. Activity ratio diagram at 25 °C and 1 bar, showing stability fields for P-9(KNa) merlinoite, "phillipsite" [approximated by ΔG_f^0 for P-9(NaK) merlinoite], analcime, and potassian feldspar. Activity of water was taken to be 0.754 and pH = 9.5. See text for explanation of upper salt (U.S.) and lower salt (L.S.) brines.

No accurate thermochemical data exist for phillipsite, but because it occurs in many saline, alkaline lake environments, including the tuffaceous sediments at Searles Lake, its field of stability is relevant to authigenic silicate mineral equilibria in these geochemical systems. It is therefore necessary to estimate the free energy of formation of phillipsite.

The close structural similarity of phillipsite and merlinoite (see Donahoe et al., 1990) suggests that differences in standard free-energy values result primarily from compositional contributions. The phillipsite crystals at Searles Lake have a higher Na/K ratio than the coexisting merlinoite crystals, but their Si/Al ratios are approximately the same (Donahoe et al., 1984). One approach to estimating ΔG_f^0 for the Searles Lake phillipsite is to assume that its thermochemical properties can be approximated by those for a Na-exchanged P-9 merlinoite ($\Delta G_f^0 = -3325.8$ kJ/mol). The ΔG_f^0 estimation method of Chermak and Rimstidt (1989) gives a value within the calorimetric uncertainty for this composition of phillipsite (Table 2).

Table 3 shows reactions that were written between merlinoite [P-9(KNa): $K_{0.80}Na_{0.20}AlSi_{1.94}O_{5.88} \cdot 1.81H_2O$], "phillipsite" [P-9(NaK): $Na_{0.81}K_{0.19}AlSi_{1.94}O_{5.88} \cdot 2.13H_2O$], potassian feldspar ($KAlSi_3O_8$), analcime ($NaAlSi_{2.125}O_{6.25} \cdot 1.04H_2O$), and aqueous species ($H_2O_{(l)}$, $Na_{(aq)}^+$, $K_{(aq)}^+$, and $H_4SiO_{4(aq)}$), conserving Al in the solid phases and assuming the activities of the crystalline phases to be unity. Equilibrium constants for these reactions were calculated using free-energy data for merlinoite and "phillipsite" obtained in this study, analcime (Johnson et al., 1982), $H_3SiO_4^-$ (Helgeson, 1971), and potassian feldspar, $Na_{(aq)}^+$, $K_{(aq)}^+$, $H_2O_{(l)}$, and $H_4SiO_{4(aq)}$ (Robie et al., 1979). Figure 3 was constructed to show the stability relations among "phillipsite," P-9(KNa) merlinoite, analcime, and potassian feldspar. The stability diagram is constructed for $T = 25$ °C, 1-atm pressure, and pH = 9.5. At this pH, Si_{tot}
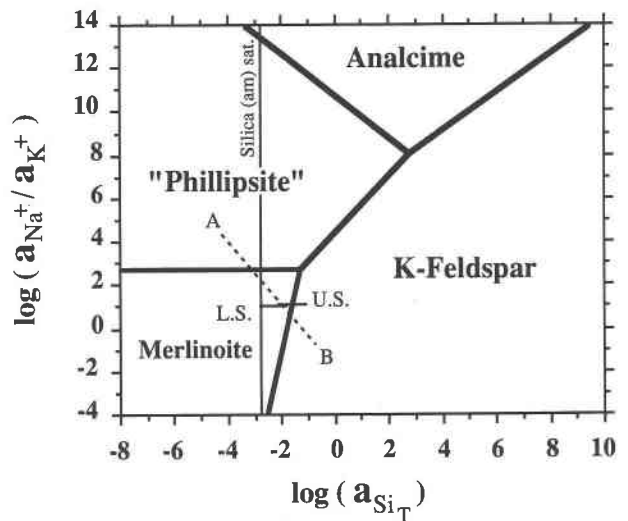
$= [H_4SiO_4] + [H_3SiO_4^-]$ and $a_{H_4SiO_4} = a_{H_3SiO_4^-}$. The activity of water was assumed to be 0.754, the value calculated for two average Searles Lake brine compositions given by Smith (1979).

