H₂O-D₂O exchange in lawsonite

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ABSTRACT

The mineral lawsonite, CaAl₂Si₂O₇(OH)₂⋅H₂O, was deuterated to about 93% in a thermobalance by H₂O-D₂O gas-phase exchange at temperatures between 375 and 425 °C. The kinetics of this reaction are reported and diffusion coefficients for the H₂O-D₂O exchange are calculated from thermogravimetric measurements.

INTRODUCTION

Lawsonite, CaAl₂Si₂O₇(OH)₂⋅H₂O, is a water-rich mineral found in low-temperature, high-pressure metamorphic rocks. Its framework structure consists of edge-sharing AlO₄(OH)₂-octahedra parallel to [100], which are interconnected by Si₂O₇-groups. Ca²⁺-ions and H₂O-molecules occupy cavities in the framework structure. The stability limits of lawsonite extend to high pressures and temperatures (Newton and Kennedy 1963; Pawley 1994). The high water content of about 11 wt% makes lawsonite a possible candidate mineral for transporting water down into the Earth’s mantle in subduction zones (Pawley 1994).

The structure of lawsonite, which contains both discrete hydroxyl groups and H₂O molecules, was refined from single-crystal X-ray diffraction data at different temperatures between 110 and 500 K by Libowitzky and Armbruster (1995). Deuteration experiments were done by Libowitzky and Rossman (1996) with polished lawsonite single-crystal slabs. They loaded the single crystal slabs and D₂O into gold capsules and sealed them by welding. The capsules were inserted into cold-seal pressure vessels and run at temperatures of 350 and 400 °C at different pressures (1.2–2.5 kbar, using Ar gas as a pressure medium) for up to 14 days. The outer regions of the lawsonite single-crystal slabs contained ~80 % D₂O whereas the inner parts showed a lower concentration of D₂O. There were indications that the H-diffusion rate along [001] (the z-direction) is at least one order of magnitude faster than along [100].

The main purpose of the deuteration procedures described here was to produce samples for neutron diffraction experiments at the high resolution powder diffractometer (HRPD) at ISIS in the UK. The neutron diffraction experiments were performed to address how does exchange of hydrogen vs. deuterium changes the critical temperatures and the thermodynamic character of the transitions, how the positions of the deuterium atoms evolve with temperature, and to clarify details of the mechanism of the transition at 273 K in terms of proton ordering and framework displacement (Meyer et al. 2001). In the present contribution, we report the experiments of deuteration and the kinetics extracted from the process.

EXPERIMENTAL METHODS

The deuteration experiments were undertaken using lawsonite from the locality at Tiburon Peninsula, Marin County, California, USA (sample no. G14555 of the South Australian Museum), and a sample from Valley Ford, Sonoma County, California, USA (sample no. 120943, Harvard University). The lawsonite samples were crushed in an agate mortar, sieved, and separated using heavy liquids. The resulting powder had an average grain size of 77 µm, which was checked by scanning electron microscopy. An electron micrograph of the lawsonite powder can be seen in Figure 1.

The H-D exchange experiments were done with a commercial CI Electronics MK2 thermobalance under controlled atmosphere at 1 atm total pressure. The use of a balance makes it possible to monitor the weight change during the H-D exchange reactions. A schematic picture of the experimental setup is shown in Figure 2. Pt wires were suspended on both arms of the thermobalance, one holding the sample in the hot zone of a tube furnace, the other holding a counter-weight crucible at room temperature. The lawsonite was contained in a platinum crucible and the counter-weight was a plastic crucible with metal pieces. About 1 g of lawsonite powder was used in each experiment.

The entire system was closed and gas-tight. Wet conditions were achieved by bubbling dried Ar at room temperature.

FIGURE 1. Lawsonite powder in the scanning electron microscope.