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Thermochemistry and phase equilibria in calcium zeolites

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ABSTRACT

Thermodynamic properties of the natural calcium zeolites laumontite, leonhardite, dehydrated leonhardite (metaleonhardite), wairakite, and yugawaralite were studied by calorimetry in lead borate solvent at 975 K. Enthalpies of formation from the elements at 298 K are as follows: -7251.0 ± 8.5 kJ/mol for laumontite, $CaAl_2Si_4O_{12}\cdot 4H_2O$; -7107.3 ± 5.6 kJ/mol for leonhardite, $CaAl_2Si_4O_{12}\cdot 3.5H_2O$; -5964.3 ± 5.1 kJ/mol for metaleonhardite, $CaAl_2Si_4O_{12}$; -6646.7 ± 6.3 kJ/mol for wairakite, $CaAl_2Si_4O_{12}\cdot 2H_2O$; and -9051.3 ± 10.4 kJ/mol for yugawaralite, $CaAl_2Si_6O_{16}\cdot 4H_2O$. The value for leonhardite is in good agreement with early values from acid calorimetry (Barany 1961) but not with revised values from Hemingway and Robie (1977). The enthalpy of dehydration of leonhardite is 140.2 ± 6.7 kJ/mol, and the loss of one mole of H_2O is associated with an endothermic effect of about 40 kJ. Standard entropies, S^0_{298}, of wairakite [400.7 J/(mol·K)] and yugawaralite [609.8 J/(mol·K)] were derived from our new enthalpy data combined with reversed *P-T* phase equilibria (Liou 1971; Zeng and Liou 1982). The upper limit of wairakite stability, the univariant curve for equilibrium of wairakite with anorthite, quartz, and fluid, was calculated from these values of enthalpy and entropy. Good agreement between thermodynamic calculations and reversed phase equilibria supports the reliability of the new thermodynamic data.

INTRODUCTION

Calcium zeolites are common in diagenetic, sedimentary, hydrothermally altered, and low-grade metamorphic environments. The major zeolites encountered are laumontite ($CaAl_2Si_4O_{12}\cdot 4H_2O$), leonhardite ($CaAl_2Si_4O_{12}\cdot 3.5H_2O$), which is the partially dehydrated form of laumontite, wairakite ($CaAl_2Si_4O_{12}\cdot 2H_2O$), which is the Ca analog of analcime, and yugawaralite ($CaAl_2Si_6O_{16}$). Laumontite phase equilibria are especially important for *P-T* boundaries of zeolite metamorphic facies (laumontite facies). Laumontite and wairakite are the index minerals of the zeolite facies.

P-T stability relations in the system $CaAl_2Si_2O_8$-SiO_2-H_2O have been investigated both experimentally and by thermodynamic calculations (Coombs et al. 1959; Koizumi and Roy 1960; Liou 1970, 1971; Thompson 1970; Zeng and Liou 1982; Senderov 1980, 1988; Ivanov and Gurevich 1975). Despite extensive experimental work, some of the zeolite phase relations have not been satisfactorily determined because of low rates of reactions under low-temperature conditions and because of the formation of metastable phases in experiments of short duration. Many experiments report only synthesis and not reversals; hence, estimations of free energies are uncertain. Thermodynamic data obtained from experimental equilibria, estimated from *P-T* data in contemporary geothermal systems, and calculated from various thermodynamic data sets show wide scatter. Thus, direct calorimetric measurement of enthalpies of formation of calcium zeolites and related minerals is desirable.

No calorimetric data exist for the enthalpies and entropies of laumontite, wairakite, and yugawaralite. The enthalpy of formation of leonhardite was obtained by Barany (1961) using hydrofluoric-acid calorimetry and later revised by Hemingway and Robie (1977). Low-temperature heat capacity and entropy of leonhardite were measured by King and Weller (1961). All published thermodynamic data for wairakite, laumontite, and yugawaralite were estimated or calculated from phase equilibrium studies and are not consistent. For instance, the standard entropy values for wairakite given by Helgeson et al. (1978) and by Glushko (1981) differ by about 80 J/(mol·K).

Several studies (Kiseleva and Ogorodova 1983; Circone and Navrotsky 1992; Smelik et al. 1994; Navrotsky et al. 1994) have shown that oxide melt solution calorimetry can determine the enthalpies of formation of hydrous minerals. The present work uses drop-solution calorimetry in molten $2PbO\cdot B_2O_3$ to measure the enthalpies of formation of natural laumontite, metaleonhardite (dehydrated laumontite), leonhardite, wairakite, and yugawaralite. The enthalpy of dehydration in the laumontite-leonhardite-metaleonhardite series was studied by transposed temperature-drop calorimetry. Stability relations of wairakite, yugawaralite, and leonhardite and the upper temperature limit for wairakite stability were calculated on the basis of these thermochemical data.

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TABLE 1. Chemical analyses and formulas of zeolites studied

	Leonhardite	Wairakite	Yugawaralite
	Chemical analysis (wt%)		
SiO_2	51.72	55.20	61.78
TiO_2	0.01	0.00	0.01
Al_2O_3	21.93	23.08	17.01
MnO	0.09	0.00	0.00
MgO	0.04	0.01	0.01
CaO	12.14	12.48	9.35
Na_2O	0.05	0.01	0.02
K_2O	0.13	0.02	0.01
P_2O_5	0.11	—	—
H_2O*	13.67	8.44	11.98
Total	99.98	99.23	100.25
	Cations and H_2O molecules per unit cell		
Si	15.96 (16)**	32.17 (32)	12.08 (12)
Ti	0.00	0.00	0.00
Al	7.98 (8)	15.86 (16)	3.92 (4)
Mn	0.02	0.00	0.00
Mg	0.02	0.01	0.00
Ca	4.02 (4)	7.79 (8)	1.96 (2)
Na	0.03	0.06	0.00
K	0.05	0.01	0.00
P	0.03	—	—
H_2O	14.07 (14)	16.41 (16)	7.80 (8)

* H_2O contents also verified by thermogravimetric analysis.

** Values in parentheses represent ideal molar ratios.

ZEOLITE CHARACTERIZATION

We chose well-crystallized natural samples of laumontite, wairakite, and yugawaralite. The laumontite is from Nidym River (left tributary of Nizhnyaya Tunguska River), Siberia. White to pinkish nontransparent crystals up to 10 mm in length were separated from hydrothermal veins in Triassic basalts.

Wairakite from Bondai-Atami, Koriyama City, Japan (Mineralogical Museum of the Russian Academy of Sciences, catalog no. 87622), was provided by A.A. Godovikov. It had been separated under a microscope from an aggregate of white semitransparent crystals with some admixture of quartz and calcite. Clean, transparent, colorless tabular crystals were used.

Yugawaralite from Obora Toi-cho, Shizuoko Prefecture, Japan (Mineralogical Museum of the Russian Academy of Sciences, catalog no. 87616), was provided by A.A. Godovikov. Transparent and semitransparent colorless platy crystals up to 1–2 mm in dimension from the central parts of the small veins (10–15 mm thick) in hydrothermally altered brecciated volcanic rock were chosen.

