Influence of layer charge on the hydroxyl stretching of trioctahedral clay minerals:
A vibrational study of synthetic Na- and K-saponites

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ABSTRACT

To understand the behavior of octahedral hydroxyl-stretching modes (νOH) as a function of increasing tetrahedral layer charge, infrared and Raman spectroscopic studies were carried out on a series of synthetic saponites. The nature of the monovalent interlayer cation (Na or K) and the hydration of the samples were shown to strongly influence spectral features. In the case of hydrated Na-samples, the νOH position shifts from 3678 to 3686 cm⁻¹ with increasing layer charge. For hydrated K-saponites, two components are observed around 3720 and 3680 cm⁻¹, assigned to OH perturbed by compensating cation and free OH groups, respectively. In the case of dehydrated samples both K and Na-saponites exhibit two components at 3677 and 3720 cm⁻¹. A linear relationship between the relative area of these two νOH components and the layer charge was then evidenced. To assign the features obtained for hydrated Na-samples in the OH-stretching modes domain, the Raman spectra were decomposed using four νOH components around 3675, 3680, 3685, and 3690 cm⁻¹. The evolution with layer charge of the relative proportions of these four components can be described by taking into account the location of hydrated cations, related to the distribution of tetrahedral substitutions. Such an assumption was confirmed using a simple statistical model that yields four populations of OH groups in the octahedral layer of hydrated Na-saponites.

INTRODUCTION

Vibrational spectroscopic studies have been widely used for characterizing clay minerals. In particular, numerous works have been dedicated to deriving various relationships between structure, composition, and infrared (IR) spectra. Indeed, the environment of octahedral hydroxyl groups can be determined from the position and intensity of IR vibrational modes that are sensitive to the nature and number of octahedral cationic species in di- or trioctahedral phyllosilicates (Stubican and Roy 1961; Vedder 1964; Farmer 1974; Velde 1983; Slonimskaya et al. 1986; Besson et al. 1987; Robert and Kodama 1988; Robert et al. 1989; Decarreau et al. 1992; Robert et al. 1993; Madejova et al. 1994; Petit et al. 1995; Besson and Drits 1997a, b; Komadel et al. 1999; Vantelon et al. 2001; Madejova 2002). OH stretching and bending vibrational modes are also affected by the presence of hydration water molecules in the case of smectites (Prost 1975; Suquet et al. 1982; Xu et al. 2000), and by the amount of tetrahedral charge (Farmer and Russell 1967). Indeed, using synthetic Al-phlogopite with variable composition, Papin et al. (1997) have shown that changes in the composition of 6(TO₄) rings influence OH-stretching vibrations: for a given octahedral composition, the OH-stretching band must be simulated using two elementary components corresponding to two types of ditrigonal cavities present in the tetrahedral layer.

The aim of the present paper is to extend such a study to low charge clay minerals using a series of 12 synthetic saponites with layer charge varying between 0.70 and 2.0 per unit cell. For such trioctahedral minerals, all hydroxyl groups are linked to three Mg atoms, which allows us to systematically investigate the influence of tetrahedral composition. For such a range of structural charge, the interlayer region is accessible to water molecules that can interact with both the clay layer and the interlamellar cation (Suquet et al. 1977; Suquet et al. 1982). To take into account the role of hydration water, the saponite samples were studied for various water contents using two monovalent cations with distinct hydration properties, sodium and potassium. Indeed, in solution Na⁺ is considered as a structure-making cation, whereas K⁺ is a structure-breaking ion (Ohtaki and Radnai 1993). However, the presence of hydration water induces some broadening of IR signals and an increase in the OH-stretching absorption intensity (due to in-

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1 In principle, the high charge materials cannot be considered as true saponites. However, as they belong to a continuous series of samples, we still chose to identify them as saponites.