

## Crystal properties and energetics of synthetic kaolinite

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### ABSTRACT

Six kaolinite  $[Al_2Si_2O_5(OH)_4]$  samples were synthesized under different conditions of temperature, pressure, and pH from two different starting materials. Chemical composition and properties of the samples were characterized using classical methods (electron microprobe, atomic absorption spectrometry, X-ray diffraction, differential and thermal analyses, and Fourier transform infrared spectrometry). All synthetic kaolinite samples contained various amounts of a boehmite impurity. The defect density was different for each kaolinite, ranging from high to low. The enthalpy of formation of these kaolinites at 25 °C was investigated by drop solution calorimetry into molten lead borate at 700 °C. All data were corrected for impurities. Whatever the synthesis conditions and the kaolinite properties, the enthalpy of kaolinite dissolution into molten lead borate at 700 °C and the standard enthalpy of kaolinite formation from the oxides and from the elements at 25 °C are constant:  $372.3 \pm 1.0$  kJ/mol,  $-46.6 \pm 2.6$  kJ/mol, and  $-4115.3 \pm 4.1$  kJ/mol respectively. Using entropy data from the literature, the standard Gibbs free energy of kaolinite formation from the elements at 25 °C is  $-3793.9 \pm 4.1$  kJ/mol. This value is in excellent agreement with most of the literature data obtained for natural kaolinites. Furthermore, the standard Gibbs free energy of kaolinite formation at 25 °C and 1 atm is very close to that obtained using the same method for the San Juanito dickite, which is commonly used as a standard mineral, the value for kaolinite being slightly more negative than the value for dickite. This trend is also true for all the temperature and pressure range of kaolin minerals occurrences. Thus, dickite is a metastable phase relative to kaolinite, and kaolinite seems to be thermodynamically more stable than dickite, as already proposed by DeLigny and Navrotsky (1999) and Anovitz et al. (1991). The natural occurrence of dickite must result from specific reaction paths and be controlled by kinetic factors.

### INTRODUCTION

Kaolinite is the most widespread mineral of the kaolin group, which also contains dickite, nacrite, and halloysite. Kaolinite can be formed as a residual weathering product or as an authigenic sedimentary mineral (Murray 1988). In soils, kaolinite is formed at *P-T* conditions of the Earth's surface (i.e., 25–30 °C and atmospheric pressure; Singer and Munns 1996; Środoń 1999). However, kaolinite and dickite also persist until late diagenesis (e.g., Beaufort et al. 1998) at temperature lower than 200 °C, and lithostatic pressure lower than 1 kbar or hydrostatic pressure of 300–400 bars. Kaolinite can also result from hydrothermal alteration, at 100–200 °C and 1–100 bars (Murray et al. 1993).

Numerous attempts to synthesize dickite have been performed (e.g., Eberl and Hower 1975; Fialips et al. 2000a, 2000b). But, whatever the starting material (crystalline or amorphous) and the synthesis conditions (200 to 450 °C, 150 to 3000 bars, 0.3 to 182 d), no *P-T-X* domain of dickite formation was found. In contrast, kaolinite was formed in a wide range of synthesis conditions (Fialips et al. 2000a), suggesting that kaolinite is thermodynamically more stable than dickite.

The relative stability of kaolinites and dickites was widely investigated using different thermodynamic approaches (e.g., Anovitz et al. 1991; Zotov et al. 1998; DeLigny and Navrotsky 1999), but the results are still not completely clear. Some authors concluded that kaolinite is the only stable kaolin mineral and that dickite is a metastable mineral whose natural genesis must be explained in terms of kinetics and/or special reaction paths (e.g., DeLigny and Navrotsky 1999). Others concluded that dickite is more stable than kaolinite (Zotov et al. 1998).

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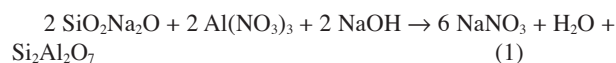
However, several criticisms can be made of the previous approaches. (1) Only few data exist for dickite, and Gibbs free energies of kaolinite and dickite are so close that discussions are sometimes prejudiced. (2) Energetics of kaolinite were studied using only natural samples. These samples were generally well crystallized and/or of large grain size; only DeLigny and Navrotsky (1999) studied the effect of crystallinity on kaolinite energetics, but error bars were larger than the possible effect of the HI index of crystallinity (Hinckley 1963) on the standard enthalpy of formation of well-ordered to disordered natural kaolinites. (3) The use of natural samples results in large corrections for impurities.

Fialips et al. (1999, 2000a, 2000b) showed that the pH of synthesis has an important effect on kaolinite crystal properties (defect density, crystal size, coherence, etc.). Thus, in this work, six syntheses were performed from two different starting materials under different conditions of temperature and pH to obtain six kaolinites possessing different defect densities. A thermodynamic study of these synthetic kaolinites was then performed by oxide melt solution calorimetry. The objectives of this study were to obtain better knowledge of the effect of defect density on kaolinite energetics, to compare the energetics of synthetic kaolinites to those of natural kaolin minerals, and thus to learn more about energetic stability of kaolinite relative to dickite.

#### MATERIALS AND METHODS

Two different starting gels named *A* and *B* were prepared according to Fialips et al. (1999).

Gel *A* was prepared with 0.2 *M* sodium metasilicate ( $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ ) and 0.2 *M* aluminum nitrate [ $(\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O})$ ], with 1 *M* sodium hydroxide added according to the following reaction:



After completion, the coprecipitate was centrifuged to remove sodium nitrate. Gel *A* was then dehydrated at 70 °C for 12 h and crushed. It was X-ray amorphous.

Gel *B* was obtained after hydrothermal treatment of gel *A* (5 g) with distilled water (75 mL; initial pH~5) at  $220 \pm 3$  °C, under equilibrium water pressure (23.2 bar), for 14 d. X-ray diffraction, infrared spectrometry, and thermogravimetric analyses of gel *B* revealed that it contained almost 50 wt% of kaolinite of medium defect density (based on the Hinckley index; Hinckley 1963), associated with amorphous product and a small amount of pseudoboehmite (undeniably identifiable by infrared spectrometry).

