

Thermochemistry of natural potassium sodium calcium leonhardite and its cation-exchanged forms

IRINA KISELEVA,¹ ALEXANDRA NAVROTSKY,¹ IGOR A. BELITSKY,² AND BORIS A. FURSENKO²

¹Department of Geological and Geophysical Sciences, Princeton University, Princeton, New Jersey 08544, U.S.A.

²Institute of Mineralogy and Petrography, Academy of Sciences, Novosibirsk, 630090, Russia

ABSTRACT

Leonhardite, a partially dehydrated laumontite, and its alkali variety, primary leonhardite, have been studied by high-temperature calorimetry. The enthalpies of formation from oxides and elements at 298 K are -306.7 ± 7.1 and -14214.6 ± 11.2 kJ/mol, respectively, for leonhardite, $\text{Ca}_2\text{Al}_4\text{Si}_8\text{O}_{24} \cdot 7\text{H}_2\text{O}$, and -521.2 ± 10.5 and -14253.7 ± 13.5 kJ/mol, respectively, for primary leonhardite of composition $\text{Ca}_{1.3}\text{Na}_{0.6}\text{K}_{0.8}\text{Al}_4\text{Si}_8\text{O}_{24} \cdot 7\text{H}_2\text{O}$. The values for primary leonhardite are significantly more negative. New calorimetric data for sodium and potassium oxides were obtained on the basis of thermochemical cycles involving carbonates. The enthalpies of drop solution are -113.10 ± 0.83 kJ/mol for Na_2O and -193.68 ± 1.10 kJ/mol for K_2O , giving enthalpies of solution of -170.78 ± 0.90 kJ/mol for Na_2O and -260.98 ± 1.20 kJ/mol for K_2O . The effects of exchange cations (K,Na) on energetics and dehydration were studied using cation-exchanged samples. Alkali substitution decreases thermal stability (decomposition on heating in air) but increases thermodynamic stability with respect to the oxides and elements. Equilibrium relations between leonhardite and alkali-feldspar, calculated on the basis of these data, show that primary leonhardite can form only from geothermal solutions having rather high ratios of alkali ions to Ca.

INTRODUCTION

Laumontite and its partially dehydrated variety, leonhardite, form in a wide range of conditions, from near-surface and diagenetic to metamorphic and hydrothermal environments. Fersman (1909) found two varieties of leonhardite. The first, $\text{Ca}_2\text{Al}_4\text{Si}_8\text{O}_{24} \cdot 7\text{H}_2\text{O}$, forms reversibly by dehydration of laumontite near room temperature in air. The second differs in having high alkali content, $\text{Ca}_{2-x}(\text{K},\text{Na})_{2x}\text{Al}_4\text{Si}_8\text{O}_{24} \cdot 7\text{H}_2\text{O}$. The sample described by Fersman (1909), with $(\text{Na} + \text{K})/\text{Ca}$ higher than 1, does not hydrate to form the corresponding laumontite and is called "primary leonhardite" to differentiate it from alkali-poor leonhardite formed from laumontite as a secondary mineral. Fersman (1909) and Belitsky and Bukin (1966) showed that primary leonhardite differs from the Ca variety in chemical, mechanical, optical, and other physico-chemical properties. Fedorov and Belitsky (1975) showed that the structure of leonhardite accepts up to 20% K substitution, but at higher K content it breaks down to two-phase mixtures with $\text{K}/(\text{K} + \text{Ca})$ of about 0.2 and 0.6.

Knowledge of the effects of exchangeable cation substitution, of varying Si/Al ratio, and of H_2O content on the thermodynamic properties is essential for modeling geochemical processes and for understanding adsorption, ion-exchange, and other properties. The present study concentrates on the determination of the thermochemical properties of primary leonhardite and its cation-ex-

changed forms and extends our earlier work on the Ca end-members (Kiseleva et al. 1996).

ZEOLITE CHARACTERIZATION

Primary leonhardite was collected by I. Belitsky in a quarry dissecting a diorite-porphiry stock in the same locality (Ukrainka Village, Crimea, Ukraine) where primary leonhardite was first described by Fersman (1909). The sample consisted of pink to deep pink radiating aggregates and crusts of primary leonhardite filling the cracks and cavities in the upper part of the diorite porphyry stock. Its composition, based on the wet-chemical analysis of Fersman (1909), is shown in Table 1. The compositions of zeolites used in this study are illustrated in Figure 1.

The optical properties of leonhardite (Table 2) are similar to those described by Coombs (1952). Primary leonhardite is optically biaxial negative, the refractive indices lower than those of leonhardite, and the extinction angle anomalously low. Lattice parameters were measured using a DRON-3 powder diffractometer, $\text{CuK}\alpha$ radiation, a graphite monochromator, and corundum as an internal standard. Data for leonhardite (see Table 3) agree well with previous studies (Pipping 1966; Yamazaki et al. 1991), but the lattice parameters of the alkali variety, measured for the first time, are smaller than those of calcium leonhardite.

