Quantum mechanical calculations of dioctahedral 2:1 phyllosilicates: Effect of octahedral cation distributions in pyrophyllite, illite, and smectite

C. IGNACIO SAINZ-DÍAZ,1,* VICENTE TIMÓN,2 VICENTE BOTEILLA,2 EMILIO ARTACHO,3 AND ALFONSO HERNÁNDEZ-LAGUNA1

1Departamento de Ciencias de la Tierra y Química Ambiental, Estación Experimental del Zaidín (C.S.I.C.), C/Profesor Albareda,1, 18008 Granada, Spain
2Instituto de Estructura de la Materia (C.S.I.C.), C/Serrano 113, 28006 Madrid, Spain
3Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge CB2 3EQ, U.K.

ABSTRACT

The structure of dioctahedral 2:1 phyllosilicates with different interlayer charge was studied theoretically using ab initio calculations. The standard Kohn-Sham self-consistent density functional method was used in the generalized gradient approximation (GGA), with numerical atomic orbitals as the basis set, by means of the SIESTA program. Once the method had been checked satisfactorily, the theoretical study was extended beyond the systems for which there are experimental information, and structural characteristics were predicted. The SIESTA program was shown to be a useful tool in studying the crystallographic properties of 2:1-dioctahedral phyllosilicates. The crystal structures of pyrophyllite, beidellite, and other smectites and illites were simulated. The experimental crystallographic properties of phyllosilicates with high, medium, and low interlayer charge were reproduced. The calculated structures agree with the main experimental structural features of the crystal lattice of these minerals. The effect of cation substitutions in the octahedral and tetrahedral sheets was also studied. The calculated effects are consistent with experimental results. The Mg2+ cations were found to have a tendency to be distributed in the octahedral sheet, in contrast to Fe3+ ions that tend to be clustered.

INTRODUCTION

The 2:1 phyllosilicate clay minerals share the common structural feature of single sheets of octahedrally coordinated cations sandwiched between two layers of tetrahedra. The great diversity of these layered silicates is due to isomorphous substitution of various cations in the octahedral and tetrahedral sheets. These substitutions include Al3+ by Mg2+, Fe3+, and Fe2+ in the octahedral sheet, and Si4+ by Al3+ in the tetrahedral sheet, and can result in a net negative charge of the layers. This charge is compensated by the presence of additional cations in the interlayer space. In this space, the cations can be exchanged easily. Organic or water molecules can intercalate between the layers, inducing swelling of the clays (Karaborni et al. 1996). The geometric similarity of the layers of these minerals facilitates the formation of structures containing different kinds of layers and in different arrangements, ordered and disordered. Cation substitutions (in the octahedral and tetrahedral sheets) also give rise to disorder in these minerals. All these types of structural disorder and the small size of the crystals in clays make it difficult to obtain good experimental structural data by means of X-ray, neutron, or electron diffraction techniques, especially in the case of smectites and illites. The valuable catalytic and adsorptive properties of clays demand a firm theoretical understanding of their structure and behavior. Our understanding of some of the important issues in the experimental behavior of these minerals is aided by the application of theoretical studies. Such issues include mineral transformations, chemical transport in the environment and some industrial applications of clays, in catalysis, and as a barrier component for nuclear waste and other pollutant deposits.

The cation distribution in the tetrahedral sheet of micas has been studied experimentally and theoretically (Herrero and Sanz 1991; Palin et al. 2001). These authors found a random distribution of cations in the tetrahedral sheet with the Loewenstein rule of AlAl pair avoidance. Reverse Monte Carlo simulations have been used to study the octahedral cation distribution in illite-smectite systems taking into account experimental NMR and IR spectra (Cuadros et al. 1999; Sainz-Díaz et al. 2001a). A short-range ordering in the Fe and Mg distribution was found in these studies.

Much effort has been dedicated to the modeling of mineral structures at the atomic level, thanks to the important advances in theory and computer technology in recent years (Lasaga 1995; Sauer et al. 1994). Modeling of layered phyllosilicates with high interlayer charge, such as muscovite, has been reported, where models of empirical interatomic potentials were applied (Collins and Catlow 1992; Bosenick et al. 2001). However, clay structures with low interlayer charge are difficult to treat using empirical potentials. In general, these methods describe reasonably well the experimental crystal lattice structure of clays (Teppen et al. 1997; Sainz-Díaz et al. 2001b). However, some geometrical features, such as the interlayer