Assignment of infrared OH-stretching bands in calcic amphiboles through deuteration and heat treatment

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ABSTRACT

Infrared OH-stretching bands of calcic amphiboles in the magnesiohornblende-tschermakite/ferrotschermakite and edenite-pargasite/hastingsite series have been assigned by deuteration and heat treatment in air. Mössbauer spectra indicate that with increasing temperature for heat-treatment in air, Fe²⁺ at the M1 and M3 sites is first converted to Fe³⁺ through dehydrogenation, and then Fe²⁺ at the M2 site is oxidized at higher temperature. The quadrupole-splitting parameters of (oxidized) Fe³⁺ at the M1 and M3 sites and Fe³⁺ at the M2 site are much larger than in natural (= non-dehydrogenated) amphiboles, indicating that dehydrogenation of O3H causes large electric-field-gradients at the M1-3 sites. The intensity of absorption of Fe³⁺ at M2 decreases with heating temperature, which is consistent with the migration of Fe³⁺ at M2 to the M1 and/or M3 sites. The (MgMgAl)-OH band, designated K*, occurs at ~3678 cm⁻¹ in Fe²⁺-poor pargasitic amphiboles, and is assigned to the configuration (MgMgAl)-OH-(Na,K):1⁰Si²⁺Al. Three (2–4) of the following types of band systems occur with decreasing band frequency: (1) A*-D* bands at 3730–3675 cm⁻¹, associated with (M1M1M3)-OH-(Na,K):1⁰Si²⁺Si configurations; (2) A*-D* bands at 3725–3650 cm⁻¹, associated with (M1M1M3)-OH-(Na,K):1⁰Si²⁺Si configurations; (3) A-D bands at 3680–3620 cm⁻¹, associated with (M1M1M3)-OH-(Na,K):1⁰Si²⁺Si configurations; and (4) A-D bands at 3560–3580 cm⁻¹, associated with (M1M1M3)-OH-(Na,K):1⁰Si²⁺Si configurations. In addition, A**T, E**T, and K**T bands ascribed to the configurations (MgMgMg)-OH-(Na,K)-O³O²–:T1SiT1Al, (MgMgFe³⁺)-OH-(Na,K)-O³O²–:T1SiT1Al, and (MgMgAl)-OH-(Na,K)-O³O²–:T1SiT1Al are important constituents of the spectra of oxidized magnesiohornblende and pargasite. The high frequency bands, A*-D*, are particularly weak, indicating short-range order involving local association of the 1⁰Si²⁺Al configuration with a locally occupied A-site.

Keywords: Infrared OH-stretching spectra, tetrahedral Al, calcic amphibole, pargasite, deuteration, heat-treatment

INTRODUCTION

The OH-stretching bands in the infrared region contain much information on chemical composition and short-range order, and several FTIR studies have shown that this is the case for amphiboles (e.g., Della Ventura et al. 1999; Melzer et al. 2000; Hawthorne et al. 2000; Ishida et al. 2002). It can be difficult to interpret the infrared OH-stretching bands for calcic amphiboles containing tetrahedrally coordinated Al because of their chemical complexity. Assignment of the component bands in the infrared spectrum of tremolite containing A(Na,K), TAl, and 0.67 F apfu (Hawthorne et al. 1996) shows that the non-tremolite components are not randomly distributed throughout the structure but show extreme short-range order: Na and K at the A site are locally associated with Al at an adjacent T1 site. Subsequent to this study, more extensive work has been done on interpreting the FTIR spectra of synthetic amphiboles along the richterite-pargasite join (Della Ventura et al. 1999; Jenkins et al. 2003), the tremolite-aluminoschermakite join (Hawthorne et al. 2000), and the tremolite-tschermakite join (Najorka and Gottschalk 2003).

In calcic amphiboles, there are two types of substitution involving Al at octahedral and tetrahedral sites: the Tschermak substitution (⁴⁰Al⁴⁰Al⁴⁰Mg-1⁰Si-) and the edenite substitution (⁴⁰Al⁴⁰Na⁴⁰Si-, which, taken together, give the pargasite substitution (Jenkins et al. 2003). Della Ventura et al. (1998) showed that in synthetic end-member Co-pargasite, only the (CoCoCo)-OH stretching band is observed, and hence in this Co-pargasite, ⁴⁰Al is completely ordered at the M2 site. Ordering of ⁴⁰Al at M2 occurs in Fe²⁺-containing tschermakite and pargasite, but not in Mg-rich compositions (Oberti et al. 1995a; Della Ventura et al. 1998; Hawthorne et al. 2000).

There are two tetrahedrally coordinated sites in the C2/m amphibole structure, T1 and T2. Normally, ⁴⁰Al is strongly ordered at the T1 site (Oberti et al. 1995a, 1995b). The effect of Al at the T1 site on the infrared spectra of monoclinic amphiboles has been discussed by Della Ventura et al. (1999) and Hawthorne et al. (2000). The hydrogen bond formed between H and the adjacent