The effect of heat treatment (60 min at temperature followed by rapid cooling) on the refractive index of leon-

TABLE 1. Chemical analyses and formulas of leonhardite

Leonhardite* (Siberia, Russia)	Primary** leonhardite (Crimea, Ukraine)	Ca-Le†	Na-Le†	K-Le† no. 9	K-Le† no. 11	K-Le† no. 12	K-Le no. 28
Chemical analysis (wt%)							
SiO ₂	51.72	50.94	51.20	52.68	51.29	52.12	54.19
TiO ₂	0.01	—	0.01	0.01	0.01	0.01	0.03
Al ₂ O ₃	21.93	22.30	21.99	22.45	22.04	22.62	22.78
Fe ₂ O ₃	0.00	0.12	0.00	0.00	0.00	0.00	0.00
MnO	0.09	—	0.09	0.09	0.10	0.09	0.10
MgO	0.04	—	0.10	0.04	0.00	0.00	0.10
CaO	12.14	7.65	12.12	2.43	8.76	6.69	7.88
Na ₂ O	0.05	2.06	0.00	10.31	0.99	0.69	0.00
K ₂ O	0.13	4.01	0.06	0.58	9.59	9.60	9.01
P ₂ O ₅	0.11	—	0.10	0.06	0.16	0.13	0.12
H ₂ O	13.67	13.42	14.06	10.98	6.63	8.01	6.08
Total	99.89	100.50	99.73	99.63	99.57	99.76	100.29
Structural formula on the basis of 48 O atoms							
Si	15.96(16)‡	15.87	15.90	15.99(16)	15.57	15.84	15.80
Ti	0.00	—	0.00	0.00	0.00	0.00	0.00
Al	7.98(8)	8.19	8.05	8.03(8)	7.89	8.03	7.95
Mn	0.02	—	0.02	0.02	0.03	0.02	0.03
Mg	0.02	—	0.05	0.02	0.00	0.00	0.02
Ca	4.02(4)	2.55	4.03	0.79	2.25	2.18	2.49
Na	0.03	1.24	0.00	6.07	0.58	0.41	0.00
K	0.05	1.59	0.02	0.23	3.71	3.72	3.39
P	0.03	—	0.03	0.02	0.06	0.03	0.00
H ₂ O	14.07(14)	13.93	14.56	11.11	6.71	8.12	5.97

* Sample in calorimetric study of Kiseleva et al. (1996).
 ** Natural sample in this work.
 † Ion-exchanged samples.
 ‡ Values in parentheses represent ideal molar ratios.

hardite was investigated from room temperature to 1273 K. The refractive index showed a decrease at 523–543 K for leonhardite and 443 K for primary leonhardite followed by a continuous increase. These changes correspond to stages of lattice contraction during dehydration.

High-temperature thermal behavior was studied using a Mettler TA 3000 thermoanalyzer. In contrast to leonhardite, primary leonhardite shows broadened dehydration steps, though the total number of peaks on the thermogravimetry curve is the same, four, at 393, 483, 523 K, and a high temperature shoulder at 593 K. Generally, primary leonhardite loses water at temperatures about 200 K lower than leonhardite. This is also confirmed by dilatation studies using a Mettler TMA-40 dilatometer. Rehydration also differs. The main structural changes preventing rehydration occur above 653 K in leonhardite, whereas in primary leonhardite rehydration becomes impossible above 543 K.

CALORIMETRY

The enthalpies of formation and dehydration of zeolites were determined using a Tian-Calvet high-temperature heat-flux microcalorimeter described in detail by Navrotsky (1977). Drop-solution calorimetry into molten $2\text{PbO} \cdot \text{B}_2\text{O}_3$ at 975 K was chosen to avoid decomposition of unstable zeolite samples at the calorimeter temperature prior to calorimetry. Heats of dehydration and heat contents were obtained using the transposed

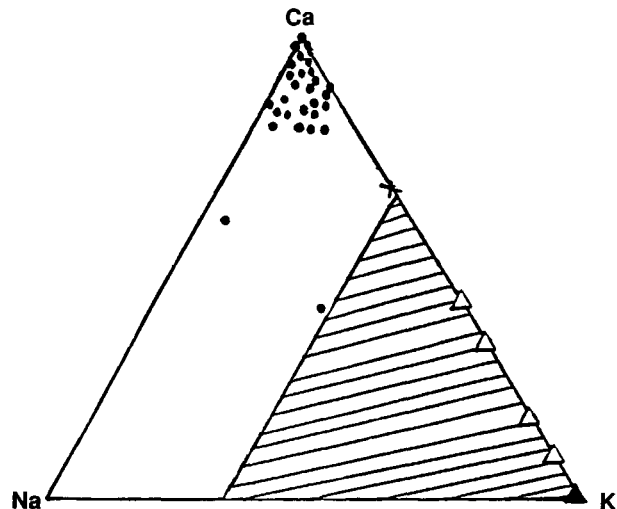


FIGURE 1. The compositions (cation ratios) of natural leonhardite (solid circles) and cation-exchanged forms (triangles, cross) (from Fedorov and Belitsky 1975): cross = one-phase sample with calcium leonhardite structure, open triangles = two-phase samples, solid triangle = one-phase sample with structure different from calcium leonhardite, and the hatched region is the assumed two-phase region.

TABLE 2. Optical data for leonhardite and primary leonhardite

	Leonhardite (Siberia, Russia) (sample used by Kiseleva et al. 1996)	Leonhardite (Transylvania) (Coombs 1952)	Primary leonhardite (Crimea, Ukraine) (this work)
α	1.506(2)	1.507(2)	1.502(2)
β	1.516(2)	1.516(2)	1.511(2)
γ	1.518(2)	1.518(2)	1.513(2)
$(-)\Delta V (^{\circ})$	38(4)	38(5)	32(4)
$\gamma \wedge c (^{\circ})$	32(3)	35(2)	11(4)

temperature-drop technique. The methods used were essentially the same as those for the calcium zeolites (Kiseleva et al. 1996). Calibration, as in that study, used pellets of α - Al_2O_3 of weight comparable to that of the zeolite samples. All experiments were performed under a flowing atmosphere of dry air at rates of 30–40 cm^3/min (Navrotsky et al. 1994).