Leonhardite was chemically analyzed by X-ray fluorescence using a Carl Zeiss VRA 20R instrument. Wairakite and yugawaralite were analyzed by electron microprobe (Camebax MICRO). Table 1 shows the analytical data.

High-temperature thermal behavior was studied using a TA 3000 (Mettler) thermoanalyzer consisting of a thermogravimeter (293–1273 K), a scanning calorimeter (103–873 K), and a differential dilatometer (173–1273 K). The thermograms are similar to those published by Gottardi and Galli (1985) and are discussed further below.

TABLE 2. Lattice parameters of zeolites

a (Å)	*b* (Å)	*c* (Å)	*β* (°)	*V* (Å³)	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
		Wairakite			
13.700 (15)	13.666 (9)	13.559 (10)	90.44 (8)	882.9 (8)	1
13.692 (3)	13.643 (3)	13.560 (3)	90.50 (10)		4
		Yugawaralite			
6.728 (5)	14.007 (6)	10.049 (9)	111.20 (4)	882.9 (8)	1
6.729	14.008	10.050	111.18		5

Note: For unit cells on the basis of 48 (leonhardite), 96 (wairakite), and 32 (yugawaralite) O atoms in the framework. Values in parentheses represent confidence interval (for 95% probability). References are as follows: 1 = this work, 2 = Pipping (1966), 3 = Yamazaki et al. (1991), 4 = Takéuchi et al. (1979), and 5 = Eberlein et al. (1971).

Lattice parameters of samples studied are shown in Table 2. They agree well with previous studies (Gottardi and Galli 1985).

CALORIMETRY

The enthalpies of formation and dehydration were determined using a Tian-Calvet high-temperature heat-flux microcalorimeter described in detail by Navrotsky (1977). Drop-solution calorimetric methods (Chai and Navrotsky 1993; Navrotsky et al. 1994) were chosen to avoid decomposition of zeolites at the calorimeter temperature prior to dissolution. The samples were dropped from room temperature into molten $2PbO \cdot B_2O_3$ at 975 K. Most calorimetric experiments were performed using pressed pellets about 3 mm in diameter, 0.5–1 mm in height, and 10–25 mg in weight. A few experiments used pieces of single crystals. The heat of drop solution was a sum of the heat of solution in the melt plus the heat content $(H^0_{975} - H^0_{298})$.

Heats of dehydration and heat contents at 975 K were obtained using transposed temperature-drop calorimetry (sample dropped into an empty platinum crucible equilibrated in the calorimeter). The heat effect contained two contributions, the enthalpy of dehydration at 975 K and the heat content of the mineral $(H^0_{975} - H^0_{298})$. When the solid decomposition products were dropped into the calorimeter, the heat effect contained only the heat content $(H^0_{975} - H^0_{298})$ of the dehydrated zeolite.

We were concerned that when the small samples used in this study were dropped into the calorimeter, the heat picked up during the drop, before the sample reached the region of the thermopile, might be a different fraction of the total heat effect than seen for more massive platinum-encapsulated samples, for 30–50 mg pellets, or for platinum calibration pieces weighing about 200 mg. Rather than using such large platinum pieces for calibration in the usual procedure (Navrotsky 1977), we chose to calibrate using corundum pellets of weight similar to that of the samples. The corundum (Johnson Matthey 99.999%)

TABLE 3. Results of calorimetric experiments at 975 K

			Observed enthalpy			
			Drop**		Dropsol†	
Mineral	Formula	F.W.*	(J/g)	(kJ/mol)	(J/g)	(kJ/mol)‡
Laumontite	$CaAl_2Si_4O_{12} \cdot 4H_2O$	470.44	1502.8 ± 13.2(9)	707.0 ± 6.2(9)		
Leonhardite	$CaAl_2Si_4O_{12} \cdot 3.5H_2O$	461.44	1450.6 ± 13.1(6)	669.4 ± 6.0(6)	1390.8 ± 6.4(9)	641.8 ± 3.0(9)§
Dehydrated leonhardite (metaleonhardite)	$CaAl_2Si_4O_{12}$	398.39	722.3 ± 7.0(7)	287.8 ± 2.8(7)	646.9 ± 4.9(6)	257.7 ± 2.0(6)§
Wairakite	$CaAl_2Si_4O_{12} \cdot 2H_2O$	434.41			1171.3 ± 9.7(10)	(508.8 ± 4.2(10)§) 506.4 ± 4.2(10)‖
Yugawaralite	$CaAl_2Si_6O_{16} \cdot 4H_2O$	590.62			1235.1 ± 13.5(7)	(729.5 ± 8.0(7)§) 734.2 ± 8.0(7)‖
Corundum	Al_2O_3	101.96			1058.6 ± 9.6(8)	107.9 ± 1.0(8)§
Quartz	SiO_2	60.08	715.0 ± 5.3(12)	43.0 ± 0.3(12)	551.3 ± 5.2(9)	39.1 ± 0.3(9)§
Calcite	$CaCO_3$	100.09			1931.8 ± 6.8(10)	193.4 ± 0.7(10)§

* F.W. = gram formula weight.

** Drop = transposed temperature-drop calorimetry, no solvent present.

† Dropsol = drop solution into $2PbO \cdot B_2O_3$ solvent.

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

§ Assuming ideal stoichiometry.

‖ Corrected for nonideal H_2O content; this is the preferred value.

was heated at 1773 K for 15 h to ensure dryness, crystallinity, and complete conversion to α-Al_2O_3. The calibration factor obtained (using $H^0_T - H^0_{298}$ from the National Bureau of Standards Certificate, 1982) for corundum was indeed about 2% higher than that obtained for the same calorimeter using large platinum pieces. We believe that this modified calibration method better reflects the conditions used in the present experiments. For the calibrations, an uncertainty of about ±0.5% (two standard deviations of the mean) was obtained.

Because laumontite is not stable at room temperature in air, it was obtained from leonhardite by keeping the sample in water-saturated conditions for 10–16 h. Laumontite with a little excess water (not more than 6×10^{-5} mole H_2O per mole laumontite) was wrapped in a small platinum capsule and dropped from room temperature into an empty platinum crucible in the calorimeter. The measured heat effect contained four contributions: the enthalpy of dehydration at 975 K, the heat content of the mineral, the platinum capsule heat content, and the excess water heat content. Using platinum capsules introduced the need for additional calibration by dropping empty platinum capsules. The platinum heat content was 10–12% of the total measured heat effect, and the excess water heat effect was about 2%.

All experiments were performed under a dry-air atmosphere flowing through the calorimeter at 30–40 cm^3/min. Navrotsky et al. (1994) showed that calorimetry under flowing gas results in a negligible enthalpy of interaction between the evolved H_2O and the solvent. Under flowing gas conditions we have been able to obtain reproducible results with excellent baseline stability.

$CaCO_3$, rather than CaO, was used as the Ca reference material because pellets of CaO did not dissolve reproducibly and showed evidence of partial hydration. Chai and Navrotsky (1993) showed that $CaCO_3$ can be used reliably for calorimetric purposes under flowing atmosphere at 975 K. The calcite (Aldrich, 99.995%) and quartz (Fluka, >99.9%) were commercial products, dried at 383 K prior to calorimetry.