It is apparent from Figure 3 that there is no continuous solution-composition path that will result in a zonation pattern of phillipsite → merlinoite → analcime → potassian feldspar. Analcime is not stable at the low Na/K ratios in solution required for merlinoite formation. If the mineral zonation is controlled by "equilibrium" fluid-mineral reactions, the presence of analcime in the carbonate sediments at Searles Lake must be the result of a different pore-solution chemistry.

The vertical zonation of phillipsite → phillipsite + merlinoite → potassian feldspar with increasing depth could be the result of a decreasing (a_{Na^+}/a_{K^+}) ratio in the solution and an increasing silica activity along a closed-system path such as from point A to point B in Figure 3. Few published analyses of brine compositions from Searles Lake exist (Gale, 1914; Haines, 1959; Garrett, 1960; White et al., 1963; Smith, 1979), and only four of these analyses report dissolved silica concentration. The four analyses are of brine samples from the upper and lower salt bodies [units at depths of about 30–40 ft (9.1–12.2 m) and 100–110 ft (30.5–33.5 m), respectively] that contain only 0–1% authigenic silicate minerals (Hay and Moiola, 1963).

Brine compositions from the upper and lower salt units are plotted on Figure 3. The analysis of brine from the upper salt body is from Gale (1914), well A21, and the analysis of brine from the lower salt body is from Smith (1979), well L-31. The calculated ionic strengths of the upper and lower salt brines are 9.58 and 9.18, respec-

tively. Brine Na and K activities were estimated by using the approach of Pitzer (1973, 1979) and the model of Harvie et al. (1984) in the EQ3 computer program (Wollery, 1979). No model exists by which the activity of aqueous silicate species can be estimated accurately at high ionic strengths. Minimum values of log a_{Si} for the brines were plotted as analyzed silica molalities on Figure 3. Maximum values of log a_{Si} were estimated by assuming that all silica exists as H_4SiO_4 and by estimating activity coefficients from the Plummer and Mackenzie (1974) approximation. For pH = 9.5, log $a_{H_4SiO_4}$ = log $a_{H_3SiO_4^-}$, and the activity coefficient corrections for these two species should partially offset each other. The true values of log a_{Si} therefore lie along lines connecting the minimum and maximum values. Correction of silica concentrations to activities has the effect of moving the plotted points toward the stability field of potassian feldspar.

The composition of brine from the lower salt body plots within the merlinoite stability field near amorphous silica saturation. The composition of brine from the upper salt body plots near the merlinoite–potassian feldspar boundary (Fig. 3). Factors that may complicate activity-diagram interpretations include simplification of the chemical system (both solution and solid compositions), lack of compositional and thermochemical data for all pertinent phases, failure to consider temperature changes, and possible nonequilibrium relationships between fluids and solids.

The activity diagram represents the extremely restricted chemical system $Na_2O-K_2O-Al_2O_3-SiO_2-H_2O$. Because Al is conserved in the solid phases for the mineral reactions in Table 3, its concentration is a hidden quantity on the diagram. Al was not analyzed in any published brine analyses from Searles Lake. Besides Na and K, natural zeolites incorporate various amounts of Ca, Mg, Ba, and Fe; potassian feldspar may take in variable amounts of these elements. Incorporation of additional components can increase the stability of a mineral, and this effect is probably more important for zeolites than for potassian feldspar. Expansion of the merlinoite stability field relative to that for potassian feldspar will move the plotted brine compositions farther away from the stability field of potassian feldspar. Thermodynamic data for the impure phases are needed to predict to what extent the zeolite stability fields will expand relative to potassian feldspar upon the addition of other components to the system.

The brines from the upper and lower salt units show an increase in pH and decrease in Na/K ratio with increasing depth within the individual units (Smith, 1979). Both of these chemical controls favor the zonation from phillipsite → merlinoite → potassian feldspar with depth. However, the decrease in Na/K ratio is not sufficient to account for the mineral-zonation pattern, and the Na/K ratio is approximately constant when average brine compositions of the upper and lower units are compared. The limited data on silica concentration in the brine suggest a decrease in dissolved silica with increasing depth across

both salt units, which would not favor the observed vertical mineral zonation. The data given by Gale (1914) for the upper salt brine is suspect, however, because the analytical method used was not reported.

