Temperature dependence of IR absorption of OH species in clinopyroxene

YAN YANG, QUNKE XIA,* MIN FENG, AND PEIPEI ZHANG

CAS Key Laboratory of Crust-Mantle Materials and Environments, School of Earth and Space Sciences, University of Science and Technology of China, Hefei 230026, China

ABSTRACT

The behavior of structural OH in clinopyroxene (augite and omphacite) during successive heating has been investigated by in situ micro-FTIR measurements under temperatures ranging from room temperature to 500 °C at 100 °C increment. The first group of OH band (3620–3640 cm⁻¹) exhibits a systematic decrease of peak position upon successive heating, while the other two groups (3520–3535 and 3450–3465 cm⁻¹) show only little change. Both augite and omphacite display a decrease of integral absorbance of OH fundamental stretching vibration upon successive heating. The IR spectra of OH band are reversible when the temperature decreases from 500 °C to room temperature, suggesting that changes in IR indicate changes in molecular state of OH. Based on: (1) the decreases of integral absorbance of OH bands with increasing temperature, and (2) comparison with Paterson’s relationship (Paterson 1982), we suggest that OH absorption coefficients are temperature dependent, so it is necessary to apply different absorption coefficients when determining OH content from Beer-Lambert law at different temperatures and sample temperatures should be reported in quantitative IR studies.

Keywords: IR, varying temperature, OH, clinopyroxene

INTRODUCTION

It is well known that OH incorporated in nominally anhydrous minerals (NAMs) has significant effects on their chemical and physical properties. IR is a powerful tool to detect trace amount of OH in NAMs because of its high sensitivity. With the improvement of analytical technique, the study of OH in NAMs becomes more precise. Methods exploring incorporation mechanisms of OH defects in NAMs are limited, and sometimes different methods come to different conclusions. For example, Skogby (1994) observed a band at 3530 cm⁻¹ in clinopyroxene by synthesis experiment and suggested that it was related to Fe, while Koch-Müller et al. (2004) suggested that the band was related to Al³⁺ using the relationship between absorbance intensity and Al⁴⁺ content. So, it is necessary to find a new way to study OH incorporation mechanisms in NAMs. Because IR spectroscopy can give crystal-structure information on a local scale and the bonds with different chemical and structural environment have different thermal expansion, we expect to find the relationships between OH frequency shifts (dv/dT) value and the chemical composition by successive heating experiments. This in turn can be used to explore the incorporation mechanisms of OH defects.

At present, calculations of OH concentrations in NAMs are based on absorption coefficients obtained at room temperature (Rossman 2006). Although some researchers investigated temperature dependence of OH absorption coefficients and H₂O in some minerals and glasses (Yamagishi et al. 1997; Suzuki and Nakashima 1999; Withers and Behrens 1999; Okumura and Nakashima 2005; Zhang et al. 2007), the knowledge on the temperature dependence of OH absorption coefficients in natural NAMs is still uncertain.

In this paper, we use in situ IR spectroscopy to study the OH behavior in clinopyroxene at varying temperatures. We try to address: (1) whether a relationship exists between OH frequency shifts (dv/dT) and specific chemical compositions, and (2) whether absorption coefficients of OH in clinopyroxene are temperature dependent.

EXPERIMENTAL METHODS

Sample description

Clinopyroxene samples include diopsides (labeled as fs18, ms25, p17, and p6) from peridotite xenoliths and augite megacryst (labeled as T4) hosted by Cenozoic basalts from different localities of eastern China, as well as omphacite (labeled as SH-6) from an ultrahigh-pressure (UHP) metamorphic eclogite from Dabieshan, China. All samples are prepared as doubly polished grains with 3–5 mm size and 0.1–0.5 mm thickness.

Electron microprobe

The chemical compositions of these samples were determined using a JEOL Superprobe (JXA 8100) electron microprobe (EMP) at Nanjing University, China, with the following operating conditions: 15 kV accelerating voltage, 10 nA beam current, and <5 µm beam diameter. Natural minerals and synthetic oxides were used as standards, and a program based on the ZAF procedure was used for data correction. The standards for EMP analysis are as follows: natural samples (quartz, olivine, almandine, wollastonite, rutile, jadeite, and sandidine) and synthetic oxides (NiO, MnO, and Cr₂O₃). Multi-point measurements were carried out from the core to the rim of each mineral grain. The EMP analyses demonstrate the chemical homogeneity of the samples and the average values are reported in Table 1.

Methods

A Linkam FTIR600 heating and cooling stage was placed on the sample stage of the IR microscope. The temperature was increased from room temperature to 500 °C in 100 °C increments and then cooled to room temperature at a rate of 10 °C/min. At every temperature step, the holding time was 20 min. The temperature was controlled by Linkam TMS94 with 0.1 °C accuracy. Unpolarized spectra were obtained from 1250 to 4000 cm⁻¹ on a Nicollet 5700 FTIR spectrometer coupled with a Continuum microscope at the University of Science and Technology of China (USTC), using a KBr beam-splitter and a liquid-nitrogen cooled MCT-A detector.