CALORIMETRIC RESULTS

Calorimetric data are summarized in Table 3. 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 (in joules per gram or kilojoules per mole) varied with sample mass. This consistency, see Figure 1, indicates proper equipment performance and reproducible sample dissolution. 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 cleanly to the original baseline in almost all experiments. The statistical errors reported (two standard deviations of the mean) are ±1% or better, which also indicates problem-free dissolution.

Table 4 compares the enthalpies of drop solution, solution, and transposed temperature drop obtained for corundum, quartz, and calcite in this work with values from previous studies at the same temperature. In general the agreement is good. Our value for the enthalpy of drop solution of calcite is slightly higher than that of Chai and Navrotsky (1993); this may reflect the difference between using calibration factors based on small alumina pellets and large platinum pieces. However, similar differences are not seen for quartz and corundum. We note that both solution calorimetry and drop-solution calorimetry on quartz and corundum are frequently performed in our laboratory to train new users and check calorimeter operation; this accounts for the large amount of unpublished data in Table 4. Because the enthalpy of solution of quartz

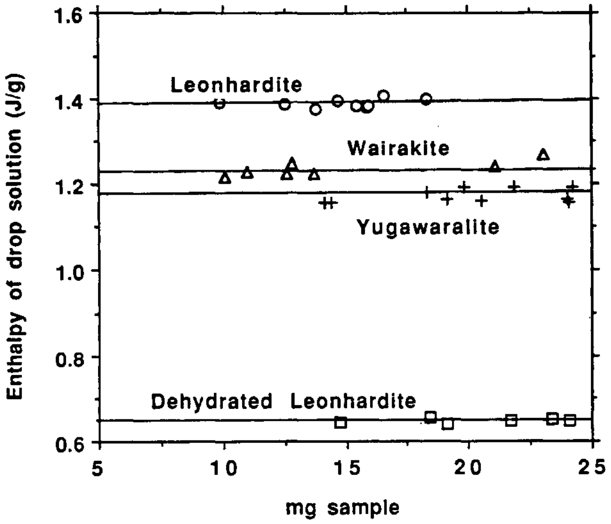

Figure 1. Observed enthalpy of drop solution vs. mass of sample used for leonhardite, wairakite, and yugawaralite.

appears to depend significantly on temperature, only data at 973–978 K are included in Table 4. Lastly, we note considerable scatter in the tabulated heat contents of quartz; this largely reflects the different ways of treating the energetics of the α-β transition.

Table 4. Comparison of enthalpies of drop solution of quartz, corundum, and calcite obtained at various times in this laboratory

Drop solution	Solution	Transposed temperature drop (heat content)
	Corundum, α-Al_2O_3	
107.9 ± 1.0[a]	33.5 ± 0.8[b]	74.3 ± 0.4[a]
107.4 ± 2.1[c]	33.0 ± 0.8[d]	74.2 ± 0.8[e]
107.9 ± 0.7[f]	32.8 ± 0.3[g]	75.3[h]
	(33.6 ± 1.0)[i]	
	Quartz, SiO_2	
39.1 ± 0.3[a]	−4.3 ± 0.2[e]	43.0 ± 0.3[a]
40.0 ± 0.2[j]	−4.3 ± 0.2[i]	42.3[k]
39.3 ± 0.4[e]	−3.9 ± 0.4[g]	44.0[l]
		45.1[m]
	Calcite, $CaCO_3$	
193.4 ± 0.7[a]		
189.9 ± 0.7[j]		

Note: a = this work, alumina calibration; b = Brown and Navrotsky (1989, unpublished), Pt calibration; c = Tinker and Navrotsky (1993, unpublished), Pt calibration; d = Hovis and Navrotsky (1994, unpublished), Pt calibration; e = Petrovic and Navrotsky (1994, unpublished), Pt calibration; f = Gerardin et al. (1994), Pt calibration; g = calculated as enthalpy of drop solution minus enthalpy of transposed temperature drop, this work; h = Robie et al. (1978), values for corundum similar in other tabulations; i = Ellison and Navrotsky (1992), Pt calibration; j = Chai and Navrotsky (1993), Pt calibration; k = Berman (1988), Holland and Powell (1990); l = Richet et al. (1982); and m = Hemingway (1987).

ENTHALPIES OF DEHYDRATION OF LEONHARDITE AND LAUMONTITE

The enthalpy of dehydration of leonhardite may be calculated (see thermodynamic cycle A in the Appendix Table). For the reaction

$$CaAl_2Si_4O_{12}\cdot 3.5H_2O\ (\mathrm{xl},\ 298\ \mathrm{K}) = CaAl_2Si_4O_{12}\ (\mathrm{xl},\ 298\ \mathrm{K}) + 3.5H_2O\ (\mathrm{l},\ 298\ \mathrm{K}),\quad \Delta H = 140.2 \pm 6.7\ \mathrm{kJ/mol}. \tag{1}$$

The enthalpy of dehydration of laumontite (see cycle B) is given by

$$CaAl_2Si_4O_{12}\cdot 4H_2O\ (\mathrm{xl},\ 298) = CaAl_2Si_4O_{12}\ (\mathrm{xl},\ 298) + 4H_2O\ (\mathrm{l},\ 298),\ \Delta H = 143.4 \pm 6.8\ \mathrm{kJ/mol}. \tag{2}$$

The enthalpy of partial dehydration of laumontite to leonhardite is represented by

$$CaAl_2Si_4O_{12}\cdot 4H_2O\ (\mathrm{xl},\ 298\ \mathrm{K}) = CaAl_2Si_4O_{12}\cdot 3.5H_2O\ (\mathrm{xl},\ 298\ \mathrm{K}) + 0.5H_2O\ (\mathrm{l},\ 298\ \mathrm{K}). \tag{3}$$

Its enthalpy (see cycle C) is 3.2 ± 4.6 kJ/mol. This value is essentially zero.

Because this reversible transition takes place in air at near room temperature, Crawford and Fyfe (1965) suggested that the free-energy change of this reaction is extremely small, not exceeding a few hundred joules. If we assume that ΔG^0 for the laumontite-leonhardite reaction is zero, we can calculate its enthalpy change using entropy values from Helgeson et al. (1978). The estimated enthalpy change is 3.1 kJ/mol, in excellent agreement with experimental data. Thus, our experiments show that the loss of H_2O from laumontite at room temperature is indeed associated with a very small endothermic effect of about 6 kJ/mol H_2O lost. In contrast, the dehydration of leonhardite is associated with more significant endothermic effects (about 40 kJ/mol H_2O).

The enthalpy of dehydration of the sodium zeolite analcime was measured by acid calorimetry by Barany (1961), who obtained about 30 kJ/mol H_2O, similar to our value for leonhardite. However, such comparisons can be misleading. Dehydration is a very complicated process that can occur continuously or stepwise and may be accompanied by changes in the aluminosilicate framework. For example, as shown by Belitsky et al. (1992, 1993), dehydration can be followed by compression of the crystal structure owing to framework polyhedral tilting. Different zeolite frameworks deform differently and have different positions of the H_2O molecules within the channels. Thus, the dehydration process related to such structural changes may be accompanied by different energy effects.

