

# Solubility of kaolinite in alkaline solutions at hydrothermal conditions

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## Introduction

Clays minerals generated by hydrolysis of primary minerals often control the physical and chemical conditions of their environments. The understanding of natural systems requires knowledge of the thermodynamic properties of these minerals, particularly for kaolinite, which is the most abundant aluminosilicate clay.

## Previous work

Values of the Gibbs free energy of kaolinite have been deduced from solubility measurements, mineral stability relations in the system  $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ , and calorimetric determinations. Kaolinite hydrolysis constants ( $K_{s4}$ ) generated from these works, depend on the thermodynamic properties of aluminum hydroxydes and on the equilibrium constants required to calculate the distribution of silica and aluminum aqueous species. To compare these results, we recalculated the various published values of  $K_{s4}$ , using a self-consistent set of thermodynamic constants (Castet *et al.* (1993) and Naumov *et al.* (1974)). Results of this analysis are depicted versus reciprocal absolute temperature in fig. 1. A large discre-

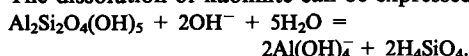
pancy is observed between the constants obtained at 25°C, while good agreement between  $pK_{s4}$  deduced from mineral stability relations is obtained at temperatures above 200°C. Note the lack of data between 25 and 200°C, with the exception of Nagy *et al.* (1991). To fill up this gap, solubility measurements of kaolinite have been experimentally determined from 60 to 170°C.

## Experimental

A natural hydrothermal kaolinite from Decazeville (France), free of defects and impurities, was chosen for this study. Spectrochemical analysis indicated a Si/Al ratio of  $0.99 \pm 0.02$ . B.E.T. surface area was determined to be  $3.17 \text{ m}^2/\text{g}$ ; particle size ranged between 5 and 10  $\mu\text{m}$ . Solubility measurements were conducted at temperatures from 60 to 170°C in  $\text{NH}_4\text{Cl}/\text{NH}_4\text{OH}$  buffered solutions of low ionic strength (0.025). At temperatures below 100°C, the experiments were performed in a polypropylene vessel immersed in water bath held at constant temperature. The solutions were continuously mixed by use of a suspended magnetic stirred. At temperatures above 100°C, the experiments are carried out in reactors which allowed the injection of the solid into the system after it had reached the experimental temperature. The evolution of solution composition were monitored from periodically extracted aliquots. Total aluminum and silica were analyzed colorimetrically using the pyrochatechol violet and molybdat blue methods respectively.

## Calculation of the ionic activity quotient

The dissolution of kaolinite can be expressed as:



Activities of the aqueous species needed for the calculation of the corresponding ionic activity ( $Q_{s4}$ ) are deduced from the measured concentrations using hydrolysis constants from Castet *et al.* (1993) and Naumov *et al.* (1974) for aluminum and silica respectively. Steady state is assumed to

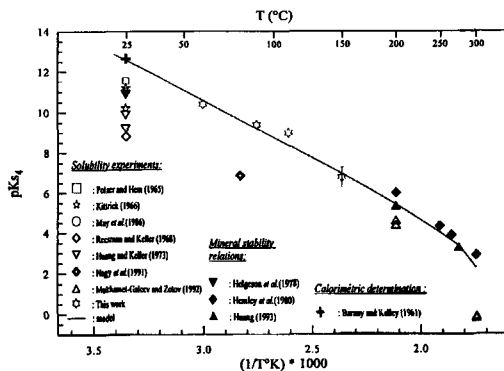


FIG. 1. Negative logarithm of the dissociation constant of kaolinite versus the reciprocal of the absolute temperature.

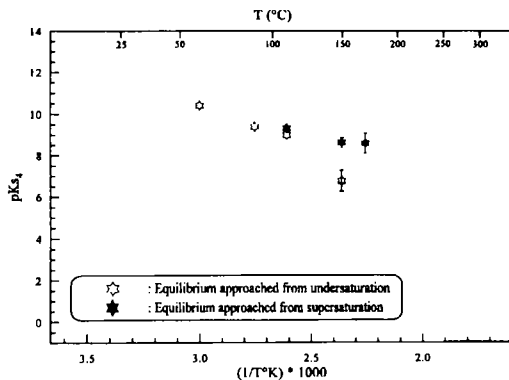


FIG. 2. Values of  $pKs_4$  calculated from the results of this study versus the reciprocal of the absolute temperature.

be reached when no variation of  $Qs_4$  is obtained after several successive samplings.

### Results and discussion

At temperatures below 100°C, equilibrium was approached from undersaturation. Three successive periods are observed during dissolution at 60 and 90°C: a short initial period of incongruent dissolution, where Si is preferentially removed over Al; a long term of stoichiometric dissolution period; and a stationary state period. At 110 and 150°C two different steady states can be reached: the first from undersaturation and the second from supersaturation. At 170°C, the stationary state is always reached after a precipitation stage during which a simultaneous decrease of Si and Al in solution is observed. At this temperature, Si concentration is always below quartz saturation and Al concentration is first controlled by boehmite solubility. The coprecipitation of boehmite with an aluminosilicate prevents identification of the Si/Al ratio of this solid phase.

The values of  $pKs_4$  calculated from all experiments are presented in fig. 2. Two trends can be clearly identified. The first trend is consistent with equilibrium constants obtained from undersaturation, while the second gathers solubility products of runs where precipitation of an aluminosilicate was observed.

At the end of each run, the solid phases were examined by X-ray diffraction, I-R and Raman

spectroscopy. No changes were discerned using X-ray and I-R spectroscopy. The Raman spectra of solids obtained from undersaturated runs are similar to that of the starting kaolinite. In contrast, the Raman spectra of solids obtained after a precipitation stage show important change in the OH-stretching region. Four of the five OH-bands were replaced by a single, broad absorption band. This residual spectrum seems to be characteristic of illite with a Si/Al ratio close to one. This information suggests that the data obtained from the precipitation experiments do not reflect kaolinite solubility. Thus only  $pKs_4$  obtained from the runs reaching equilibrium from undersaturation are characteristic of kaolinite solubility. Regression of these data (fig. 1) led to a Gibbs free energy value for kaolinite (25°C, 1 bar): -907.68 kcal/mol. This value is more negative than corresponding values obtained from solubility measurements at 25°C. Furthermore, the thermodynamic parameters generated in this study are in close agreement with those deduced from boehmite-kaolinite equilibrium data above 200°C and from calorimetric measurements at 25°C.

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