Montmorillonite under high $H_2O$ pressures: Stability of hydrate phases, rehydration hysteresis, and the effect of interlayer cations

TZY-CHUNG WU, WILLIAM A. BASSETT, WUU-LIANG HUANG, STEPHEN GUGGENHEIM, AND AUGUST F. KOSTER VAN GROOS

Mineral Physics Laboratory, Department of Geological Sciences, Snee Hall, Cornell University, Ithaca, New York 14853, U.S.A.

Exxon Production Research Company, Houston, Texas 77252-2189, U.S.A.

Department of Geological Sciences, University of Illinois at Chicago, Chicago, Illinois 60680, U.S.A.

ABSTRACT

Dehydration of Ca- and Mg-exchanged montmorillonite was studied along $H_2O$ isochors in the hydrothermal diamond-anvil cell by in situ X-ray diffraction using a synchrotron radiation source. At pressures between the $H_2O$ liquid-vapor (L-V) boundary and ~10 kbar, the dehydration temperature for the conversion from the 19 Å hydration state to the 15 Å hydration state occurred over the temperature range 260–350 °C for Ca-exchanged montmorillonite and 200–250 °C for Mg-exchanged montmorillonite, with a slight increase with increasing pressure. For both materials, the rehydration from the 15 Å to 19 Å states occurred at the same temperature as dehydration at pressures along the $H_2O$ L-V boundary, thus showing no hysteresis. The rehydration hysteresis increased to nearly 75 °C at 6 kbar for Ca-exchanged montmorillonite and to the same amount at 2.5 kbar for Mg-exchanged montmorillonite. Dehydration experiments on Mg-exchanged montmorillonite along the isochors of 1.024 and 0.75 g/cm³ showed conversion from the 15 Å hydrate to the 12.5 Å hydrate at 590–605 °C. The 12.5 Å hydrate only partially rehydrated after cooling to room temperature along those two isochors. In an experiment started from the 15 Å state, in which the pressure was below the $H_2O$ L-V curve, dehydration occurred at 400–500 °C and rehydration at 430–350 °C. When our previous results on Na-exchanged montmorillonite are combined with the current experimental data, systematic trends can be found in the effect of pressure and interlayer-cation species on the dehydration temperature and rehydration hysteresis.

INTRODUCTION

The interlayer in montmorillonite is composed of hydrated cations. Because of the low charge of silicate layers (<0.6 unit charge per one-half unit cell), montmorillonite readily hydrates and has a large swelling capability.

For divalent interlayer cations, at a pressure of 1 atm, many previous studies (e.g., McEwan and Wilson 1980) show three discrete hydration states with (001) layer spacings at ~12.5, ~15, and ~19 Å, depending on the $H_2O$ activity in the system. Although those states have been called one-, two-, and three-layer hydrates, respectively, those terms do not accurately represent the real interlayer structures. The configuration of interlayer $H_2O$ depends greatly on the cation size, charge, and charge distribution within the silicate layers (e.g., Clementz et al. 1973; McBride et al. 1975). Therefore, we simply refer to them as the 12.5 Å, 15 Å, and 19 Å hydration states as or the first, second, and third hydration states.

The dehydration of the interlayer is of special interest to geologists because dehydration processes influence pore pressure in rocks, affect rock strength, and contribute to subsurface fluid migration. Evolved water may also be subducted along with the lithospheric plates to the upper mantle. Thus, understanding the effects of temperature, pressure, and other variables on the dehydration reaction in montmorillonite, which is abundant in sedimentary settings, is of considerable importance.

Because of experimental limitations, most earlier studies concentrated on the pressure dependence of smectite dehydration temperature at lower pressures, in which hydrated smectite dehydrates to $H_2O$ in gas phase or in supercritical vapor phase plus dehydrated smectite. Although the earlier data cannot be applied directly to geologic $P-T$ conditions, they are valuable because they provide insight into dehydration phenomena and can be compared in part to our data. Stone and Rowland (1955) first studied the pressure dependence of the dehydration temperature in a Ca-rich montmorillonite using differential thermal analysis (DTA) between 1 and 6 bars $H_2O$ pressure. They showed that the temperature for dehydration of the second hydration state to the first hydration state increased from 150 °C at 1 bar to 240 °C at 6 bars. For dehydration from the first hydration state to the an-