Yakubovich and Simonov (1985) refined the crystal structure of leonhardite, giving it the structural formula $Ca(H_2O)_{2.8}(Al_2Si_4O_{12})\cdot 0.5H_2O$ to represent better the different roles of H_2O in the crystal structure. Four positions were occupied by H_2O molecules. Our differential scanning calorimetry (DSC) and differential thermogravimetry curves show three peaks, but the third peak is asymmetric and its high-temperature shoulder may be related to removal of the most tightly bonded H_2O molecules.

Using DSC we measured the total heat effects associated with dehydration of leonhardite, $CaAl_2Si_4O_{12} \cdot 3.5H_2O$, from 298 to 863 K to be about 139 kJ/mol, which agrees with the value measured by transposed temperature calorimetry (143 kJ/mol). DSC measurements show the disproportionate distribution of energy into several peaks. The first peak reflects the loss of weakly bonded zeolitic water without changes in the Al-Si framework and has a small heat effect corresponding to about 6–8% of the total heat of dehydration. The second peak represents removal of H_2O molecules bonded to both framework O atoms and Ca and comprises about 20% of the total heat effect. The third peak is related to loss of water from the Ca coordination sphere and the formation of a metastable dehydrated phase, accompanied by changes in the framework structure. It accounts for 70–80% of the total energy. The loss of one mole of H_2O during the first and the second peaks has an endothermic effect about 10–20 kJ/mol, but removing H_2O molecules from the Ca coordination sphere requires about 70–80 kJ/mol.

The enthalpy of dehydration of yugawaralite was evaluated only by DSC to be about 150 kJ/mol $CaAl_2Si_6O_{16} \cdot 4H_2O$, or about 37.5 kJ/mol H_2O. Kerr and Williams (1969) found four water sites, each with 75% occupancy and each linked to a Ca site. All hydrogen bonds were described as long or very long. The DSC curve shows three main peaks, but the third peak, as for leonhardite, has an asymmetric high-temperature shoulder. The first peak (about 10–15% of the total heat effect) presumably corresponds to loss of weakly bonded H_2O molecules with the longest hydrogen bonds. The loss of one mole of such H_2O requires 5–20 kJ. The second peak corresponds to 15–20% of the total heat effect with an endothermic effect of about 10–20 kJ/mol H_2O. The third peak (about 70% of the total heat effect) probably corresponds to the removal of H_2O molecules with shorter hydrogen bonds. This is associated with a larger endothermic effect of about 70 kJ/mol.

ENTHALPIES OF FORMATION OF CALCIUM ZEOLITES

Leonhardite and metaleonhardite

The enthalpy of formation of leonhardite from the oxides at 298 K was calculated using two thermochemical cycles for the reaction

$$CaO + Al_2O_3 + 4SiO_2 + 3.5H_2O = CaAl_2Si_4O_{12} \cdot 3.5H_2O. \tag{4}$$

One uses the enthalpy of drop solution of leonhardite and of constituent oxides (see cycle D). The second cycle (E) is used to derive the enthalpy of formation of leonhardite and metaleonhardite. It involves dehydration and subsequent dissolution of fully dehydrated samples.

The enthalpy of formation of leonhardite from the oxides at 298 K is −153.3 ± 3.5 kJ/mol using the first cycle and −150.9 ± 7.2 kJ/mol using the second cycle. Because the first cycle requires fewer steps, it yields a value with smaller uncertainty and we adopt this as our preferred value. The agreement between the first and second cycles indicates the overall consistency of the data.

Per mole H_2O, the difference between the enthalpies of formation obtained from the first and second cycles is 0.7 ± 2.3 kJ/mol. Because the second cycle does not use any reactions that dissolve a hydrous phase in lead borate, whereas the first cycle does, their good agreement once more validates the methodology of drop-solution calorimetry under flowing atmosphere for volatile-bearing phases (Navrotsky et al. 1994).

The standard enthalpy of formation of leonhardite from oxides obtained in this work is −153.3 ± 3.5 kJ/mol. This agrees within experimental error with the value of −154.2 ± 2.7 kJ/mol (Barany 1961) previously obtained from solution calorimetry in aqueous hydrofluoric acid for a natural sample with slightly higher (by 0.33%) water content. Later, Hemingway and Robie (1977) recalculated Barany's data. They considered that the enthalpy of formation of gibbsite, $Al(OH)_3$, obtained by Barany and Kelley (1961) was incorrect and that the heat of solution value used for α-quartz refers to very small particles. They revised Barany's data and recommended a value of −169.2 ± 3.5 kJ/mol for the enthalpy of formation. Our new determination supports the original rather than the revised HF value.

For the formation of metaleonhardite (fully dehydrated leonhardite),

$$CaO + Al_2O_3 + 4SiO_2 = CaAl_2Si_4O_{12}, \quad \Delta H = -10.7 \pm 2.8 \text{ kJ/mol} \tag{5}$$

(see cycle F). Thus, the dehydrated zeolite has only a rather modest energetic stability with respect to the oxides and is metastable with respect to other anhydrous phase assemblages. For the reaction (see cycle G)

$$CaAl_2Si_4O_{12} \text{ (metaleonhardite)} = CaAl_2Si_2O_8 \text{ (anorthite)} + 2SiO_2 \text{ (quartz)}, \quad \Delta H = -78.7 \text{ kJ/mol}. \tag{6}$$

On the basis of two moles of O ($Ca_{1/6}Al_{1/3}Si_{2/3}O_2$), metaleonhardite is only 13.1 kJ/mol higher energetically with respect to its stable phase assemblage of anorthite + quartz. Petrovic et al. (1993) found that a series of synthetic zeolites of SiO_2 composition were 10–15 kJ/mol higher in energy than quartz, and Hu et al. (1995) found that several aluminophosphate zeolites ($Al_{0.5}P_{0.5}O_2$) were only 7–10 kJ/mol higher in energy than berlinite. Thus, the present data support the observation that anhydrous open zeolite frameworks are only slightly destabilized with respect to their dense anhydrous stable assemblages.

The enthalpies of formation from the elements were calculated with the use of the thermodynamic values of the constituent oxides taken from Robie et al. (1978) and the enthalpies of formation from the oxides obtained in this study: ΔH_f at 298 K = −7107.3 ± 5.6 kJ/mol for leonhardite ($CaAl_2Si_4O_{12} \cdot 3.5H_2O$), and −5964.3 ± 5.1 kJ/mol for metaleonhardite ($CaAl_2Si_4O_{12}$).