The expected atomic Si/Al/Na ratio of the starting materials was 2/2/0 (kaolinite stoichiometry). The measured atomic Si/Al/Na ratios of gels *A* and *B*, as determined by atomic absorption spectrometry (AAS), were 2.00/2.15/1.79 and 2.00/2.10/0.09, respectively, showing small excesses in Al owing to the fact that reaction 1 did not go to completion. Moreover, gel *A* contained a substantial amount of the remaining Na that was not eliminated by centrifugation, whereas gel *B* was almost Na free.

#### HYDROTHERMAL AGING

400 to 5000 mg of powdered starting material and 30 to 100 mL of distilled water (12 to 100 wt%) were placed in experimental vessels with a metal body and a removable Teflon liner for temperatures lower than 250 °C and in Ti reactors for higher temperatures. In some cases, HCl or Na(OH) was added to produce an initial pH ( $\text{pH}_i$ ) within the range 2.0–9.1. This  $\text{pH}_i$  was adjusted and measured directly in the vessel, after mixing and stabilization, at room temperature. Vessels were held at 220, 240, 260, or 280 °C ( $\pm 3$  °C), under equilibrium water pressure (respectively 23.2, 33.5, 46.9, and 64.1 bar). Synthesis duration was from 14 to 91 days. Final pH ( $\text{pH}_f$ ) was measured on quenched synthesis fluids.

#### ANALYTICAL TECHNIQUES

##### Electron microprobe (EMP)

The chemical composition of four samples (in wt% of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{Na}_2\text{O}$ ) was determined using a Cameca SX-50 fully automated EMP. The samples were dehydroxylated at 800 °C, compacted, mounted with epoxy in a sample holder, polished, and carbon coated. The analytical conditions were 10 nA and 15 keV. The standards used were albite for Na, corundum for Al, and quartz for Si.

##### Atomic absorption spectrometry (AAS)

Chemical analyses for Si, Al, and Na were performed on two samples by AAS using a Perkin Elmer 2380 spectrometer. Samples were prepared by fusion with  $\text{SrB}_2\text{O}_4$  and dissolution in  $\text{HNO}_3$  (Jeanroy 1974).

##### Water content measurements

The water content (in wt%) of the products was determined by measuring the weight loss of a known mass of sample (50 to 100 mg) after total dehydration at 800 °C overnight. This procedure was repeated 2–3 times. The results were reproducible within 0.1 to 0.2 wt%. Thus, the uncertainty in water content values is  $\pm 0.2$  wt%.

##### X-ray diffraction (XRD)

All products were analyzed by XRD, by reflection mode on randomly oriented powder preparations, using a Philips PW 1050/25 DY 5249 diffractometer equipped with a Ni-filtered  $\text{CuK}\alpha$  radiation (40 kV, 40 mA), combined with a SOCABIM system (DACO-MP) for numerical data acquisition. Diffraction patterns were recorded by step scanning, using a step interval of  $0.02^\circ 2\theta$  and a counting time of 5 s per step. Defects in kaolinite (Hinckley 1963) were characterized using the Hinckley index (HI) and the  $R_2$  index of Liétard (Liétard 1977; Cases et al. 1982).

HI is the most commonly used index of kaolinite defect density (e.g., Plançon et al. 1988, 1989). HI is calculated from the (020), (1 $\bar{1}$ 0), and (1 $\bar{1}$  $\bar{1}$ ) X-ray reflections of kaolinite, in the range  $19\text{--}23^\circ 2\theta \text{ CuK}\alpha$ . HI is sensitive to all the crystalline defects of kaolinite (i.e.,  $\pm nb/3$  translations,  $\pm n\pi/3$  rotations, and random defects). The HI of natural kaolinites is in the range 1.5 (low defects) to 0.2 (high defects) (Liétard 1977).

$R_2$  is calculated from the intensities of the (131) and ( $\bar{1}\bar{3}1$ ) reflections, in the range 37–40 °2 $\theta$  CuK $\alpha$ .  $R_2$  is only sensitive to the random defects.  $R_2$  is an independent index (no relation with HI) that decreases with the increase of the monoclinic character of kaolinite. Well-resolved (131) and ( $\bar{1}\bar{3}1$ ) reflections indicate triclinic character and correspond to a high  $R_2$  value whereas the overlapping of the two peaks indicates monoclinic character and corresponds to a low  $R_2$  value (Plançon and Tchoubar 1977; Liétard 1977; Brindley and Porter 1978; Plançon et al. 1989). The  $R_2$  of natural kaolinites is in the range 1.2 (low defect) to 0.3 (high defect) (Liétard 1977).

The apparent coherent scattering thickness of kaolinite was calculated along the  $c^*$  axis, using the (001) reflection ( $CS_{001}$ ) and along the  $b$  axis using the (060) reflection ( $CS_{060}$ ), according to the Scherrer formula (Guinier 1956). The calculations used the full width at half maximum (FWHM) of the considered X-ray peak, the corresponding Bragg angle, the wavelength of the CuK $\alpha_1$  radiation (1.540562 Å), and the constant for our instrument (0.9).

#### Differential and thermal analyses (DTA-TG)

DTA-TG analyses were performed with an electrobalance NETZSCH STA 409 EP. The thermocouple was calibrated using seven standard minerals with well-known onset temperatures (temperature at which the DTA curve begins to deviate from the baseline, e.g., CsCl: onset temperature of 476.0 °C). The measurements were performed with ~20 mg of sample, heated in air, at 10 °C/min, from 20 to 1100 °C. The temperature of kaolinite dehydroxylation ( $T_{max}$ ) was measured at the maximum deviation from background of the endotherm.

#### Fourier transform infrared spectrometry (FTIR)

FTIR spectra were recorded in the 400–4000  $cm^{-1}$  range on a Nicolet 510 FTIR spectrometer with 4  $cm^{-1}$  resolution. Spectra were obtained in transmission mode from KBr pressed pellets, which were previously heated at 110 °C overnight. These pellets were prepared by mixing 3–4 mg of sample with 300 mg of KBr. Kaolinite FTIR spectra were normalized by equalizing the total integrated intensity of the Si-O-<sup>VI</sup>Al band located at 538–542  $cm^{-1}$  (Stubican and Roy 1961; Pampuch 1966; Hlavay et al. 1977) to an arbitrarily chosen value to allow a quantitative comparison of the samples. The measurements of the integrated intensity of the absorption bands were made with OMNIC software from Nicolet Instrument.