For calculations of the enthalpy of formation of potassium sodium calcium zeolites we need the heat of drop solution (or solution) of all constituent oxides under the same calorimetric conditions. Potassium, sodium, and calcium carbonates, rather than oxides, were used as reference materials. K_2CO_3 (99.99%) and Na_2CO_3 (99.995%) were commercial products (Aldrich) dried at 413 and 473 K, respectively, prior to calorimetry. Because Na_2CO_3 and especially K_2CO_3 are hygroscopic we minimized the time the samples were exposed to air. We checked the formation of hydration products using room- and high-temperature X-ray diffraction. The carbonates were dried at 413 K for a few hours and then were immediately transferred to a vacuum desiccator. Each sample was ground under acetone and immediately X-rayed. The total time of preparation and air exposure was about 38 min for K_2CO_3 and 45 min for Na_2CO_3 . The K_2CO_3 sample was a two-phase mixture of potassium carbonate (~60%) and potassium carbonate hydrate (~40%). Na_2CO_3 was also a mixture of carbonate and hydrate, although the hydrate component was <10%. Thus, these materials cannot remain unaltered in air for half an hour, or possibly the acetone used for grinding was not anhydrous.

The XRD at high temperature showed that the hydrate phase disappeared upon heating at 413–473 K, and the remaining material was pure carbonate. Thus, before calorimetry, the K_2CO_3 and Na_2CO_3 pellets were pressed and kept at 413 K for 30 h in air and then at 473 K in vacuum for 50 h. Then the pellets were rapidly transferred to the balance and into the calorimeter. The time the samples were exposed to air during weighing and dropping was <2 min. Constant weight during this weighing procedure suggested that the hydrate did not form in this time period.

Chai and Navrotsky (1993) and Navrotsky et al. (1994) showed that CaCO_3 can be used reliably for drop-solution calorimetry under a flowing-gas atmosphere at 975 K. The calcite (Aldrich, 99.995%) and quartz (Fluka, >99.9%) used in this study were commercial products and were dried at 383 K prior to calorimetry.

TABLE 3. Lattice parameters of zeolites

a (Å)	b (Å)	c (Å)	β (°)	V (Å ³)	Ref.
Leonhardite					
14.747(5)*	13.067(3)	7.532(4)	111.9(3)	1346(1)	1
14.770	13.056	7.595	112.8		2
14.77(2)	13.09(2)	7.58(2)	112.0(1)		3
Primary leonhardite					
14.545(8)	13.223(5)	7.522(5)	110.77(6)	1352(2)	4

Note: Parameters are for unit cells containing 48 O atoms in the framework. References are as follows: 1 = Kiseleva et al. (1996), 2 = Pipping (1966), 3 = Yamazaki et al. (1991), and 4 = this work.
* The number in parentheses is the confidence interval (for 95% probability).

RESULTS AND DISCUSSION

Calorimetric data are given in Table 4. Six to 12 enthalpy measurements were made for each substance. The calibration factor did not depend on the mass of the alumina dropped, which ranged from 10 to 25 mg, and neither the heat of drop solution nor the heat of transposed temperature drop varied with sample mass. The heats of drop solution did not depend on the amount of sample previously dissolved (up to about 150 mg in 30 g lead borate), and the calorimetric curves returned to the original baseline in almost all cases. The statistical errors reported (two standard deviations of the mean) are on the order of $\pm 1\%$ or better, indicating problem-free dissolution.

The enthalpy values for CaCO_3 , α - Al_2O_3 , and α - SiO_2 were discussed in our recent paper on calcium zeolites (Kiseleva et al. 1996). We performed two series of experiments for K_2CO_3 and Na_2CO_3 with pellets heated at different temperatures (see Table 4). They show no systematic differences, with uncertainties of $\pm 0.5\%$ or better. These observations suggest no problems arising from slight hydration, which might show up as scatter in the data.

The heats of drop solution were calculated using thermodynamic cycle A in Table 5 to be -113.1 ± 0.8 kJ/mol for Na_2O and -193.7 ± 1.1 kJ/mol for K_2O (Table 6). There are no previous data for the enthalpy of drop solution of Na_2O and K_2O , but the enthalpies of solution of Na_2O calculated by Zygan et al. (1978) are -172.2 ± 4.3 kJ/mol using a carbonate cycle and -170.8 ± 4.9 kJ/mol using NaAlO_2 . To compare our results with these previous data we calculated the heat of solution of Na_2O and K_2O from the enthalpy of drop solution using heat contents of Na_2O and K_2O at 975 K (JANAF 1986). Our value of the heat of solution of Na_2O is -170.8 ± 0.8 kJ/mol (Table 6), which is in good agreement with the previous data but has significantly less error. Our calculated heat of solution of K_2O is -261.0 ± 1.2 kJ/mol, significantly less negative than that obtained previously by Zygan et al. (1978) (-266.2 ± 3.1 kJ/mol) using the carbonate cycle. It is very difficult to analyze this discrepancy because these authors gave no details concern-

TABLE 4. Calorimetric data for natural leonhardite and constituent substances

Mineral and formula	F.W.	Observed enthalpy (kJ/mol)*	
		Drop	Dropsol
Leonhardite** (Ca ₂ Al ₄ Si ₆ O ₂₄ ·7H ₂ O)	922.87	1338.7 ± 12.1(6)	1283.5 ± 5.9(9)
Dehydrated leonhardite** (Ca ₂ Al ₄ Si ₆ O ₂₄)	796.77	575.5 ± 5.6(7)	515.4 ± 3.9(6)
Primary leonhardite (Ca _{1.3} Na _{0.6} K _{0.8} Al ₄ Si ₆ O ₂₄ ·7H ₂ O)	939.89	1355.5 ± 9.3(6)	1398.8 ± 9.8(9)
Dehydrated primary leonhardite (Ca _{1.3} Na _{0.6} K _{0.8} Al ₄ Si ₆ O ₂₄)	813.78	671.3 ± 9.3(6)	
Quartz (SiO ₂)	60.08		39.1 ± 0.3(9)
Corundum (Al ₂ O ₃)	101.96		107.9 ± 1.0(8)
Potassium carbonate (K ₂ CO ₃)	38.21		234.4 ± 1.1(18)†
Sodium carbonate (Na ₂ CO ₃)	105.99		241.2 ± 0.8(10)‡
Calcite (CaCO ₃)	100.09		193.4 ± 0.7(10)

Note: F.W. = gram formula weight. Drop = transposed temperature-drop calorimetry, no solvent present. Dropsol = drop solution into 2PbO·B₂O₃ solvent.