TABLE 5. Thermodynamic properties at 298 K of some Ca-zeolites obtained from this study and from the literature

Mineral and formula	ΔH°_{f} (kJ/mol)	Ref. (methods)	S° [J/(mol·K)]	Ref. (methods)
Laumontite ($CaAl_2Si_4O_{12} \cdot 4H_2O$)	−7251.0 ± 8.5*	1, C	485.3 ± 20.9	2, E
	−7268.9 ± 6.3	2, PE	485.76	3, E
	−7231.3 ± 10.1	4, PE	499.2 ± 19.2	5, E
	−7233.6	3, PE		
	−7265.6	6, E		
Leonhardite ($CaAl_2Si_4O_{12} \cdot 3.5H_2O$)	−7107.3 ± 5.6	1, C	461.1 ± 5.45	7, C
	−7123.2 ± 4.8	8, PE		
	−7108.3 ± 5.2	9, C		
Metaleonhardite ($CaAl_2Si_4O_{12}$)	−5964.3 ± 5.1	1, C	255.0	1, E
Wairakite ($CaAl_2Si_4O_{12} \cdot 2H_2O$)	−6646.7 ± 6.3	1, C	400.7	1, PE, C
	−6678.9 ± 5.0	2, PE	376.6 ± 20.9	2, PE
	−6606.9 ± 8.1	4, PE	439.7	3, PE
	−6608.8	3, PE	463.6 ± 4.2	5, E
Yugawaralite ($CaAl_2Si_6O_{16} \cdot 4H_2O$)	−9051.3 ± 10.4	1, C	609.8	1, C, PE
	−9036.19	10, PE	609.9	10, PE
	−9087.6	6, E		

Note: References are as follows: 1 = this study, 2 = Glushko (1981), 3 = Helgeson et al. (1978), 4 = Senderov (1980), 5 = Zen (1972), 6 = Chermak and Rimstidt (1989), 7 = King and Weller (1961), 8 = Hemingway and Robie (1977), 9 = Barany (1961), and 10 = Zeng and Liou (1982). Methods are as follows: C = calorimetry, PE = phase equilibrium, and E = estimation.

* Enthalpy of formation from elements.

Laumontite

Calorimetric study of laumontite under excess water allows us to calculate the enthalpy of formation of laumontite using two cycles. First (cycle H), we can use the enthalpy of the reaction leonhardite = laumontite, the enthalpy of formation of leonhardite obtained in this work, and the data for H_2O from Robie et al. (1978). The enthalpy of formation from the elements of laumontite ($CaAl_2Si_4O_{12} \cdot 4H_2O$) is −7253.4 ± 10.3 kJ/mol. The second cycle (I) uses the complete dehydration of laumontite to metaleonhardite, the enthalpy of formation of metaleonhardite, and data for H_2O. The calculated enthalpy of formation from the elements is −7251.0 ±8.5 kJ/mol. This value is close to that obtained using the first cycle, but the second cycle yields a value with smaller uncertainty and we adopt this as our preferred value (Table 4). Our value lies between previously reported data based on phase equilibria, −7233.6 kJ/mol (Helgeson et al. 1978) and −7268.9 ± 6.3 kJ/mol (Glushko 1981).

Wairakite

The wairakite used has a nearly stoichiometric composition, except for a slightly higher water content (0.15%), as is very common for natural samples of wairakite (Gottardi and Galli 1985). The very small amounts of Na, K, and Mg have a negligible effect on the enthalpy, but we made a correction to the enthalpy of drop solution for 0.05 mole of excess H_2O. We subtracted the heat content of 0.41 moles of H_2O from the measured heat effect and obtained the heat of drop solution of stoichiometric wairakite, 506.4 ± 4.2 kJ/mol (Table 3). This preferred value was used to calculate the enthalpy of formation. For the reaction

$$CaO + Al_2O_3 + 4SiO_2 + 2H_2O = CaAl_2Si_4O_{12} \cdot 2H_2O \quad (7)$$

we obtained $\Delta H^{\circ}_{f,ox}$ = −123.5 ± 4.7 kJ/mol at 298 K using thermodynamic cycle J. The enthalpy of formation from the elements, $\Delta H^{\circ}_{f,el}$, is −6646.7 ± 6.3 kJ/mol. Without correction for water, $\Delta H^{\circ}_{f,el}$ would be −6649.2 ± 6.3 kJ/mol. Previous data for $\Delta H^{\circ}_{f,el}$ of wairakite calculated from phase equilibria or otherwise estimated differ significantly from each other, ranging from −6606.9 ± 5.0 kJ/mol (Senderov 1980) to −6678 ± 5.0 kJ/mol (Glushko 1981). Our value, the first direct calorimetric measurement, is close to the middle of this range (see Table 5). It is worth noting that solid solution exists between wairakite and its Na analog, analcime, and that this substitution influences crystal structure, thermodynamic properties, and phase equilibria (Aoki and Minato 1980).

Yugawaralite

The yugawaralite studied is nearly stoichiometric (Eberlein et al. 1971; Gottardi and Galli 1985), but the H_2O content is about 0.1 mole less than theoretical. The experimental value for the enthalpy of drop solution was corrected by adding the heat content of 0.1 moles of H_2O (Table 3). The thermodynamic cycle K was used to calculate the enthalpy of formation from the oxides at 298 K. For the reaction

$$CaO + Al_2O_3 + 6SiO_2 + 4H_2O = CaAl_2Si_6O_{16} \cdot 4H_2O \quad (8)$$

$\Delta H^{\circ}_{f,ox}$ = −133.0 ± 8.4 kJ/mol. The enthalpy of formation from the elements is −9051.3 ± 10.4 kJ/mol. Without correction for the missing H_2O, $\Delta H^{\circ}_{f,el}$ would be −9046.5 ± 10.4 kJ/mol. Table 5 shows that only two estimates of ΔH°_{f} are available in the literature: −9036.19 kJ/mol (Zeng and Liou 1982) calculated from phase equilibria involving somewhat uncertain data for wairakite

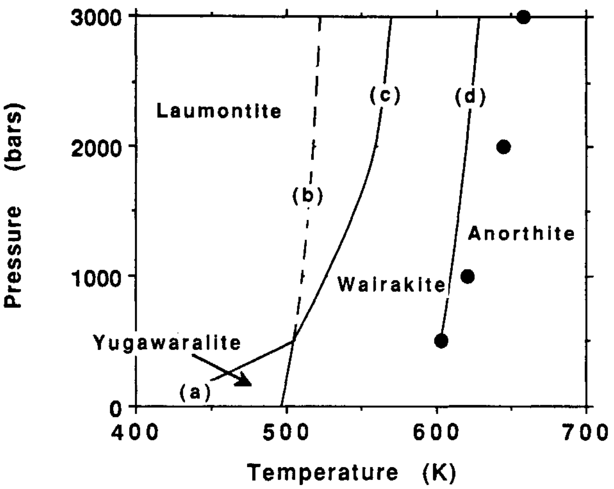

Figure 2. *P-T* diagram, showing the relations among zeolites in the presence of excess quartz and H_2O fluid. The curves marked a, b, and c represent the laumontite + yugawaralite, yugawaralite + wairakite, and laumontite + wairakite equilibria, respectively, calculated from thermochemical data and in agreement (to ±5 K) with curves calculated by Zeng and Liou (1982). The metastable extension of the yugawaralite + wairakite reaction, reversed by Zeng and Liou (1982), is shown as a dashed curve. Curve d represents the breakdown of wairakite to anorthite as calculated from thermochemical data. The four solid circles represent the reversals of that equilibrium by Liou (1970). The error in these points is approximately ±5 K and ±20 bars.

from Helgeson et al. (1978), and a significantly more exothermic value estimated by Chermak and Rimstidt (1989). Our value is closer to the value calculated from phase equilibria.