#### Calorimetric measurements

The enthalpies of formation of the synthetic kaolinites were determined using a Tian Calvet high-temperature heat-flux microcalorimeter as described by Navrotsky (1997). The enthalpy of sample dissolution was measured by drop-solution calorimetry under flowing Ar. This method avoids the decomposition of highly hydrated minerals at the high temperature of the calorimeter prior to dissolution (Navrotsky et al. 1994). Powdered samples were dried at 120 °C overnight. Fresh pressed pellets weighing 14.5–15.5 mg were dropped from room temperature into molten lead borate (2PbO·B<sub>2</sub>O<sub>3</sub>) at 700 °C. An Ar flow of ~100 mL/min was maintained in the calorimeter

during all the experiments. A good return of the signal to baseline was observed within 80 min. The calorimeter was calibrated by measuring the heat content of ~15 mg pellets of corundum.

The enthalpy of drop solution of oxides needed to complete the thermochemical cycles was measured under the same conditions, but without Ar flushing.

### EXPERIMENTAL RESULTS AND DISCUSSION

Synthesis conditions, parageneses obtained, and kaolinite crystal properties are given in Table 1. All samples contained impurities of boehmite. Actually, synthetic kaolinite is rarely obtained as a pure phase (e.g., Tomura et al. 1985; Satokawa et al. 1994). Boehmite is the most common auxiliary phase because it commonly occurs as a precursor mineral (e.g., Fialips et al. 1999; Tsuzuki 1976). The amount of impurities is easily quantifiable from chemical analyses (Table 2), assuming that the kaolinite has the theoretical composition: [Si<sub>2</sub>Al<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>].

#### Kaolinite characterization

**XRD.** X-ray diffractograms of the samples are presented in Figure 1. Small XRD peaks of boehmite are observed at 14–16 and 27–29° 2 $\theta$  in the P043, P187, P065, and P180 diffractograms.

The HI and  $R_2$  indexes of kaolinite defect density (Table 1) of the synthetic kaolinites are in the range of those of natural kaolinites (Liétard 1977). However, the HI index of all the synthetic kaolinites is almost constant (HI  $\approx$  1) whereas their  $R_2$  indexes are all different (Table 1). XRD patterns (Fig. 1) and  $R_2$  values (Table 1) show that all the synthetic kaolinites are different in terms of monoclinic or triclinic character, ranging from a relatively high triclinic character (i.e., P180) to a high monoclinic character (i.e., P043). The  $R_2$  index is plotted vs. pH<sub>F</sub> in Figure 2.  $R_2$  decreases with increasing pH<sub>F</sub>, as already observed by Fialips et al. (1999, 2000a, 2000b).

The  $CS_{001}$  and  $CS_{060}$  values of the synthetic kaolinites are spread over the ranges 240–336 Å and 241–305 Å respectively (Table 1). Contrary to Fialips et al. (2000a), no effect of final pH on kaolinite  $CS_{001}$  and  $CS_{060}$  values was observed. However, Fialips et al. (2000a) performed their study using a series of kaolinites synthesized under the same conditions of temperature, pressure, time, solid/solution ratio, and nature and composition of the starting material. In the present study, synthetic kaolinites were not synthesized under the same  $P$ - $T$  conditions. Thus, the possible effect of the  $P$ - $T$  variations may have obscured the effect of pH<sub>F</sub> on CS values.

**DTA.** The dehydroxylation temperature,  $T_{max}$ , of the synthetic kaolinites are given in Table 1.  $T_{max}$  values are spread over the range 511–523 °C.

**FTIR.** Infrared spectra in the hydroxyl-stretching region of the synthetic samples are presented in Figure 3. All the four characteristic hydroxyl bands of kaolinite are well resolved for P180. These bands, located at 3693, 3667, 3651, and 3620  $cm^{-1}$ , were named  $\nu_1$ ,  $\nu_2$ ,  $\nu_3$ , and  $\nu_4$  respectively by Brindley et al. (1986). From P180 up to P043, the intensity of the 3667  $cm^{-1}$  band decreases compared to the 3651  $cm^{-1}$  band, reflecting an increase of the kaolinite defect density (Liétard 1977; Brindley

**TABLE 1.** Synthesis conditions, parageneses obtained, and crystal properties of the kaolinites

| Sample                          | P180     | P065     | P187     | P059       | P042       | P043       |
|---------------------------------|----------|----------|----------|------------|------------|------------|
| Starting gel                    | <i>B</i> | <i>A</i> | <i>B</i> | <i>B</i>   | <i>B</i>   | <i>A</i>   |
| Solid/solution (g/L)            | 100      | 67       | 17       | 13         | 12         | 13         |
| $T$ ( $\pm 3$ °C)               | 220      | 220      | 220      | 240        | 280        | 260        |
| $t$ (days)                      | 91       | 35       | 28       | 21         | 15         | 14         |
| PH <sub>i</sub> ( $\pm 0.2$ )   | 2.0      | 3.5      | 5.1      | 9.1        | 5.6        | 6.2        |
| PH <sub>F</sub> ( $\pm 0.2$ )   | 2.0      | 1.5      | 3.9      | 5.2        | 5.6        | 6*         |
| Paragenesis                     | Kaol +   | Kaol +   | Kaol +   | Kaol +     | Kaol +     | Kaol +     |
|                                 | (Boehm)  | (Boehm)  | (Boehm)  | Boehm      | (Boehm)    | Boehm      |
| HI                              | 1.1(0.1) | 0.9(0.2) | 1.0(0.1) | 1.02(0.06) | 0.9(0.1)   | 1.1(0.1)   |
| R <sub>2</sub>                  | 0.9(0.1) | 0.8(0.1) | 0.7(0.1) | 0.54(0.07) | 0.41(0.09) | 0.33(0.08) |
| CS <sub>001</sub> ( $\pm 20$ Å) | 300      | 296      | 242      | 269        | 240        | 336        |
| CS <sub>060</sub> ( $\pm 15$ Å) | 247      | 241      | 305      | 255        | 242        | 273        |
| $T_{max}$ ( $\pm 5$ °C)         | 523      | 511      | 519      | 512        | 512        | 522        |

Note:  $T$  = temperature of synthesis.  $t$  = run time. pH<sub>i</sub>, pH<sub>F</sub> = initial and final pH (Boehm). HI, R<sub>2</sub> = Hinckley and Liétard indexes of kaolinite crystallinity. CS<sub>001</sub>, CS<sub>060</sub> = kaolinite coherent crystal sizes measured along the  $c$  and  $b$  axis.  $T_{max}$  = temperature of kaolinite dehydroxylation. Numbers in parentheses are errors associated with the data.