* Uncertainty is two standard deviations of the mean; number in parentheses is number of experiments.

** Kiseleva et al. (1996).

† Average including experiments on samples heated for 30 h at 413 K in air, which gave 234.5 ± 1.3(11), and samples heated for 50 h at 473 K in vacuum, which gave 234.2 ± 2.1(7).

‡ Including samples heated at 413 and 473 K.

ing experimental procedure and sample preparation. We suspect, on the basis of observations, that there may have been problems of hydrate formation in the K₂CO₃ of Zyg-an et al. (1978).

The enthalpies of drop solution of Na₂O and K₂O may also be calculated using the recently measured heats of solution of analbite and sanidine (Hovis and Navrotsky 1995), their enthalpies of formation and heat contents (Robie and Hemingway 1995), and the enthalpies of drop solution of SiO₂ and Al₂O₃ obtained in this study. The results (see Table 6) are in good agreement with those obtained using the carbonate cycle.

ENTHALPIES OF DEHYDRATION OF LEONHARDITE AND PRIMARY LEONHARDITE

The enthalpy of dehydration was calculated for both the pure Ca end-member (see our companion work, Kiseleva et al. 1996) and the primary leonhardite (see thermodynamic cycle B in Table 5). The loss of one mole of H₂O in calcium leonhardite is associated with an endothermic effect of about 40 kJ, but removing one mole of H₂O from primary leonhardite requires only 30 kJ/mol. The latter value is similar to data for the sodium zeolite, analcime, measured by Barany (1961) by acid calorimetry. Thus, the energy of hydration of divalent cations (Ca²⁺) is significantly more exothermic than that of monovalent cations (K⁺ and Na⁺).

ENTHALPIES OF FORMATION OF LEONHARDITE AND PRIMARY LEONHARDITE

The enthalpy of formation of leonhardite (Kiseleva et al. 1996) is -306.7 ± 7.1 kJ/mol from the oxides, which corresponds to -14214.6 ± 11.2 kJ/mol from the elements. The enthalpy of formation of primary leonhardite from the oxides at 298 K, calculated from the enthalpies of drop solution (Table 4 and thermodynamic cycle C in Table 5), is -521.2 ± 10.5 kJ/mol. This value is signif-

TABLE 5. Thermodynamic cycles used in calculations

A. Enthalpy of drop solution of alkali oxides (M = Na, K)	
M ₂ CO ₃ (xl, 298 K) = M ₂ O (sol, 975 K) + CO ₂ (g, 975 K)	(1)*
M ₂ O (xl, 298 K) + CO ₂ (g, 298 K) = M ₂ CO ₃ (xl, 298 K)	(2)**
CO ₂ (g, 975 K) = CO ₂ (g, 298 K)	(3)†
M ₂ O (xl, 298 K) = M ₂ O (sol, 975 K)	(4)
$\Delta H_4 = \Delta H_1 + \Delta H_2 + \Delta H_3$	
B. Enthalpy of dehydration (where Le = Ca ₂ Al ₄ Si ₆ O ₂₄ ·7H ₂ O for Ca-leonhardite and Ca _{1.3} Na _{0.6} K _{0.8} Al ₄ Si ₆ O ₂₄ ·7H ₂ O for primary leonhardite)	
Le (xl, 298 K) = dehydrated-Le (xl, 975 K)	(5)*
Dehydrated-Le (xl, 975 K) = dehydrated-Le (xl, 298 K) + 7H ₂ O (g, 975 K)	(6)*
7H ₂ O (g, 975 K) = 7H ₂ O (xl, 298 K)	(7)†
Le (xl, 298 K) = dehydrated-Le (xl, 298 K) + 7H ₂ O (xl, 298 K)	(8)
$\Delta H_8 = \Delta H_5 + \Delta H_6 + \Delta H_7$	
C. Enthalpy of formation of primary leonhardite	
1.3CaCO ₃ (xl, 298 K) = 1.3CaO (sol, 975 K) + 1.3CO ₂ (g, 975 K)	(9)*
1.3CaO (xl, 298 K) + 1.3CO ₂ (g, 298 K) = 1.3CaCO ₃ (xl, 298 K)	(10)**
0.3Na ₂ CO ₃ (xl, 298 K) = 0.3Na ₂ O (sol, 975 K) + 0.3CO ₂ (g, 975 K)	(11)*
0.3Na ₂ O (xl, 298 K) + 0.3CO ₂ (g, 298 K) = 0.3Na ₂ CO ₃ (xl, 298 K)	(12)**
0.4K ₂ CO ₃ (xl, 298 K) = 0.4K ₂ O (sol, 975 K) + 0.4CO ₂ (g, 975 K)	(13)*
0.4K ₂ O (xl, 298 K) + 0.4CO ₂ (g, 298 K) = 0.4K ₂ CO ₃ (xl, 298 K)	(14)**
2CO ₂ (g, 975 K) = 2CO ₂ (g, 298 K)	(15)†
2Al ₂ O ₃ (xl, 298 K) = 2Al ₂ O ₃ (sol, 975 K)	(16)*
8SiO ₂ (xl, 298 K) = 8SiO ₂ (sol, 975 K)	(17)*
7H ₂ O (xl, 298 K) = 7H ₂ O (g, 975 K)	(18)†
1.3CaO (sol, 975 K) + 0.3Na ₂ O (sol, 975 K) + 0.4K ₂ O (sol, 975 K) + 2Al ₂ O ₃ (sol, 975 K) + 8SiO ₂ (sol, 975 K) + 7H ₂ O (g, 975 K) = Ca _{1.3} Na _{0.6} K _{0.8} Al ₄ Si ₆ O ₂₄ ·7H ₂ O (xl, 298 K)	(19)*
1.3CaO + 0.3Na ₂ O + 0.4K ₂ O + 2Al ₂ O ₃ + 8SiO ₂ + 7H ₂ O = Ca _{1.3} Na _{0.6} K _{0.8} Al ₄ Si ₆ O ₂₄ ·7H ₂ O	(20)
$\Delta H_{20} = \Sigma \Delta H_{9-19}$	

* Measured, this work.