Mud temperatures near the base of the alkalic zeolite zone and the top of the potassian feldspar zone are reported by Smith (1979) to be about 26 °C. Temperature, therefore, is not likely to have been important in causing the diagenetic transition from phillipsite through merlinoite to potassian feldspar.

Although Figure 3 is oversimplified for application to the Searles Lake system, all considerations suggest that the size of the merlinoite stability field relative to potassian feldspar is underestimated.

The vertical mineral zonation at Searles Lake could also be caused by kinetically controlled nonequilibrium growth and dissolution reactions. Hay and Guldman (1987) studied the diagenetic alteration of silicic tephra layers in the sediments of Searles Lake and interpreted pore-water chemistry evolution through consideration of the authigenic mineral assemblages. The upper 291 m of sediment, which contains the diagenetic sequence phillipsite → merlinoite → potassian feldspar, is interpreted by Hay and Guldman (1987) to have formed in contact with highly saline, alkaline pore fluid (pH ≈ 9.5). The lower portion of the lacustrine sediments that contain the diagenetic sequence smectite → clinoptilolite → analcime, was interpreted to have formed in contact with moderately saline, slightly alkaline pore fluid (pH ≈ 7.5). On the basis of the measured geothermal gradient in the upper 80 m of sediments, the temperature at the base of the potassian feldspar zone is believed to be less than 48 °C (Hay and Guldman, 1987). Hay and Guldman attributed the alteration of phillipsite and/or merlinoite to form potassian feldspar to be the result of kinetically controlled disequilibrium processes.

The analyses of salt unit brines plot near the potassian feldspar–merlinoite stability-field boundary, possibly supporting the interpretation that the highly saline, alkaline pore fluids are in equilibrium with potassian feldspar and that the transition of phillipsite through merlinoite to potassian feldspar represents the transformation of metastable phases to a stable one. The upper and lower salt units for which brine compositions are available lie in the uppermost part of the stratigraphic section. The tuff units at this depth do not contain potassian feldspar (Hay and Guldman, 1987, Fig. 2), but rather contain the alkalic zeolites phillipsite and merlinoite. No brine compositions are available from the lower units. Based on the fact that saline minerals in the lake sediments show almost no evidence of solution or reaction, Hay and Moiola (1963) theorized that the chemical character and pH of the interstitial waters do not vary significantly with depth.

However, studies of silicate diagenesis by Hay and Guldman (1987) indicate that some vertical changes in pore-water chemistry have occurred within the tuffaceous layers. It is probable that the two analyses of brines for the upper and lower salt units are not representative of

the composition of a brine that is in equilibrium with authigenic silicates. Authigenic silicates occur primarily within tuffaceous sediment layers. These tuffs are commonly sandwiched between layers of mud and should have a separate hydrologic regime with interstitial water that varies in composition from the pore waters in equilibrium with the more permeable saline beds. Higher silica concentrations would place tuffaceous sediment brines within the potassian feldspar stability field and support kinetically controlled mineral zonation. Decreasing Na/K ratio and increasing alkalinity with depth would support control by "equilibrium" fluid-mineral reactions. Samples of interstitial fluids from tuffaceous sediments in the salt units and lower stratigraphic units are needed to determine which of these mechanisms is responsible for the pattern of silicate diagenesis observed at Searles Lake.

It is not possible to conclusively demonstrate whether the chemistry of the pore water, nonequilibrium kinetic factors, or a combination of the two control the mineral reactions seen in the Searles Lake core samples. However, the data do not support the interpretation of Smith (1979) that changes in the composition of the pore-fluid brines probably explain the vertical zonation pattern in the tuffaceous sediments. Depending upon the position of the merlinoite–potassian feldspar stability-field boundary and the effect of activity-coefficient corrections for silica, the salt brines may be approximately in equilibrium with potassian feldspar. If the composition of pore fluids in tuffaceous sediment layers is the same as that of the salt brines, kinetically controlled processes may have to be called upon to explain the observed transition from alkalic zeolites to potassian feldspar in this saline, alkaline lake environment.