\* Measured using a pH-paper,  $\pm 1$ .

**TABLE 2.** Compositions of the synthetic samples in weight percent of oxides determined by electron microprobe analysis of dehydroxylated samples or by atomic adsorption spectrometry; corresponding amount of kaolinite in the samples (wt%); amount of adsorbed water (wt%)

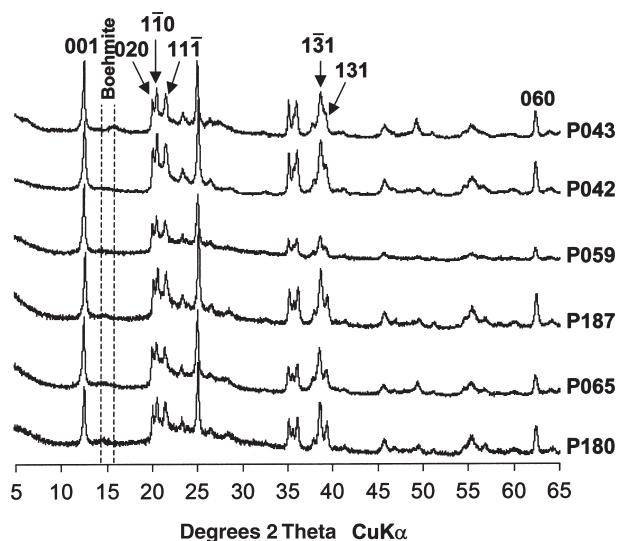
|                                | P180*       | P065†      | P187*       | P059*       | P042*       | P043‡       |
|--------------------------------|-------------|------------|-------------|-------------|-------------|-------------|
| SiO <sub>2</sub>               | 45.28(0.42) | 45.39(0.5) | 45.93(0.57) | 43.60(0.90) | 46.12(0.87) | 36.96(0.50) |
| Al <sub>2</sub> O <sub>3</sub> | 40.31(0.42) | 40.08(0.5) | 39.51(0.57) | 41.77(1.03) | 39.36(0.86) | 47.10(0.50) |
| Na <sub>2</sub> O              | 0.00        | 0.45(0.5)  | 0.05(0.01)  | 0.33(0.14)  | 0.32(0.03)  | 1.24(0.50)  |
| H <sub>2</sub> O <sup>†</sup>  | 14.4(0.2)   | 14.1(0.2)  | 14.5(0.2)   | 14.3(0.2)   | 14.2(0.2)   | 14.7(0.2)   |
| %Kaol (wt%)                    | 97.3        | 97.5       | 98.7        | 93.7        | 99.1        | 79.4        |
| H <sub>2</sub> O ads (wt%)     | 0.8         | 0.5        | 0.7         | 1.2         | 0.4         | 3.6         |

Note: %Kaol = amount of stoichiometric kaolinite deduced from chemical analyses. H<sub>2</sub>O ads = amount of adsorbed water deduced from thermal and chemical analyses. The numbers in parentheses are errors associated with the analyses. For EMP they represent two standard deviations of at least five analyses. For AAS they represent the maximum deviation observed between 2–3 analyses.

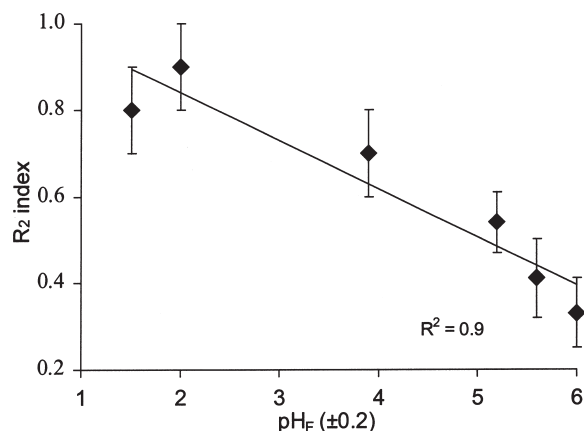
\* EMP analyses.

† AAS analyses.

‡ Weight loss obtained by total dehydration at 800 °C.

**FIGURE 1.** X-ray diffraction patterns of the synthetic kaolinites.

et al. 1986), as already observed by XRD. The FTIR spectrum of P043, which is characteristic of a highly disordered kaolinite, also shows a shoulder at 3600 cm<sup>-1</sup>. Fialips et al. (2000a) observed the same shoulder for kaolinites synthesized at high pH and proposed that it could be generated by a perturbation of hydroxyl groups due to interactions with Na cations adsorbed on the kaolinite surface. Furthermore, they showed that the in-

**FIGURE 2.** R<sub>2</sub> index of "crystallinity" of the synthetic kaolinites vs. their final pH of synthesis.

tensity of the 3600 cm<sup>-1</sup> shoulder is proportional to the amount of adsorbed Na. The more than two times higher content of Na in P043 compared with all the other samples (Table 3) supports this hypothesis. As other samples also contain some Na, but in smaller amounts, the perturbation of their hydroxyl groups, though possible, is not obvious in the spectra.