** Enthalpy of formation of carbonate from oxides at 298 K (JANAF 1986) for Na₂CO₃; Kubaschewski (1991) for K₂CO₃; Robie et al. (1978) for CaCO₃.

† Heat content (Robie et al. 1978).

TABLE 6. Enthalpies of solution and drop solution of potassium and sodium oxides at 975 K in 2PbO·B₂O₃ melt

Method	$\Delta H_{\text{sol},975}$ (kJ/mol)	$\Delta H_{\text{drop},975}$ (kJ/mol)
Na₂O		
Na ₂ CO ₃	-170.78 ± 0.90	-113.10 ± 0.83
Drop solution (this study)	(this study)	(this study)
Na ₂ CO ₃	-172.21 ± 4.31	
Solution (Zygan et al. 1978)	(Zygan et al. 1978)	
NaAlO ₂	-170.79 ± 4.89	
Solution (Zygan et al. 1978)	(Zygan et al. 1978)	
Analcite		-116.7 ± 4.0
Solution (this study)		(this study)
K₂O		
K ₂ CO ₃	-260.98 ± 1.20	-193.68 ± 1.10
Drop solution (this study)	(this study)	(this study)
K ₂ CO ₃	-266.23 ± 3.14	
Solution (Zygan et al. 1978)	(Zygan et al. 1978)	
Sanidine		-196.0 ± 4.0
Solution (this study)		(this study)

icantly more negative than the enthalpy of formation of calcium leonhardite, as expected from the greater basicity of K₂O than of CaO. The enthalpy of formation of primary leonhardite from the elements is -14253.7 ± 13.5 kJ/mol. Throughout this paper, we use the formula Ca_{2-x}(K,Na)_{2x}Al₄Si₈O₂₄·nH₂O ($n = 7$ for natural samples) to report thermochemical data. In our companion paper (Kiseleva et al. 1996), we used a formula half as large (CaAl₂Si₄O₁₂·3.5H₂O) to make it easier to compare directly the energetics of different calcium zeolites (laumontite, leonhardite, wairakite, ugawaralite) on the basis of one mole of Ca. For leonhardite itself, the 2Ca, 7H₂O formula is a convenient and usual choice.

CALCULATION OF THE ENTROPY AND THE FREE ENERGY OF LEONHARDITE AND SOME GEOLOGIC APPLICATIONS

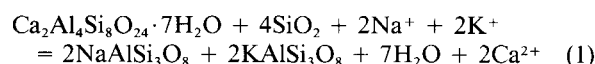
Low-temperature heat capacity and entropy at 298 K have been measured only for leonhardite (King and Weller 1961). From these data we can approximate the entropy of primary leonhardite using the entropies of substitutional oxides (2CaO = 1.3CaO + 0.3Na₂O + 0.4K₂O) taken from Robie et al. (1978) to be 956 J/(mol·K) (Table 6).

The calculated standard Gibbs free energies of formation from the elements for leonhardite and primary leon-

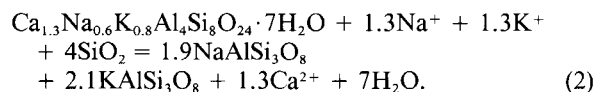
hardite are shown in Table 7. The substitution Ca = 2(Na,K) results in a more negative enthalpy and free energy of formation from oxides and elements.

The free-energy change for hydration of leonhardite is near zero ($\Delta G_{298}^0 = -26 \pm 20$ kJ/mol, Kiseleva et al. 1996). Belitsky and Bukin (1966) showed that keeping primary leonhardite in water for 15 d did not result in any further hydration, suggesting a positive standard free-energy change for hydration. Because the other H₂O molecules in primary leonhardite appear less tightly bound, it seems likely that the enthalpy of hydration for the additional H₂O would also be less exothermic.

Using the new thermodynamic data, we estimate conditions of leonhardite and primary leonhardite formation. We consider equilibrium in hydrothermal solutions of zeolites with alkali feldspars and quartz, which are always abundant in the wall rocks. The feldspars that coexist with both zeolites are represented by low albite and microcline because the temperature is well below the alkali feldspar solvus. The following reactions are considered:



and



Solutions acting in geothermal areas are dilute enough for water activity in the reaction to be equal to one, as are activities of solid decomposition products. The equilibrium constants may be calculated along the water-vapor saturation curve to 473 K using the following relationship:

$$-RT \ln K(T) = \Delta G_{\text{fs}(T)} + \Delta G_{\text{li}(T)} + \Delta G_{\text{f,H}_2\text{O}(T)}. \quad (3)$$

R is the gas constant, T is temperature in kelvins, $\Delta G_{\text{fs}(T)}$ is the Gibbs free energy of formation from the elements of the solid phases for reactions at T and 1 atm, $\Delta G_{\text{li}(T)}$ is the Gibbs free energy of formation of ions for the reaction, and $\Delta G_{\text{f,H}_2\text{O}(T)}$ is the Gibbs free energy of formation of liquid water at T and saturated vapor pressure. Thermodynamic data for ions and water were taken from Naumov et al. (1971), and for the solid phases from Robie et al. (1978). For microcline the revised data of Ber-

TABLE 7. Recommended values of thermodynamic properties of natural zeolites

Mineral	$\Delta H_{\text{dehyd},298,15}$	$\Delta H_{\text{f,ox},298,15}$ (kJ/mol)	$\Delta H_{\text{f,el},298,15}$	$S_{298,15}$ [J/(mol·K)]	$\Delta G_{\text{f},298,15}$ (kJ/mol)
Leonhardite	280.4 ± 13.3	-306.7 ± 7.1	-14214.6 ± 11.2	922.2*	-13165.3
Primary leonhardite	201.3 ± 13.1	-521.2 ± 10.5	-14253.7 ± 13.5	956** 979†	-13198.0† -13205.9†

* King and Weller (1961).