Calculation of the entropies of wairakite and yugawaralite

Low-temperature heat capacity and entropy at 298 K have been measured only for leonhardite (King and Weller 1961). There are many estimates of the entropies of the other minerals in the various datasets (Table 5).

Because leonhardite is related to laumontite, the standard entropy of laumontite has been estimated rather consistently by different authors using the leonhardite data (see Table 5). In contrast, estimates of the entropy of wairakite from phase equilibria scatter from 376.6 ± 20.9 J/(mol·K) (Glushko 1981) to 463.6 ± 4.2 J/(mol·K) (Zen 1972). The standard entropy of yugawaralite was calculated in only one study (Zeng and Liou 1982) on the basis of a value for the entropy of wairakite from Helgeson et al. (1978).

The standard entropies of wairakite and yugawaralite were derived from our new, independently determined enthalpy data, in combination with experimentally reversed *P-T* phase equilibria. The equilibrium decomposition of laumontite to wairakite is the most suitable reaction for calculating the entropy of wairakite:

$$\text{laumontite} = \text{wairakite} + 2H_2O. \qquad (9)$$

Because the breakdown product of laumontite may be either ordered or disordered wairakite depending on the length of the experiments, we did not consider studies that had no proof of reaction reversal and for which the products may have represented various intermediate stages of this reaction. The equilibria demonstrated by Liou (1971) appear reliable. From these reversals, we calculated the entropy of wairakite using

$$\Delta G_{P\text{-}T} = \Delta H_r^0 - T\Delta S_r^0 + \Delta V_s^0 P + RT \ln f_{H_2O} = 0 \qquad (10)$$

where $\Delta G_{P\text{-}T}$, ΔH_r^0, and ΔS_r^0 are the total free energy, enthalpy, and entropy change of the reaction, respectively, ΔV_s^0 is the volume change among the solid phases of the reaction, and f_{H_2O} is the fugacity of H_2O (Burnham et al. 1969). Because no experimental heat-capacity data are available for laumontite and wairakite we assume as a first approximation that ΔC_P for the reaction is 0 and that ΔV of the solid phases is constant. These assumptions are reasonable at the low-*P* and low-*T* conditions in these studies. Using the new calorimetric data for the enthalpies of formation of laumontite and wairakite we calculated the enthalpy of the laumontite-wairakite equilibrium. We used the value for entropy of laumontite of 485.76 J/(mol·K) from Helgeson et al. (1978). Using the molar volumes of laumontite and wairakite from Helgeson et al. (1978) we calculated $\Delta V_s = -2.07$ J/bar. The resulting standard entropy of wairakite is 400.7 J/(mol·K). This is in the midrange of estimates from different datasets (Table 5).

The entropy of yugawaralite at 298 K can be derived analogously. At present there is only one experimental study (Zeng and Liou 1982) of the univariant equilibrium curve for the dehydration of yugawaralite:

$$\text{yugawaralite} = \text{wairakite} + 2\ \text{quartz} + 2H_2O. \qquad (11)$$

Even though this reaction was studied in a metastable field (see Fig. 2), the steep slope of the *P-T* curve was established reliably. We obtained a value for the standard entropy of yugawaralite of 609.8 J/(mol·K) (Table 5). Our value for S^0 of yugawaralite is in excellent agreement with the value calculated by Zeng and Liou (1982).

The thermochemical calculations give stability fields of laumontite, wairakite, and yugawaralite that agree with reversed phase equilibria (Liou 1971; Zeng and Liou 1982) (see Fig. 2). Because the entropies used were based in part on these reversals, such agreement is expected. Nevertheless, the simultaneous good fit to several equilibria using the calorimetric results strongly suggests internal consistency in both the calorimetric and phase-equilibrium studies.

Recommended values for heats and entropies of formation, and for standard entropies based on the above considerations, are listed in Table 6 for all the zeolites studied.

Table 6. Recommended values of thermodynamic properties of zeolites obtained in this study

Mineral and formula	$\Delta H^{0}_{f,298.15}$ (kJ/mol)	$S^{0}_{298.15}$ [J/(mol·K)]	$\Delta G^{0}_{f,298.15}$ (kJ/mol)
Laumontite ($CaAl_2Si_4O_{12} \cdot 4H_2O$)	−7251.0 ± 8.5	485.5*	−6698.9
Leonhardite ($CaAl_2Si_4O_{12} \cdot 3.5H_2O$)	−7107.3 ± 5.6	461.1**	−6582.7
Metaleonhardite ($CaAl_2Si_4O_{12}$)	−5964.3 ± 5.1	255.0	−5621.6
Wairakite ($CaAl_2Si_4O_{12} \cdot 2H_2O$)	−6646.7 ± 6.3	400.7	−6208.3
Yugawaralite ($CaAl_2Si_6O_{16} \cdot 4H_2O$)	−9051.3 ± 10.4	609.8	−8402.6

* Helgeson et al. (1978).
** King and Weller (1961).

Geologic applications

Several reactions constrain minerals in the zeolite facies; one such reaction that determines the upper limits of wairakite stability is

$$\text{wairakite} = \text{anorthite} + 2\ \text{quartz} + 2\ H_2O. \quad (12)$$

Coombs et al. (1959) reported that the equilibrium temperature for this reaction at 2 kbar is near 623 K. Koizumi and Roy (1960) suggested that the maximum temperature for this reaction is 733 K at 1 kbar and 743 K at 2 kbar. These studies were synthesis experiments rather than reversals. Seki (1968) noted that the synthetic wairakite used in these studies was a tetragonal modification, disordered wairakite. The equilibrium dehydration of wairakite to anorthite, quartz, and water (Liou 1970) (see Fig. 2) yielded temperatures of the breakdown curve of wairakite much lower than the earlier data.

Using our new enthalpy and entropy values, we calculated the univariant curve of the equilibrium of wairakite with anorthite, quartz and fluid. The Gibbs free energy of reaction at P and T was calculated as above, and we assumed constant ΔC_P and ΔV_s. We used values for the molar volume, standard entropy, and enthalpy of quartz and H_2O from Robie et al. (1978), volume and entropy of anorthite from Robie et al. (1978), the enthalpy of synthetic anorthite from a recent publication of Zhu et al. (1994) and the volume of wairakite from Helgeson et al. (1978). Thermodynamic properties of H_2O at P and T were taken from Burnham et al. (1969).

The calculated breakdown curve of wairakite (Fig. 2) agrees reasonably with Liou's (1970) phase equilibria. The temperature of the calculated univariant curve at 500 bars is near the experimental value, but at 1000–2000 bars calculated temperatures are slightly lower than experimental temperatures. At a given pressure, the calculated temperature can change by as much as 50 K depending on the values of ΔH, ΔS, and ΔV chosen within their allowable ranges. The assumptions of negligible ΔC_P and constant ΔV_s add other uncertainties. However, these factors probably do not vary independently, and a rigorous assessment of uncertainties is impossible. We consider the agreement with experimental values encouraging, especially because the wairakite breakdown reaction was not used to constrain the thermochemical data. Thus, this thermochemical calculation of the upper thermal stability limit of wairakite supports the consistency and reliability of our new calorimetric data. The calculated P-T field of wairakite agrees with field observations in low-grade metamorphic and hydrothermally altered rocks (Coombs et al. 1959). The thermochemical data confirm that wairakite requires higher temperatures for its formation than laumontite. They also support the topology of the laumontite-wairakite-yugawaralite phase diagram, with an invariant point (in the presence of excess quartz and water) near 500 bars and 500 K.