### Thermochemistry

**Enthalpies of drop solution.** Enthalpies of drop solution of the synthetic samples,  $\Delta H_{ds}$  (in kJ/g) and  $\Delta H_{ds}^0$  (in kJ/mol)

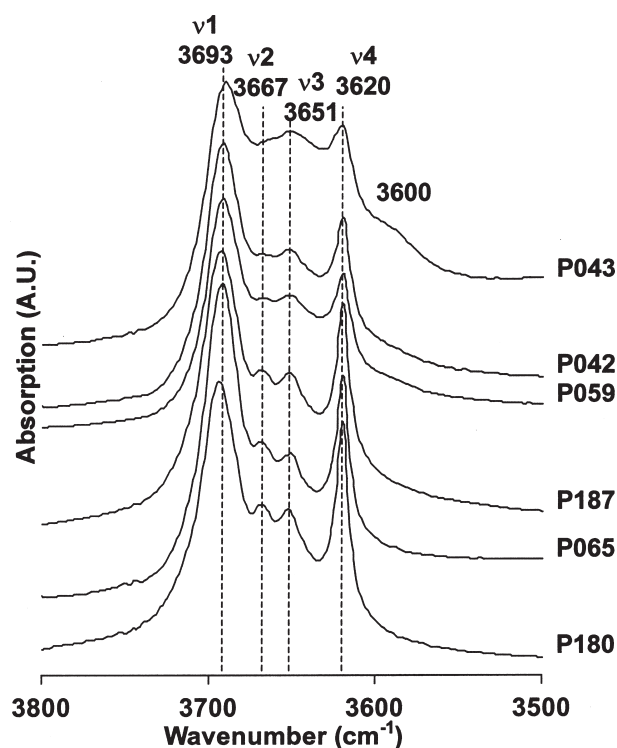


FIGURE 3. Normalized Fourier transform infrared spectra of the synthetic samples in the OH-stretching region. A.U. = arbitrary unit.

are given in Table 3.  $\Delta H_{\text{ds}}^{\text{no}}$  was normalized to one mol of kaolinite plus the impurities  $[\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + \Sigma \text{impurities}]$  (see cycle below) from the chemical analyses (Table 2).

According to XRD, FTIR, and microprobe data, all the samples contain some boehmite  $[\text{AlO}(\text{OH})]$ . Moreover, except for P180, all the samples contain small amounts of Na. We know from Fialips et al. (2000) and from our FTIR data that the Na could be adsorbed on the kaolinite and, thus, is unlikely present in a separate identifiable impurity phase. However, as it was impossible to know the exact composition of the kaolinite (particles are too small for individual analysis), we had to make some

assumptions to permit corrections for impurities. We assumed that: (1) the synthetic kaolinite stoichiometry is ideal  $[\text{Si}_2\text{Al}_2\text{O}_5(\text{OH})_4]$ ; (2) the excess of Al corresponds only to boehmite; and (3) the Na corresponds to an NaOH phase. The choice of NaOH was deliberate because the contribution of Na to the total enthalpy of solution should be similar to that of NaOH, even if the Na is effectively linked to the kaolinite structure, owing to the presence of excess water in all the samples.

To correct  $\Delta H_{\text{ds}}^{\text{no}}$  for impurities [i.e.,  $\text{AlO}(\text{OH})$ , NaOH, and  $\text{H}_2\text{O}_{\text{adsorbed}}$ ], and to calculate the enthalpies of kaolinite formation from the oxides, enthalpies of drop solution of the pure oxides or impurities were necessary and are summarized in Appendix Table 1. The enthalpy of drop solution of pure boehmite  $[\text{AlO}(\text{OH})]$  was determined from the data of Majzlan et al. (2000) for slightly hydrated boehmite  $[\text{AlO}(\text{OH}) \cdot n\text{H}_2\text{O}]$  using the enthalpy of drop solution of liquid water from Robie and Hemingway (1995). The enthalpies of drop solution of NaOH and  $\text{Na}_2\text{O}$  were obtained by cycles involving  $\text{Na}_2\text{CO}_3$  (Table 4). Using the data in Table 2,  $x_i \Delta H_{\text{ds}}^i$ , the contribution of each impurity to  $\Delta H_{\text{ds}}^{\text{no}}$ , was determined (Table 3). The contribution of NaOH to  $\Delta H_{\text{ds}}^{\text{no}}$  is very small ( $<2$  kJ/mol for all samples except P043). The contribution of boehmite is lower than 10 kJ/mol ( $<3\%$  of the enthalpy of drop solution) for most of the samples, but that for P059 and P043 is larger.

Both these synthetic materials and the natural kaolinites used by De Ligny and Navrotsky (1999) required corrections for impurities. Nevertheless, because the impurities in the synthetic materials are only boehmite (in quantifiable amounts and having a known enthalpy) and possibly a very small amount of an Na-bearing phase ( $<0.07$  mol of Na for 1 mole of kaolinite), in contrast to the natural materials that contained significant and variable amounts of many different impurities, we consider the impurity correction on the synthetic samples to be more reliable. The agreement between natural and synthetic kaolinites (see below) suggests that the corrections for impurities in the former were done correctly as well.

Enthalpies of drop solution of the synthetic kaolinites,  $\Delta H_{\text{ds}}^{\text{no}}$ , were determined using the following cycle:

$$[\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + \Sigma \text{impurities}]_{\text{(crystal, 298 K)}} = \text{Oxides}_{\text{(solution, 975 K)}} - \Delta H_{\text{ds}}^{\text{no}}$$

$$\text{Impurities}_{\text{(crystal, 298 K)}} = \text{Oxides}_{\text{(solution, 975 K)}} - \Delta H_{\text{ds}}^i$$

TABLE 3. Enthalpies of drop solution at 975 K in  $2\text{PbO} \cdot \text{B}_2\text{O}_3$ , and derived standard formation enthalpies of the synthetic kaolinites

|  | P180           | P065           | P187           | P059           | P042           | P043           |
|--|----------------|----------------|----------------|----------------|----------------|----------------|
| $\Delta H_{\text{ds}}$ (kJ/g)                          | 1.462(0.008)   | 1.449(0.005)   | 1.477(0.006)   | 1.472(0.005)   | 1.436(0.009)   | 1.483(0.006)   |
| $\Delta H_{\text{ds}}^{\text{no}}$ (kJ/mol)            | 387.86(2.01)   | 383.71(1.35)   | 386.47(1.56)   | 405.79(1.48)   | 374.22(2.26)   | 482.12(2.10)   |
| $x_i \Delta H_{\text{ds}}^i$ AlO(OH) impurity          | 9.71           | 8.03           | 2.73           | 25.49          | 1.15           | 99.08          |
| $x_i \Delta H_{\text{ds}}^i$ NaOH impurity             | 0.00           | 2.04           | 0.23           | 1.56           | 1.43           | 6.90           |
| $x_i \Delta H_{\text{ds}}^i$ H <sub>2</sub> O adsorbed | 6.13           | 1.03           | 7.64           | 3.74           | 2.93           | 7.32           |
| Total impurities                                       | 15.84          | 11.10          | 10.60          | 30.79          | 5.51           | 113.30         |
| $\Delta H_{\text{ds}}^{\text{co}}$ (kJ/mol)            | 372.02(4.72)   | 372.60(5.12)   | 375.88(5.50)   | 375.01(8.77)   | 368.71(7.76)   | 368.83(6.50)   |
| $\Delta H_{\text{ds}}^{\text{oxides}}$ (kJ/mol)        | -46.32(5.30)   | -49.90(5.66)   | -50.18(6.00)   | -49.31(9.10)   | -43.01(8.12)   | -43.13(6.94)   |
| $\Delta H_{\text{ds}}^{\text{elements}}$ (kJ/mol)      | -4115.02(5.82) | -4115.60(6.15) | -4118.88(6.46) | -4118.01(9.41) | -4111.71(8.47) | -4111.83(7.34) |