** Without configurational entropy, see text.

† With configurational entropy, see text.

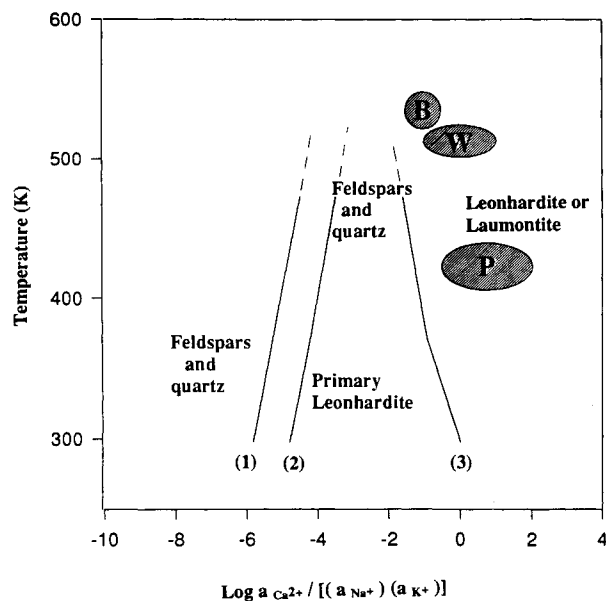


FIGURE 2. Equilibrium curves of zeolites in equilibrium with alkali feldspars and quartz at saturated water-vapor pressure. Curve 1 represents primary leonhardite, configurational entropy neglected; curve 2 represents primary leonhardite, configurational entropy included; curve 3 represents laumontite. The region to the left of each curve is the phase field of albite, orthoclase, and quartz, that to the right represents the stability field of the zeolites (with excess quartz). The shaded ovals are compositions of natural thermal waters from areas where calcium zeolites are formed in rocks: Pauzhetka (P) in Kamchatka, Russia, and Wairakei (W) and Broadlands (B) in New Zealand (Senderov 1980). The phase field shown for leonhardite or laumontite includes some fully hydrated laumontite at low T and low alkali content.

man (1988) were used, and the Gibbs free energy of formation of leonhardite and primary leonhardite were taken from this study. No experimental heat-capacity data are available for leonhardite and primary leonhardite. We assumed that ΔC_p of the solid phases is zero, which is reasonable for the P - T range considered. With these simplifications, the equilibrium constant is the ratio of the activity of the Ca ion to the activity of the alkali ions.

$$K(T) = a_{Ca^{2+}} / (a_{Na^+} a_{K^+}). \quad (4)$$

The calculated stability fields for leonhardite and primary leonhardite are shown in Figure 2. Two curves are shown for primary leonhardite. Curve 1 does not include any configurational entropy resulting from the mixing of Ca, Na, and K. Curve 2 assumes ideal mixing of Ca, Na, and K, which gives, for primary leonhardite of the composition studied, $Ca_{1.3}Na_{0.6}K_{0.8}Al_4Si_8O_{24} \cdot 7H_2O$,

$$S_{conf} = -2.7R(0.482 \ln 0.482 + 0.222 \ln 0.222 + 0.296 \ln 0.296) = 23.48 \text{ J}/(\text{mol} \cdot \text{K}). \quad (5)$$

Nonrandom distribution of cations over several inequivalent sites in the channels would lower the configurational entropy, but considering partial site occupancy and

TABLE 8. Preparation conditions of cation-exchanged forms

Sample	Salt	Expt. conditions		Autoclave conditions	
		T (K)	t (d)	T (K)	t (d)
Ca leonhardite	Ca(NO ₃) ₂	453	1	403	1
Na leonhardite	NaCNS	603	1	413	1
K leonhardite (no. 12)	KNO ₃	613	6	413	1
K leonhardite (no. 28)	KCNS	510	10	420	1
K leonhardite (no. 11)	KCNS	450	6	420	2
K leonhardite (no. 9)	KCNS	500	6	570	1

the mixing of cations and vacancies would raise it. Thus, the configurational entropy cannot be defined uniquely at present, but the above calculation probably gives the right order of magnitude. The effect of including the configurational entropy is to increase the stability of primary leonhardite by about an order of magnitude of activity ratio.

Figure 2 indicates that calcium leonhardite would form from alkali feldspars at 373–473 K at activity ratios of about 10^{-1} . Formation of primary leonhardite from alkali feldspars may be possible from more alkaline hydrothermal solutions with activity ratios of about 10^{-4} . The equilibrium relations between the calcium and alkali leonhardite and feldspars depend rather weakly on temperature.

Senderov (1980) reported chemical analyses of geothermal waters from which wairakei and laumontite form at Pauzhetka in Kamchatka, Russia, and at Wairakei and Broadlands, New Zealand. The calculated activity ratios are shown in Figure 2; they fall within the calculated stability field of laumontite.

Figure 2 shows that the calculated stability field of (alkali-free) laumontite overlaps the field of natural geothermal fluid compositions, but the calculated equilibrium curves of primary leonhardite lie rather far from Ca to alkali ratios in natural waters. This explains why primary leonhardite has rather limited occurrence (Senderov 1988). However, in natural assemblages there are many intermediate members of the Ca-Na-K series of leonhardite (Coombs 1952), which could form in a significantly wider range of conditions.