These thermochemical data can be used to calculate other equilibria involving these minerals. P_{CO_2} and P_{H_2O} may significantly affect the stability of calcium zeolites. These minerals are unstable in the presence of even a moderate amount of CO_2 because the partial pressure of CO_2 lowers the fugacity of water and because Ca is consumed in carbonates. Such conditions are rather common for the calcium zeolite assemblages in uranium deposits (Mironenko and Naumov 1982). Thus, P-T conditions of calcium zeolite formation strongly depend on the geothermal gradient, P_{H_2O}/P_{tot}, P_{CO_2}, and other factors, including solution composition (Na,K). With appropriate care, the thermochemical data produced by this study are useful in understanding zeolite stability in complex natural systems. Equally important, a knowledge of thermodynamic stability helps distinguish equilibrium from nonequilibrium conditions, a constant problem in low-temperature environments.

Acknowledgments

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Appendix Table. Thermodynamic cycles

A. Leonhardite dehydration	
$CaAl_2Si_4O_{12}\cdot 3.5H_2O$ (xl, 298 K) = $CaAl_2Si_4O_{12}$ (xl, 975 K) + $3.5H_2O$ (g, 975 K)	(1)[a]
$CaAl_2Si_4O_{12}$ (xl, 975 K) = $CaAl_2Si_4O_{12}$ (xl, 298 K)	(2)[a]
$3.5H_2O$ (g, 975 K) = $3.5H_2O$ (l, 298 K)	(3)[b]
$CaAl_2Si_4O_{12}\cdot 3.5H_2O$ (xl, 298 K) = $CaAl_2Si_4O_{12}$ (xl, 298 K) + $3.5H_2O$ (l, 298 K)	(4)
$\Delta H_4 = \Delta H_1 + \Delta H_2 + \Delta H_3$	
B. Laumontite dehydration	
$CaAl_2Si_4O_{12}\cdot 4H_2O$ (xl, 298 K) = $CaAl_2Si_4O_{12}$ (xl, 975 K) + $4H_2O$ (g, 298 K)	(5)[a,c]
$CaAl_2Si_4O_{12}$ (xl 975 K) = $CaAl_2Si_4O_{12}$ (xl, 298 K)	(2)[a,b]
$4H_2O$ (g, 975 K) = $4H_2O$ (l, 298 K)	(6)
$CaAl_2Si_4O_{12}\cdot 4H_2O$ (xl, 298 K) = $CaAl_2Si_4O_{12}$ (xl, 298 K) + $4H_2O$ (l, 298 K)	(7)
$\Delta H_7 = \Delta H_5 + \Delta H_2 + \Delta H_6$	
C. Laumontite-leonhardite reaction	
$CaAl_2Si_4O_{12}\cdot 4H_2O$ (xl, 298 K) = $CaAl_2Si_4O_{12}$ (xl, 975 K) + $4H_2O$ (g, 298 K)	(5)[a]
$CaAl_2Si_4O_{12}$ (xl, 975 K) + $3.5H_2O$ (g, 975 K) = $CaAl_2Si_4O_{12}\cdot 3.5H_2O$ (xl, 298 K)	−(1)[a]
$0.5H_2O$ (g, 975 K) = $0.5H_2O$ (l, 298 K)	(8)[b]
$CaAl_2Si_4O_{12}\cdot 4H_2O$ (xl, 298 K) = $CaAl_2Si_4O_{12}\cdot 3.5H_2O$ (xl, 298 K) + $0.5H_2O$ (l, 298 K)	(9)
$\Delta H_9 = \Delta H_5 - \Delta H_1 + \Delta H_8$	
D. Formation of leonhardite (using drop-solution calorimetry of leonhardite)	
$CaCO_3$ (xl, 298 K) = CaO (sol, 975 K) + CO_2 (g, 975 K)	(10)[a]
CaO (xl, 298 K) + CO_2 (g, 298 K) = $CaCO_3$ (xl, 298 K)	(11)[b]
CO_2 (g, 975 K) = CO_2 (g, 298 K)	(12)[b]
Al_2O_3 (xl, 298 K) = Al_2O_3 (sol, 975 K)	(13)[a]
$4SiO_2$ (xl, 298 K) = $4SiO_2$ (sol, 975 K)	(14)[a]
$3.5H_2O$ (l, 298 K) = $3.5H_2O$ (g, 975 K)	(3)[b]
CaO (sol, 975 K) + Al_2O_3 (sol, 975 K) + $4SiO_2$ (sol, 975 K) + $3.5H_2O$ (g, 975 K) = $CaAl_2Si_4O_{12}\cdot 3.5H_2O$	(15)[a]
CaO (xl, 298 K) + Al_2O_3 (xl, 298 K) + $4SiO_2$ (xl, 298 K) + $3.5H_2O$ (l, 298 K) = $CaAl_2Si_4O_{12}\cdot 3.5H_2O$ (xl, 298 K)	(16)
$\Delta H_{16} = \Delta H_{10} + \Delta H_{11} + \Delta H_{12} + \Delta H_{13} + \Delta H_{14} + \Delta H_3 + \Delta H_{15}$	
E. Formation of leonhardite (using dehydration and drop-solution calorimetry of metaleonhardite)	
$CaCO_3$ (xl, 298 K) = CaO (sol, 975 K) + CO_2 (g, 975 K)	(10)[a]
CaO (xl, 298 K) + CO_2 (g, 298 K) = $CaCO_3$ (xl, 298 K)	(11)[b]
CO_2 (g, 975 K) = CO_2 (g, 298 K)	(12)[b]
Al_2O_3 (xl, 298 K) = Al_2O_3 (sol, 975 K)	(13)[a]
$4SiO_2$ (xl, 298 K) = $4SiO_2$ (sol, 975 K)	(14)[a]
CaO (sol, 975 K) + Al_2O_3 (sol, 975 K) + $4SiO_2$ (sol, 975 K) = $CaAl_2Si_4O_{12}$ (xl, 298 K)	(17)[a]
$CaAl_2Si_4O_{12}$ (xl, 298 K) = $CaAl_2Si_4O_{12}$ (xl, 975 K)	−(2)[a]
$CaAl_2Si_4O_{12}$ (xl, 975 K) + $3.5H_2O$ (g, 975 K) = $CaAl_2Si_4O_{12}\cdot 3.5H_2O$ (xl, 298 K) $3.5H_2O$ (l, 298 K) = $3.5H_2O$ (g, 975 K)	−(1)[a,c]
CaO (xl, 298 K) + Al_2O_3 (xl, 298 K) + $4SiO_2$ (xl, 298 K) + $3.5H_2O$ (l, 298 K) = $CaAl_2Si_4O_{12}\cdot 3.5H_2O$ (xl, 298 K)	(16)