Note:  $\Delta H_{\text{ds}}$  = enthalpy of dissolution measured experimentally in kJ/g.  $\Delta H_{\text{ds}}^{\text{no}}$  = enthalpy of dissolution normalized at one mol of  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + \Sigma \text{impurities}$ .  $x_i \Delta H_{\text{ds}}^i$  contribution of each impurity to  $\Delta H_{\text{ds}}^{\text{no}}$ , with  $i$  = any impurity and  $x_i$  = number of mol of the impurity normalized at one mol of kaolinite  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ , given according to data in Table 2.  $\Delta H_{\text{ds}}^{\text{co}}$  = enthalpy of dissolution of the pure kaolinite obtained after corrections.  $\Delta H_{\text{ds}}^{\text{oxides}}$  and  $\Delta H_{\text{ds}}^{\text{elements}}$  = enthalpies of kaolinite formation from the oxides and from the elements. The numbers in parentheses are errors associated with the data. Uncertainties associated with  $\Delta H_{\text{ds}}$  and  $\Delta H_{\text{ds}}^{\text{no}}$  are given as two standard deviations of the mean:  $\Delta(\Delta H_{\text{ds}}) = 2\sigma / \sqrt{n}$  where  $\sigma$  is the sample standard deviation and  $n$  the total number of experiments ( $n \geq 10$ ).

**TABLE 4.** Thermodynamic cycle used to calculate the enthalpy of drop solution of NaOH and Na<sub>2</sub>O in lead borate at 700 °C

| Thermodynamic Cycle  | Reference  |
|--|--|
| <b>NaOH</b>  |  |
| Na <sub>2</sub> CO <sub>3</sub> (crystal, 298 K) + H <sub>2</sub> O (liq, 298 K) = 2 NaOH (crystal, 298 K) + CO <sub>2</sub> (gas, 298 K)  | ΔH <sub>1</sub> Calculated from Robie and Hemingway 1995 |
| Na <sub>2</sub> CO <sub>3</sub> (crystal, 298 K) = Na <sub>2</sub> CO <sub>3</sub> (solution, 975 K)   | ΔH <sub>2</sub> This study                               |
| H <sub>2</sub> O (liq, 298 K) = H <sub>2</sub> O (gas, 975 K)  | ΔH <sub>3</sub> Robie and Hemingway 1995                 |
| NaOH (crystal, 298 K) = NaOH (solution, 975 K)   | ΔH <sub>4</sub> Robie and Hemingway 1995                 |
| CO <sub>2</sub> (gas, 298 K) = CO <sub>2</sub> (gas, 975 K)  | ΔH <sub>5</sub> Chase 1998                               |
| ΔH <sub>4</sub> = (-ΔH <sub>1</sub> + ΔH <sub>2</sub> + ΔH <sub>3</sub> - ΔH <sub>5</sub> ) / 2 = (-169.9(0.4) + 239.14(1.26) + 69.0(1.1) - 31.95) / 2 ΔH <sub>4</sub> = 53.14 ± 0.86 kJ/mol |  |
| <b>Na<sub>2</sub>O</b>   |  |
| Na <sub>2</sub> CO <sub>3</sub> (crystal, 298 K) = Na <sub>2</sub> O (solution, 975 K) + CO <sub>2</sub> (gas, 975 K)  | ΔH <sub>6</sub> This study                               |
| CO <sub>2</sub> (gas, 298 K) = CO <sub>2</sub> (gas, 975 K)  | ΔH <sub>7</sub> Chase 1998                               |
| (Na <sub>2</sub> O + CO <sub>2</sub> ) <sub>elements</sub> = Na <sub>2</sub> CO <sub>3</sub> (crystal, 298 K)  | ΔH <sub>8</sub> Robie and Hemingway 1995                 |
| (Na <sub>2</sub> O) <sub>elements</sub> = Na <sub>2</sub> O (crystal, 298 K)   | ΔH <sub>9</sub> Robie and Hemingway 1995                 |
| (CO <sub>2</sub> ) <sub>elements</sub> = CO <sub>2</sub> (gas, 298 K)  | ΔH <sub>10</sub> Chase 1998                              |
| Na <sub>2</sub> O (crystal, 298 K) = Na <sub>2</sub> O (solution, 975 K)   | ΔH <sub>11</sub> This study                              |
| ΔH <sub>11</sub> = ΔH <sub>6</sub> - ΔH <sub>7</sub> + ΔH <sub>8</sub> - ΔH <sub>9</sub> - ΔH <sub>10</sub> = 239.14(1.26) - 31.95 - 1129.2(0.3) + 414.8(0.3) + 393.52(0.05)                 |  |
| ΔH <sub>11</sub> = -113.69 ± 1.33 kJ/mol   |  |

Note: Numbers in parentheses are errors associated with the data.

$$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4(\text{crystal, 298 K}) = \text{Oxides}(\text{solution, 975 K}) \Delta H_{\text{ds}}^{\text{co}}$$

$$\Delta H_{\text{ds}}^{\text{co}} = \Delta H_{\text{ds}}^{\text{no}} - \sum_i x_i \Delta H_{\text{ds}}^i$$

Errors associated with  $\Delta H_{\text{ds}}^{\text{co}}$  were calculated using the following equation:

$$\Delta(\Delta H_{\text{ds}}^{\text{co}}) = \sqrt{[\Delta(\Delta H_{\text{ds}}^{\text{no}})]^2 + \sum_i x_i^2 [\Delta(\Delta H_{\text{ds}}^i)]^2 + \sum_i (\Delta H_{\text{ds}}^i)^2 \Delta x_i^2}$$

(see Taylor 1997)

All the kaolinites yield the same  $\Delta H_{\text{ds}}^{\text{co}}$  within error, and the average  $\Delta H_{\text{ds}}^{\text{co}}$  obtained from all drops of each sample is 372.3 ± 1.0 kJ/mol. The error associated with this value represents two standard deviations of the mean. This value of enthalpy of drop solution of the synthetic kaolinite is similar to that of natural kaolinite (370.6 ± 3.9 to 374.7 ± 10.2 kJ/mol; De Ligny and Navrotsky 1999).

