Order parameter behavior at the structural phase transition in cummingtonite from Mössbauer spectroscopy

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ABSTRACT

The microscopic behavior of the C2/m ↔ P21/m phase transition occurring in cummingtonite (36 mol% Fe) as a function of temperature has been investigated using Mössbauer spectroscopy performed in the temperature range 100–550 K. The quadrupole splitting (ΔE0) of the M4 doublet shows a change in slope at the critical temperature of the phase transition. The difference between ΔE0 of the low-symmetry phase and the values obtained at the same temperatures by extrapolating ΔE0 of the C2/m phase has been used as a measure proportional to the local order parameter associated with the phase transition. The Mössbauer data, which provide a measure of the local microscopic order parameter, scale in an identical manner to the macroscopic properties, indicating that the sub-unit scale structure of cummingtonite evolves in a parallel manner with the macroscopic average structure on a much longer length scale.

INTRODUCTION

Structural phase transitions in rock forming minerals are commonly observed under physical conditions corresponding to those of the Earth’s crust and mantle. They can have an important influence on the thermodynamic stability of solid solutions and dramatic effects on bulk elastic properties. A major focus of interdisciplinary research in the last few years has been on the development of a theoretical framework with which to quantitatively describe the changes in properties, which accompany such transitions. In this context, Landau theory has been highly effective in defining relationships between different physical properties: how these depend on the macroscopic order parameter, Q, and how they evolve with temperature and pressure (Angel 2000; Carpenter et al. 1998; Carpenter and Salje 1998; Salje 1990). While the approach provides descriptions of the macroscopic behavior, it does not necessarily yield insights into the microscopic origins of structural instabilities. In the present study, concerning a phase transition in the mineral cummingtonite, we show how Mössbauer spectroscopy can be used to characterize structural evolution from a purely local scale and microscopic perspective.

EXPERIMENTAL METHODS

The cummingtonite sample 118125 used in this study is from Bare Hills, Baltimore, Maryland (Smithsonian Institution). It was well characterized in a previous study (Boffa Ballaran et al. 2000) by means of transmission electron microscopy, microprobe analysis, X-ray diffraction, and IR spectroscopy. The composition is expressed in terms of XFe = Fe/(Fe + Mg) = 0.36 and the impurity (Al, Ca, and Na) content is negligible.

Mössbauer data were recorded in transmission mode using a constant acceleration Mössbauer spectrometer equipped with a nominal 50 mCi 57Co source in a 6 μm Rh matrix. Low temperature experiments were performed using a continuous flow cryostat with the sample held in nitrogen vapor, with temperature controlled to within ±0.5 K. High temperature experiments were performed using a vacuum furnace controlled to within ±1 K, and evacuated to 2 × 10−3 Pa using a diffusion pump to prevent oxidation. Mössbauer spectra were collected at each temperature for 10 to 20 hours. The velocity scale was calibrated relative to 25m/α-Fe foil using the position certified for National Bureau of Standards standard reference material no. 1541. The collected spectra were fit to Voigt line shapes using the commercial fitting program NORMOS written by R.A. Brand (distributed by Wissenschaftliche Elektronik GmbH, Germany).

RESULTS

Cummingtonite is a double chain silicate with the amphibole structure. Its composition can be expressed in terms of the solid solution Mg5Si8O22(OH)2–Fe5Si8O22(OH)2 (Hawthorne 1981). Crystals with intermediate compositions display a reversible C2/m ↔ P21/m (zone boundary) transition as a function of temperature, while Fe-rich crystals undergo the same transition when subjected to increasing hydrostatic pressure (Boffa Ballaran et al. 2000; Prewitt et al. 1970; Sueno et al. 1972; Yang and Hirschmann 1995; Yang et al. 1998). The structural mechanism for this transition involves rotations of SiO4 tetrahedra in the double chains such that the chains are extended parallel to ε in the C2/m structure but are contracted in the P21/m structure (Fig. 1). These rotations cause changes in the oxygen atom positions around the M4 crystallographic sites and it is these changes in coordination, which are detected in the Mössbauer signal from Fe2+. In the C2/m structure, there are four oxygen atoms at distances between 2 and 2.2 Å from the...