$\Delta H_{16} = \Delta H_{10} + \Delta H_{11} + \Delta H_{12} + \Delta H_{13} + \Delta H_{14} + \Delta H_{17} - \Delta H_2 - \Delta H_1$	
F. Formation of metaleonhardite (fully dehydrated leonhardite)	
$CaCO_3$ (xl, 298 K) = CaO (sol, 975 K) + CO_2 (g, 975 K)	(10)[a]
CaO (xl, 298 K) = CO_2 (g, 298 K) = $CaCO_3$ (xl, 298 K)	(11)[b]
CO_2 (g, 975 K) = CO_2 (g, 298 K)	(12)[b]
Al_2O_3 (xl, 298 K) = Al_2O_3 (sol, 975 K)	(13)[a]
$4SiO_2$ (xl, 298 K) = $4SiO_2$ (sol, 975 K)	(14)[a]
CaO (sol, 975 K) + Al_2O_3 (sol, 975 K) + $4SiO_2$ (sol, 975 K) = $CaAl_2Si_4O_{12}$ (xl, 298 K)	(17)[a]
CaO + Al_2O_3 + $4SiO_2$ = $CaAl_2Si_4O_{12}$	(18)
$\Delta H_{18} = \Delta H_{10} + \Delta H_{11} + \Delta H_{12} + \Delta H_{13} + \Delta H_{14} + \Delta H_{17}$	
G. Metaleonhardite = anorthite + quartz	
$CaAl_2Si_4O_{12}$ (xl, 298) = CaO (sol, 975 K) + Al_2O_3 (sol, 975 K) + $4SiO_2$ (sol, 975 K)	−(17)[a]
CaO (sol, 975 K) + Al_2O_3 (sol, 975 K) + $2SiO_2$ (sol, 975 K) = $CaAl_2Si_2O_8$ (xl, 975 K)	(19)[d]
$CaAl_2Si_2O_8$ (xl, 975 K) = $CaAl_2Si_2O_8$ (xl, 298 K)	(20)[b]
$2SiO_2$ (sol, 975 K) = $2SiO_2$ (xl, 298 K)	(21)[a]
$CaAl_2Si_4O_{12}$ (xl, 298 K) = $CaAl_2Si_2O_8$ (xl, 298 K) + $2SiO_2$ (xl, 298 K)	(22)
$\Delta H_{22} = -\Delta H_{17} + \Delta H_{19} + \Delta H_{20} + \Delta H_{21}$	
H. Laumontite formation (first cycle)	
$CaAl_2Si_4O_{12}\cdot 3.5H_2O$ (xl, 298 K) + $0.5H_2O$ (l, 298 K) = $CaAl_2Si_4O_{12}\cdot 4H_2O$ (xl, 298 K)	−(9)[a]
CaO (xl, 298 K) + Al_2O_3 (xl, 298 K) + $4SiO_2$ (xl, 298 K) + $3.5H_2O$ (l, 298 K) = $CaAl_2Si_4O_{12}\cdot 3.5H_2O$ (xl, 298 K)	(16)[a]
CaO (xl, 298 K) + Al_2O_3 (xl, 298 K) + $4SiO_2$ (xl, 298 K) + $4H_2O$ (l, 298 K) = $CaAl_2Si_4O_{12}\cdot 4H_2O$ (xl, 298 K)	(23)
$\Delta H_{23} = -\Delta H_9 + \Delta H_{16}$	
I. Laumontite formation (second cycle)	
$CaAl_2Si_4O_{12}$ (xl, 298 K) + $4H_2O$ (l, 298 K) = $CaAl_2Si_4O_{12}\cdot 4H_2O$ (xl, 298 K)	(24)[a]
CaO (xl, 298 K) + Al_2O_3 (xl, 298 K) + $4SiO_2$ (xl, 298 K) = $CaAl_2Si_4O_{12}$ (xl, 298 K)	(18)[a]
CaO (xl, 298 K) + Al_2O_3 (xl, 298 K) + $4SiO_2$ (xl, 298 K) + $4H_2O$ (l, 298 K) = $CaAl_2Si_4O_{12}\cdot 4H_2O$ (xl, 298 K)	(25)
$\Delta H_{25} = \Delta H_{24} + \Delta H_{18}$	
J. Wairakite formation	
CaO (sol, 975 K) + Al_2O_3 (sol, 975 K) + $4SiO_2$ (sol, 975 K) + $2H_2O$ (g, 975 K) = $CaAl_2Si_4O_{12}\cdot 2H_2O$ (xl, 298 K)	(26)[a]
$CaCO_3$ (xl, 298 K) = CaO (sol, 975 K) + CO_2 (g, 975 K)	(10)[a]
CaO (xl, 298 K) + CO_2 (g, 298 K) = $CaCO_3$ (xl, 298 K)	(11)[b]
CO_2 (g, 975 K) = CO_2 (g, 298 K)	(12)[b]
Al_2O_3 (xl, 298 K) = Al_2O_3 (sol, 975 K)	(13)[a]
$4SiO_2$ (xl, 298 K) = $4SiO_2$ (sol, 975 K)	(14)[a]
$2H_2O$ (l, 298 K) = $2H_2O$ (g, 975 K)	(27)[b]
CaO (xl, 298 K) + Al_2O_3 (xl, 298 K) + $4SiO_2$ (xl, 298 K) + $2H_2O$ (l, 298 K) = $CaAl_2Si_4O_{12}\cdot 2H_2O$ (xl, 298 K)	(28)
$\Delta H_{28} = \Delta H_{26} + \Delta H_{10} + \Delta H_{11} + \Delta H_{12} + \Delta H_{13} + \Delta H_{14} + \Delta H_{27}$	
K. Yugawaralite formation	
CaO (sol, 975 K) + Al_2O_3 (sol, 975 K) + $6SiO_2$ (sol, 975 K) + $4H_2O$ (g, 975 K) = $CaAl_2Si_6O_{16}\cdot 4H_2O$ (xl, 298 K)	(29)[a]
$CaCO_3$ (xl, 298 K) = CaO (sol, 975 K) + CO_2 (g, 975 K)	(10)[b]
CaO (xl, 298 K) + CO_2 (g, 298 K) = $CaCO_3$ (xl, 298 K)	(11)[b]
CO_2 (g, 975 K) = CO_2 (g, 298 K)	(12)[b]
Al_2O_3 (xl, 298 K) = Al_2O_3 (sol, 975 K)	(13)[a]
$6SiO_2$ (xl, 298 K) = $6SiO_2$ (sol, 975 K)	(30)[a]
$4H_2O$ (l, 298 K) = $4H_2O$ (g, 975 K)	−(6)
CaO (xl, 298 K) + Al_2O_3 (xl, 298 K) + $6SiO_2$ (xl, 298 K) + $4H_2O$ (l, 298 K) = $CaAl_2Si_6O_{16}\cdot 4H_2O$ (xl, 298 K)	(31)
$\Delta H_{31} = \Delta H_{29} + \Delta H_{10} + \Delta H_{11} + \Delta H_{12} + \Delta H_{13} + \Delta H_{30} - \Delta H_6$	

Note: a = this work; b = Robie et al. (1978); c = the materials produced by dehydrating laumontite and leonhardite are essentially the same and have the same heat contents, called ΔH_2 in the cycles above; and d = Zhu et al. (1994).