

## ION TRANSPORT IN SINGLE CRYSTALS OF THE CLAY-LIKE ALUMINOSILICATE, VERMICULITE

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### ABSTRACT

We have made an investigation of the ion transport properties of single crystals of the naturally occurring clay vermiculite in order to elucidate the mechanism of conductivity including the predominant charge carrier. Measurements of the ion conductivity, magnetic susceptibility and x-ray lattice parameters of ion-exchanged samples strongly suggest that the native cations and not protons are the major current carriers. We have synthesized the hydrogen form and found that it is a much preferred precursor for ion-exchange by other cations allowing the time necessary for ion-exchange to be reduced from several months to around a week.

### INTRODUCTION

Although a number of studies have been made of the diffusion of cations and water in aluminosilicate materials [1-5], there is still much disagreement as to the major charge carriers so we embarked on a study [6,7] of single crystal samples where surface diffusion is minimized. These layered clay/mica compounds have the ideal composition  $\text{Al}_3(\text{Si}_4\text{O}_{10})(\text{OH})_2$ , but substitution in the tetrahedral (Si) and octahedral (Al) sites lead to incorporation of cations in the Van der Waals layer to maintain charge balance. These cations are frequently hydrated, the degree of hydration being a function of the water partial pressure as well as of the cation and the charge density in the layers. The montmorillonite class of clays have the lowest charge density (i.e. lowest cation content) and are found only as poorly crystalline fine powders; they swell continuously as the salinity of their environment decreases [8]. At the other extreme are the micas which have the compositions  $\text{M}^+(\text{Si}_3\text{AlO}_{10})(\text{Mg}_3)(\text{OH})_2$  and  $\text{M}^{2+}(\text{Si}_2\text{Al}_2\text{O}_{10})(\text{Mg}_3)(\text{OH})_2$ ; their very high charge densities preclude the incorporation of water or other solvents except in a few special cases. In between reside the vermiculite class of aluminosilicates with the idealized formula  $\text{M}^+(\text{Si}_3\text{AlO}_{10})(\text{Mg}_3)(\text{OH})_2, y\text{H}_2\text{O}$  where  $y$  can vary from 0 to above 5; in practice the M content is somewhat less and the aluminum content somewhat greater than unity. A schematic of the three phases of sodium vermiculite is shown in fig. 1.

The vermiculites and micas are readily available from natural sources as single crystals so are ideal for studies of transport properties like conductivity. Thus in these cases the external surface area is minimal in contrast to the montmorillonites where in the presence of water the surface area can be in excess of  $100 \text{ m}^2/\text{gm}$ . We therefore do not anticipate any major contributions from surface conduction by native or foreign species such as protons. In addition, there are no grain boundaries to hinder or enhance the transport of cations. Whereas, Calvet and Mamy [1] suggested that the major charge carriers in sodium montmorillonite are proton species, possibly due to the Bronsted acidity of the