Acknowledgments

References cited

Breck, D.W. (1974) Zeolite molecular sieves. Wiley, New York.

Chen, C-H. (1975) A method of estimation of standard free energies of formation of silicate minerals at 298.15 °K. American Journal of Science, 275, 801–817.

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.

Commission on Atomic Weights, International Union of Pure and Applied Chemistry. (1976) Atomic weights of the elements 1975. Pure and Applied Chemistry, 47, 75–95.

Dibble, W.E., and Tiller, W.A. (1981) Kinetic model of zeolite paragenesis in tuffaceous sediments. Clays and Clay Minerals, 29, 323–330.

Donahoe, R.J., Guldman, S., and Liou, J.G. (1984) Synthesis and characterization of zeolites in the system Na_2O-K_2O-Al_2O_3-SiO_2-H_2O. Clays and Clay Minerals, 32, 433–443.

Donahoe, R.J., Hemingway, B.S., and Liou, J.G. (1990) Thermochemical data for merlinoite: 1. Low-temperature heat capacities, entropies, and enthalpies of formation at 298.15 K of six synthetic samples having

various Si/Al and Na/(Na + K) ratios. American Mineralogist, 75, 188–200.

Gale, H.S. (1914) Salines in the Owens, Searles and Panamint Basins, southeastern California. U.S. Geological Survey Bulletin 580-L, 251–323.

Galli, E., Gottardi, G., and Pongiluppi, D. (1979) The crystal structure of the zeolite merlinoite. Neues Jahrbuch für Mineralogie, Monatshefte, 1–9.

Garrett, D.E. (1960) Borax processing at Searles Lake. In J.L. Gilson, Ed., Industrial minerals and rocks (3rd edition), p. 119–122. American Institute of Mining, Metallurgical and Petroleum Engineers, New York.

Gottardi, G., and Galli, E. (1985) Natural zeolites. Springer-Verlag, New York.

Haines, D.V. (1959) Core logs from Searles Lake, San Bernadino Co., California. U.S. Geological Survey Bulletin 1045-E, 139–317.

Harvie, C.E., Møller, N., and Weare, J.H. (1984) The prediction of mineral solubilities in natural waters: The Na-K-Mg-Ca-H-Cl-SO_4-OH-HCO_3-CO_3-CO_2-H_2O system to high ionic strengths at 25 °C. Geochimica et Cosmochimica Acta, 48, 723–752.

Hay, R.L. (1966) Zeolites and zeolitic reactions in sedimentary rocks. Geological Society of America Special Paper 85, 130 p.

——— (1977) Geology of zeolites in sedimentary rocks. In Mineralogical Society of America Reviews in Mineralogy, 4, 53–64.

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.A. (1971) Kinetics of mass transfer among silicates and aqueous solutions. Geochimica et Cosmochimica Acta, 35, 421–469.

Hovis, G.L., and Waldbaum, D.R. (1977) A solution carlorimetric investigation of K-Na mixing in a sanadine-analbite ion-exchange series. American Mineralogist, 62, 680–686.

Johnson, G.K., Flotow, H.E., O'Hare, P.A.G., and Wise, W.S. (1982) Thermodynamic studies of zeolites: Analcime and dehydrated analcime. American Mineralogist, 67, 736–748.

——— (1983) Thermodynamic studies of zeolites: Natrolite, mesolite, and scolecite. American Mineralogist, 68, 1134–1145.

Karpov, I.K., and Kashik, S.A. (1968) Computer calculation of standard isobaric-isothermal potentials of silicates by multiple regression from a crystallochemical classification. Geochemistry International, 5, 706–713.

Khomyakov, A.P., Kurova, T.A., and Muravitskaya, T.N. (1981) Merlinoite: The first discovery in the USSR. Doklady Akademiy Nauk SSSR, 256, no. 1, 172–174.