THERMODYNAMIC PROPERTIES OF CATION-EXCHANGED LEONHARDITE

A sample of natural leonhardite (River Nidym, Siberia, Russia) has been used for the exchange $Ca^{2+} = 2M^+$ (where $M = Li, Na, K, Cs, Tl, Ag$) under equilibrium conditions

TABLE 9. Calorimetric data for cation-exchanged forms of leonhardite

Cation-exchanged material	Formula weight	ΔH_{dissol} (kJ/mol)
Ca leonhardite	928.2	1312.8 ± 6.8(7)
Na leonhardite	906.40	1194.8 ± 7.8(6)
K-Ca leonhardite (no. 12)	889.13	1021.2 ± 8.7(9)
K-Ca leonhardite (no. 28)	885.02	1034.0 ± 7.2(5)
K-Ca leonhardite (no. 9)	906.7	1121.6 ± 3.2(6)
K-Ca leonhardite (no. 11)	909.6	1216.9 ± 5.3(6)

TABLE 10. The enthalpies of formation from oxides of cation-exchanged forms at 298 K

Cation-exchanged form	Ca _{2-x} (K,Na) _{2x} Al ₄ Si ₆ O ₂₄ ·H ₂ O			H ₂ O (mol)	$\Delta H_{f,ox}$ (kJ/mol)
	Ca	Na	K		
Ca leonhardite	2	0	0	7.3	-315.3 ± 7.8*
	2	0	0	7.0	-306.6 ± 7.0*
Na leonhardite	0.4	3.0	0.1	5.6	-465.9 ± 8.5**
K leonhardite	1.1	0.1	2.1	2.6	-545.1 ± 9.4**

* Kiseleva et al. (1996).
** This work.

at various temperatures (Belitsky and Fedorov 1978). The authors of that study showed that the extent of exchange in molten salts depends upon the exchange ion and the treatment temperature. The degree of exchange decreased as the ionic radius of the substituting alkali ion increased. The maximum degree of substitution for Ca²⁺ reaches 60% at 413 K; over the range 413–513 K the degree of exchange does not change (Belitsky and Fedorov 1978). The dynamic exchange capacity of laumontite and of Na-, K-, NH₄-, Mg-, and Ba-exchanged forms obtained in aqueous salt solutions was studied by Tsitsishvili et al. (1992). They showed that the Na form of laumontite can be used as an effective adsorbent for transition metal ions.

In this study K-, Na-, and Ca-exchanged forms of leonhardite were prepared from the natural leonhardite described above by ion exchange in nitrate melts (see Table 8). Experimental products were washed in hot water and then annealed in an autoclave with distilled water to remove any excess salts and to rehydrate the zeolites. Chemical compositions of these samples are shown in Table 1. The cation substitution for K-Ca samples generally corresponds to the Ca²⁺ = 2K⁺ reaction. H₂O content clearly depends on the cation content. The K-rich leonhardite samples have a high K content with 2K/(2K + Ca) = 0.41–0.48. Fedorov and Belitsky (1975) showed that samples with >20% of the Ca substituted by K are two-phase mixtures. The X-ray diffraction patterns of samples 9, 11, and 28 in this study confirm this observation, but sample 12, which has the highest K content and very low H₂O content, appears to be a single phase. Thermal analysis showed that while the Ca- and Na-exchanged leonhardite samples lose water in three distinct steps, the K-exchanged forms lose water at 100 K lower and in one broad step.

These samples pose several difficulties for calorimetric study. The natural leonhardite starting materials vary in their cationic compositions and are heterogeneous, making it impossible to obtain a fully exchanged form. H₂O content decreases with increasing cation size from Ca (14 moles) to K (5 moles). There may also be small differences in the Si/Al ratio in the framework. Nevertheless, an exploratory drop-solution calorimetric study of these samples proved useful.

The heats of drop solution of Ca-, Na-, and Ca-K-exchanged forms of natural leonhardite are summarized in Table 9. The statistical errors reported are on the order of ±0.5%, indicative of problem-free calorimetry. The enthalpies of formation from the oxides and the elements of Ca-, Na-, and Ca-K-exchanged forms were calculated (see Table 10). The thermochemical cycles used were analogous to that for primary leonhardite but correspond to the stoichiometry of these samples.

The entropies of cation-exchanged forms of leonhardite were estimated from the entropies of substitutional oxides taken from Robie et al. (1978), and the entropy of water was estimated from the entropy of leonhardite experimentally determined by King and Weller (1961) (see Table 11). Standard Gibbs free energies of formation are also shown in Table 11. These do not include configurational entropy contributions.

The Ca²⁺ exchange by Na⁺ in leonhardite is endothermic, but the exchange for the cation of larger size, K⁺, is exothermic. Generally, H₂O content decreases with increasing ionic radius of the cation. Cations, such as K, having ionic radii significantly greater than that of Ca, possibly cause a framework deformation and occupy a significant fraction of the volume otherwise available to H₂O. Such cations may prevent mobility of H₂O within the channels.