**Standard enthalpies of formation.** The standard enthalpy of formation of each kaolinite from the oxides was derived from enthalpy of drop solution of kaolinite and the oxides (Appendix Tables 1 and 2). The standard enthalpy of formation from the elements was calculated using data from Robie and Hemingway (1995) (Table 3).  $\Delta H_f^{\text{oxides}}$  and  $\Delta H_f^{\text{elements}}$  of all the synthetic kaolinites are the same within the associated errors. Thus, as already observed by De Ligny and Navrotsky (1999) for natural kaolinites, the crystal properties of synthetic kaolinite (defect density, coherent crystal sizes, etc.) affect its energetics by an amount equal to or less than the standard error of 0.9 kJ/mol. The average  $\Delta H_f^{\text{oxides}}$  and  $\Delta H_f^{\text{elements}}$  values of the synthetic kaolinites, derived from the average  $\Delta H_{\text{ds}}^{\text{co}}$  value for all the drops of each sample (i.e., 372.3 ± 1.0 kJ/mol) are -46.6 ± 2.6 kJ/mol and -4115.3 ± 4.1 kJ/mol respectively. The increase of the error from drop solution to formation from elements is due to the error propagation generated by the large errors associated with the heats of formation of binary oxides in Robie and Hemingway (1995) used in the calculation.

$\Delta H_f^{\text{oxides}}$  and  $\Delta H_f^{\text{elements}}$  values obtained in this study are in excellent agreement with most of the literature data for natural kaolinite. Thus, no significant difference exists between natural and synthetic kaolinites: either in crystal properties (it is

possible to synthesize a kaolinite with the same properties as a natural kaolinite), or in energetics.

**Standard Gibbs free energy of formation.**  $\Delta G_f^0$  (kaolinite) was determined from  $\Delta H_f^{\text{elements}}$  (kaolinite) taking the entropy of kaolinite at 298 K and the entropy of the elements from Robie and Hemingway (1995), and yields  $\Delta G_f^0$  (kaolinite) equal to -3793.9 ± 4.1 kJ/mol. Our  $\Delta G_f^0$  (kaolinite) value is in agreement with most of the literature data (e.g., Robie and Hemingway 1995; Devidal et al. 1996; DeLigny and Navrotsky 1999). Furthermore, our  $\Delta G_f^0$  (kaolinite) value is more negative (by almost 9 kJ/mol) than the value obtained by DeLigny and Navrotsky (1999) for the San Juanito dickite (commonly used as a reference mineral; Frost 1997) using exactly the same calorimetric method of measurement.

One could ask whether the deliberate choice of NaOH to account for the presence of Na in the samples leads to this difference between the results of kaolinite and dickite energetics. To address this, we also made three other calculations, using data obtained from all drops of each sample, considering that Na is (1) in an oxide phase, using data of enthalpy of solution of Na<sub>2</sub>O (Appendix Table 1 and 2); (2) in an amorphous silicate phase, using data of enthalpy of solution of a glass of sodium metasilicate chemical composition (i.e., Na<sub>2</sub>SiO<sub>3</sub>, Appendix Table 2); and (3) in an amorphous aluminosilicate phase, using data of enthalpy of solution of a glass of albite composition (i.e., NaAlSi<sub>3</sub>O<sub>8</sub>, Appendix Table 2). We know that the presence of Na<sub>2</sub>O in our samples is highly unlikely owing to the hydrothermal synthesis conditions. However, the enthalpy of solution of Na<sub>2</sub>O in lead borate at 700 °C being strongly negative (Appendix Table 1), the corresponding  $\Delta G_f^0$  value would reflect a minimum value that could not be reached using any other type of possible Na-phase correction. Enthalpies of solution of the Na<sub>2</sub>SiO<sub>3</sub> and NaAlSi<sub>3</sub>O<sub>8</sub> glasses in lead borate at 700 °C were determined using cycles involving pure oxides (Appendix Table 2) and are summarized in Appendix Table 1. No silicate or aluminosilicate phase other than kaolinite was observed by any analysis (e.g., microprobe, FTIR). However, the energetic contribution of sodium might be interpreted as arising from small domains or clusters similar to Na<sub>2</sub>SiO<sub>3</sub> or NaAlSi<sub>3</sub>O<sub>8</sub> located within the clay. The enthalpy of NaAlSi<sub>3</sub>O<sub>8</sub>

glass solution being highly positive, the corresponding correction of the raw data would lead to the maximum value for  $\Delta G_i^0$  which could not be reached using any other type of possible Na-phase correction.

The results of standard Gibbs free energy of the synthetic kaolinite considering that Na is in an oxide  $\text{Na}_2\text{O}$ , amorphous  $\text{Na}_2\text{SiO}_3$ , or amorphous  $\text{NaAlSi}_3\text{O}_8$  phase are, respectively,  $-3796.3 \pm 4.1$  kJ/mol,  $-3789.1 \pm 4.5$  kJ/mol, and  $-3788.6 \pm 4.6$  kJ/mol, compared to the preferred value of  $-3793.1 \pm 4.1$  kJ/mol derived above using NaOH as sodium-bearing impurity. Thus, whatever Na correction we apply, the standard Gibbs free energy of the synthetic kaolinite is in agreement with most of the literature data for natural kaolinite (e.g., DeLigny and Navrotsky 1999). Furthermore, our  $\Delta G_i^0$  (kaolinite) value is still more negative than the value obtained for the San Juanito dickite (DeLigny and Navrotsky 1999;  $-3785.1 \pm 5.6$  kJ/mol) but by only 3–8 kJ/mol, depending on the Na correction we applied. It is unlikely that this difference will change much at the higher temperatures and/or pressures within the area of natural occurrence of kaolin minerals. However, errors associated with the values of  $\Delta G_i^0$  (kaolinite) and  $\Delta G_i^0$  (dickite) are respectively 4–5 and 5.6 kJ/mol. Thus, the only statement we can make is that dickite appears to be a metastable mineral.