La Iglesia, A., and Aznar, A.J. (1986) A method of estimating the Gibbs energies of formation of zeolites. Zeolites, 6, 26–29.

Mattigod, S.V., and Sposito, G. (1978) Improved method for estimating the standard free energies of formation ($\Delta G_{f298.15}$) of smectites. Geochimica et Cosmochimica Acta, 42, 1753–1762.

McDaniel, C.V., and Maher, P.K. (1976) Zeolite stability and ultrastable zeolites. Chapter 4, American Chemical Society Monograph 171, 285–331.

Nriagu, J.O. (1975) Thermochemical approximations for clay minerals. American Mineralogist, 60, 834–839.

Passaglia, E., Pongiluppi, D., and Rinaldi, R. (1977) Merlinoite, a new mineral of the zeolite group. Neues Jahrbuch für Mineralogie, Monatshefte, 335–364.

Pitzer, K.S. (1973) Thermodynamics of electrolytes: I. Theoretical basis and general equations. Journal of Physical Chemistry, 77, 268–277.

——— (1979) Theory: Ion interaction approach. In R.M. Pytkowicz, Ed., Activity coefficients in electrolyte solutions, vol. 1, p. 157–208. Chemical Rubber Company Press, Boca Raton, Florida.

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.

Robie, R.A., Hemingway, B.S., and Fisher, J.R. (1979) Thermodynamic properties of minerals and related substances at 298.15 K and 1 bar (10^5 pascals) pressure and at higher temperatures. U.S. Geological Survey Bulletin 1452, 456 p.

Sheppard, R.A., and Gude, A.J., 3rd. (1968) Distribution and genesis of authigenic silicate minerals in tuffs of Pleistocene Lake Tecopa, Inyo

County, California. U.S. Geological Survey Professional Paper 597, 38 p.

Sherman, J.D. (1977) Identification and characterization of zeolites synthesized in the $K_2O-Al_2O_3-SiO_2-H_2O$ system. In J.R. Katzer, Ed., Molecular sieves II, p. 30–42. Symposium Series 40, American Chemical Society, Washington, D.C.

Slaughter, M. (1966) Chemical binding in silicate minerals, Parts I, II, III. Geochimica et Cosmochimica Acta, 30, 299–339.

Smith, G.I. (1979) Subsurface stratigraphy and geochemistry of late Quaternary evaporites, Searles Lake, California. U.S. Geological Survey Professional Paper 1043, 129 p.

Smith, J.V., and Rinaldi, F. (1962) Framework structures formed from parallel four- and eight-membered rings. Mineralogical Magazine, 33, 202–212.

Sposito, G. (1986) The polymer model of thermochemical clay mineral stability. Clays and Clay Minerals, 34, 198–203.

Surdam, R.C. (1977) Zeolites in closed hydrologic systems. In Mineralogical Society of America Reviews in Mineralogy, 4, 65–91.

Tardy, Y., and Garrels, R.M. (1974) A method of estimating the Gibbs energies of formation of layer silicates. Geochimica et Cosmochimica Acta, 38, 1101–1116.

——— (1976) Prediction of Gibbs energies of formation—I. Relationships among Gibbs energies of formation of hydroxides, oxides and aqueous ions. Geochimica et Cosmochimica Acta, 40, 1051–1056.

——— (1977) Prediction of Gibbs energies of formation—II. Monovalent and divalent metal silicates. Geochimica et Cosmochimica Acta, 41, 87–92.

Thompson, J.B., and Hovis, G.L. (1979) Entropy of mixing in sanadine. American Mineralogist, 62, 680–686.

Waldbaum, D.R., and Robie, R.A. (1971) Calorimetric investigation of Na-K mixing and polymorphism in the alkali feldspars. Zeitschrift für Kristallographie, 134, 381–420.

White, D.E., Hem, J.D., and Waring, G.A. (1963) Chemical composition of subsurface waters. U.S. Geological Survey Professional Paper 440-E, 67 p.

Wollery, T.J. (1979) Calculation of chemical equilibria between aqueous solution and minerals, the EQ3/6 software package. UCR-52658, Lawrence Livermore Laboratory, Livermore, California.