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REFERENCES CITED

- Barany, R. (1961) Heats and free energies of formation of some hydrated and anhydrous sodium- and calcium-aluminum silicates. U.S. Bureau of Mines, 5900, 1–18.
Belitsky, I.A., and Bukin, G.U. (1966) Study of laumontite, alpha and beta leonhardite. In *Materials in Genetic and Experimental Mineralo-*

TABLE 11. Thermodynamic properties of cation-exchanged forms of leonhardite

Cation-exchanged form	$\Delta H_{f,ox,298,15}$ (kJ/mol)	$\Delta H_{f,el,298,15}$	S_{298} [J/(mol·K)]	$\Delta G_{f,el,298}$ (kJ/mol)
Ca leonhardite (Ca _{2.0} Al ₄ Si ₆ O ₂₄ ·7.3H ₂ O)	-315.3 ± 7.8	-14309.0 ± 11.5	940	-13246
Na leonhardite (Na _{3.0} K _{0.1} Ca _{0.4} Al ₄ Si ₆ O ₂₄ ·5.6H ₂ O)	-465.9 ± 8.5	-13598.2 ± 12.0	896*	-12611*
K leonhardite (K _{2.1} Na _{0.1} Ca _{1.1} Al ₄ Si _{7.9} O ₂₄ ·2.6H ₂ O)	-545.1 ± 9.4	-12933.1 ± 12.6	727*	-12102*

* Neglecting possible configurational entropy.

- gy, Siberian Branch of the Academy of Sciences of the USSR, 4, 91–115.
- Belitsky, I.A., and Fedorov, I.I. (1978) The cation behavior in (Al, Si)-O laumontite framework. In *Experimental Investigation of Minerals*, Institute of Geology and Geophysics, Siberian Branch of the Academy of Sciences of the USSR, 74–80 (in Russian).
- Berman, R.G. (1988) Internally-consistent thermodynamic data for minerals in $\text{Na}_2\text{O}-\text{K}_2\text{O}-\text{CaO}-\text{MgO}-\text{FeO}-\text{Fe}_2\text{O}_3-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{TiO}_2-\text{H}_2\text{O}-\text{CO}_2$. *Journal of Petrology*, 29, 445–522.
- Chai, L., and Navrotsky, A. (1993) Thermochemistry of carbonate-pyroxene equilibria. *Contributions to Mineralogy and Petrology*, 114, 139–147.
- Coombs, D.S. (1952) Cell size, optical properties and chemical composition of laumontite and leonhardite. *American Mineralogist*, 37, 812–830.
- Fedorov, I.I., and Belitsky, I.A. (1975) The change of Ca for monovalent ions in laumontite. In *Experimental Investigation of Minerals*, Institute of Geology and Geophysics, Siberian Branch of the Academy of Sciences of the USSR, 89–95 (in Russian).
- Fersman, A.E. (1909) Etudes sur les zeolites de la Russie: 1. Leonhardite et laumontite dans les environs de Simferopolis (Crimee). *Travail Musee Geologique Pierre Le Grand, Academie Imperiale Scientifique, Petersburg, Russia*, 2, 103–150.
- Hovis, G.L., and Navrotsky, A. (1995) Enthalpies of mixing for disordered alkali feldspars at high temperature: A test of regular solution thermodynamic models and a comparison of hydrofluoric acid and lead borate solution calorimetric techniques. *American Mineralogist*, 80, 280–284.
- JANAF (1986) JANAF thermodynamics tables (3rd edition). American Institute of Physics, New York.
- King, E.G., and Weller, W.W. (1961) Low-temperature heat capacities and entropies at 298.15 K of some sodium- and calcium-aluminum silicates. U.S. Bureau of Mines Report of Investigation, 5855, 1–8.
- Kiseleva, I., Navrotsky, A., Belitsky, I.A., and Fursenko, B.A. (1996) Thermochemistry and phase equilibria in calcium zeolites. *American Mineralogist*, 81, 658–667.
- Kubaschewski, O.O., Knacke, O., and Hesselman, H., Eds. (1991) *Thermochemical properties of inorganic substances*, 182 p. Springer-Verlag, Berlin.
- Naumov, G.B., Ryzhenko, B.N., and Khodakovskiy, I.L. (1971) Handbook of thermodynamic data, 328 p. Atomizdat, Moscow, Russia.
- Navrotsky, A. (1977) Progress and new directions in high temperature calorimetry. *Physics and Chemistry of Minerals*, 2, 89–104.
- Navrotsky, A., Rapp, R.P., Smelik, E., Burnley, P., Circone, S., Chai, L., Bose, K., and Westrich, H.R. (1994) The behavior of H_2O and CO_2 in high-temperature lead borate solution calorimetry of volatile-bearing phases. *American Mineralogist*, 79, 1099–1109.
- Pipping, F. (1966) The dehydration and chemical composition of laumontite. *Mineral Society, India IMA*, 1, 159–166.
- Robie, R.A., Hemingway, B.S., and Fisher, J.R. (1978) Thermodynamic properties of minerals and related substances at 298.15 K and 1 bar (10⁵ Pascals) pressure and at higher temperatures. U.S. Geological Survey Bulletin 1452, 456 p.
- Robie, R.A., and Hemingway, B.S. (1995) Thermodynamic properties of minerals and related substances at 298.15 K and 1 bar (10⁵ pascals) and at higher temperatures. U.S. Geological Survey Bulletin 2131, 461 p.
- Senderov, E.E. (1980) Estimation of Gibbs energy for laumontite and wairakite from conditions of their formation in geothermal areas. *Proceedings of the Fifth International Conference on Zeolites*, June 2–6, Naples, Italy.
- (1988) Physical-chemical aspects of zeolite formation in nature. In *Occurrence, Properties and Utilization of Natural Zeolites*, 111, 147 p.
- Tsitsishvili, G.V., Andronikashvili, T.G., Kirov, G.N., and Filizova, L.D. (1992) *Natural zeolites*, 295 p. Market Cross House, U.K.
- Yamazaki, A., Shiraki, T., Mishido, H., and Otsuka, R. (1991) Phase change of laumontite under relatively humidity-controlled conditions. *Clay Science*, 8, 79–86.
- Zygan, V.N., Kesler, Y.A., Gordeev, I.V., and Tretyakov, Y.D. (1978) Thermochemistry of solution of alkali metal-containing oxide phases. *Neorganicheskie Materialy*, 14(6), 1987–1989.

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