### GEOLOGICAL APPLICATIONS

Whatever their crystal properties, synthetic kaolinites have enthalpies and Gibbs free energies very close to those of natural kaolinites. Furthermore, whatever its crystal properties, kaolinite (synthetic or natural) is energetically very close to dickite (De Ligny and Navrotsky 1999; this study), with kaolinite seeming to be slightly more stable than dickite. Thus, dickite is a metastable phase relative to kaolinite.

Other observations agree with these statements: (1) in natural systems, kaolinite is much more common than dickite; (2) in the laboratory, kaolinite was crystallized under a wide range of synthesis conditions; and (3) no  $P$ - $T$ - $X$  domain of dickite crystallization was found experimentally.

One can conclude that the formation of dickite in natural system follows a specific reaction path or is controlled by kinetic factor(s). Fialips et al. (2000b) showed that only kaolinite was formed from metadickite or metanacrite, although these amorphous metakaolins inherited some chemical (trace or minor amounts of various elements), morphological (platy, blocky, or tubular shape), and/or crystalline properties (arrangement of Al and Si) from the initial dickite and nacrite.

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**APPENDIX TABLE 1.** Enthalpies of drop solution of oxides and related phases at 975 K in 2PbO·B<sub>2</sub>O<sub>3</sub>

|  | $\Delta H_f$ (kJ/mol) | Reference  |
|--|-----------------------|--|
| Corundum Al <sub>2</sub> O <sub>3</sub>  | 108.07(0.85)          | This study   |
| Boehmite AlO(OH)                         | 98.7(1.0)             | Calculated from Majzlan et al. 2000                              |
| Quartz SiO <sub>2</sub>                  | 39.82(0.17)           | This study   |
| Na <sub>2</sub> CO <sub>3</sub>          | 239.14(1.26)          | This study   |
| NaOH                                     | 53.14(0.86)           | This study   |
| Na <sub>2</sub> O                        | -113.69(1.33)         | This study   |
| NaAlSi <sub>3</sub> O <sub>8</sub> glass | 216.18(0.99)          | Calculated from Kelley 1962                                      |
| Na <sub>2</sub> SiO <sub>3</sub> glass   | 121.49(1.32)          | Calculated from Kelley 1962                                      |
| H <sub>2</sub> O liquid                  | 69.0(1.1)             | De Ligny and Navrotsky, calculated from Robie and Hemingway 1995 |
| H <sub>2</sub> O adsorbed                | 85.02(2.02)           | De Ligny and Navrotsky, calculated from Iwata et al. 1989        |

*Note:* For data obtained in this study, uncertainties represent two standard deviations from the mean.

**APPENDIX TABLE 2.** Thermodynamic cycle used to calculate the enthalpy of drop solution of Na<sub>2</sub>SiO<sub>3</sub> and NaAlSi<sub>3</sub>O<sub>8</sub> glasses in lead borate at 700 °C

| Thermodynamic Cycle  |  | Reference   |
|--|--|-------------|
|  | <b>Na<sub>2</sub>SiO<sub>3</sub></b>   |             |
| Na <sub>2</sub> O <sub>(crystal, 298K)</sub> + SiO <sub>2(crystal, 298K)</sub> = Na <sub>2</sub> SiO <sub>3(glass, 298K)</sub>   | $\Delta H_1$                           | Kelley 1962 |
| Na <sub>2</sub> O <sub>(crystal, 298 K)</sub> = Na <sub>2</sub> O <sub>(solution, 975 K)</sub>   | $\Delta H_2$                           | This study  |
| SiO <sub>2(crystal, 298 K)</sub> = SiO <sub>2(solution, 975 K)</sub>   | $\Delta H_3$                           | This study  |
| Na <sub>2</sub> SiO <sub>3(glass, 298 K)</sub> = Na <sub>2</sub> SiO <sub>3(solution, 975 K)</sub>   | $\Delta H_4$                           | This study  |
| $\Delta H_4 = -\Delta H_1 + \Delta H_2 + \Delta H_3 = 195.39 - 113.7(1.3) + 39.8(0.2) = 121.49 \pm 1.32$ kJ/mol  |  |             |
|  | <b>NaAlSi<sub>3</sub>O<sub>8</sub></b> |             |
| $1/2$ Na <sub>2</sub> O <sub>(crystal, 298K)</sub> + $1/2$ Al <sub>2</sub> O <sub>3(crystal, 298K)</sub> + 3 SiO <sub>2(crystal, 298K)</sub> = NaAlSi <sub>3</sub> O <sub>8(glass, 298K)</sub> | $\Delta H_5$                           | Kelley 1962 |
| Na <sub>2</sub> O <sub>(crystal, 298 K)</sub> = Na <sub>2</sub> O <sub>(solution, 975 K)</sub>   | $\Delta H_6$                           | This study  |
| Al <sub>2</sub> O <sub>3 (crystal, 298 K)</sub> = Al <sub>2</sub> O <sub>3 (solution, 975 K)</sub>   | $\Delta H_7$                           | This study  |
| SiO <sub>2(crystal, 298 K)</sub> = SiO <sub>2(solution, 975 K)</sub>   | $\Delta H_8$                           | This study  |
| NaAlSi <sub>3</sub> O <sub>8(glass, 298 K)</sub> = NaAlSi <sub>3</sub> O <sub>8(solution, 975 K)</sub>   | $\Delta H_9$                           | This study  |
| $\Delta H_9 = -\Delta H_5 + 1/2 \Delta H_6 + 1/2 \Delta H_7 + 3 \Delta H_8 = 99.58 - 1/2 * 113.7(1.3) + 1/2 * 108.1(0.9) + 3 * 39.8(0.2) = 216.18 \pm 0.99$ kJ/mol                             |  |             |

*Note:* Numbers in parentheses are errors associated with the data.