Aluminum ordering and clustering in Al-rich synthetic phlogopite: \{^{1}H\} \rightarrow ^{29}Si CPMAS HETCOR spectroscopy and atomistic calculations

RAMONA LANGNER,¹ MICHAEL FECHTELKORD,¹,* ALBERTO GARCÍA,² ERIKA J. PALIN,³ AND JAVIER LÓPEZ-SOLANO†

¹Institut für Geologie, Mineralogie und Geophysik, Ruhr-Universität Bochum, Universitätsstr. 150, 44780 Bochum, Germany
²Institut de Ciència de Materials de Barcelona (ICMAB-CSIC), Campus de la UAB, 08193 Bellaterra, Spain
³Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge, CB2 3EQ, U.K.
†Departmento de Física de la Materia Condensada, Facultad de Ciencia y Tecnología, Universidad del País Vasco, UPV/EHU, Apdo. 644, 48080 Bilbao, Spain

ABSTRACT

The cationic ordering in the octahedral and tetrahedral sheets of Al-rich synthetic phlogopites with composition K(Mg_{x}Al_{(1-x)})[Si_{10}O_{32}](OH)_2 (0.0 < x < 1.0) has been investigated using a combined approach of Monte Carlo simulations based on the “J formalism” (Bosenick et al. 2001; Warren et al. 2001) and \(^{1}H\), \(^{29}Si\) MAS and \{^{1}H\} \rightarrow ^{29}Si CPMAS/HETCOR solid-state NMR spectroscopic experiments. Our results are compatible with the well-established Loewenstein’s rule of Al-Al avoidance in the tetrahedral sheets, but the Si\(^{VI}\)Al and Mg\(^{III}\)Al distributions show a tendency to segregation of the excess Al atoms, and we observe a preference for \(^{VI}\)Al and \(^{IV}\)Al to occupy directly neighbored octahedral and tetrahedral sites. As a result the structure is separated into clusters of original phlogopite composition [K(Mg)][AlSi_{2}O_{5}](OH)_2 and clusters of “eastonite” composition [K(Mg,Al)][AlSi_{2}O_{5}](OH)_2 that encompass a whole T-O-T layer package, although Al is solved in the phlogopite structure homogeneously on a macroscopic level.

Keywords: HETCOR CPMAS NMR, phlogopite, Monte Carlo simulations, J formalism, total-energy calculations, GULP, SIESTA

INTRODUCTION

Phlogopite is the magnesium end-member [K(Mg)][AlSi_{2}O_{5}](OH,F)_2 of the biotite solid-solution series of the phyllosilicate mica family. It can be found in various rocks formed over a wide range of pressure and temperature conditions. One major occurrence is in contact metamorphosed limestones and dolomites, in which nearly pure Mg-phlogopites can be found (Schreyer et al. 1980). Phlogopites have also been found in kimberlites and are thought to be carriers of volatiles in the upper mantle (Virgo and Popp 2000). Moreover, the mineral is present in intrusive and extrusive magmatic rocks, where it can incorporate considerable amounts of fluorine. This element is able to influence the physical and chemical properties of a magma even in small amounts (Christiansen et al. 1983; London 1987; Pichavant and Manning 1984; Whalen et al. 1987) so that detailed information on the incorporation mechanism of fluorine into the phlogopite structure may be valuable for magmatic petrology. This, however, also depends on the incorporation and ordering of Al in the phlogopite structure, so that both topics have to be investigated.

The framework structure of phlogopite consists of two tetrahedral sheets of a two-dimensional infinite array of corner-linked TO\(_4\) tetrahedra, each of which is joined by an apical O atom to a single octahedral sheet. Three of the four tetrahedral sites per half unit-cell in natural phlogopite are occupied by Si and the remaining site by Al. Potassium ions in the interlayer sections balance the negative charge of the Al-containing tetrahedral sheets. Increasing the Al content in phlogopites according to Tschermak’s substitution (\(^{III}\)Mg\(^{IV}\)Si \rightarrow \(^{III}\)Al\(^{IV}\)Al) leads to an additional substitution of Si sites by Al, reaching toward the hypothetical end-member “eastonite,” K(Mg,Al)[Al_{2}Si_{2}O_{5}](OH,F)\(_2\).

In pure phlogopite, the octahedral sites are occupied by Mg (three sites per half unit cell). Two Mg sites (M2) are coordinated by four O atoms from the tetrahedral sheets and two (OH\(^{-}\) and/or F\(^{-}\) anions in cis-coordination. The third Mg site (M1) has a trans-coordination of the hydroxyl and/or F\(^{-}\) anions. The (OH\(^{-}\) and/or F\(^{-}\) anions are always coordinated to three Mg-sites. In the Al-rich phlogopites some of the Mg sites are substituted by Al, so that some of the (OH\(^{-}\) and/or F\(^{-}\) anions are coordinated by two Mg cations and one Al cation.

In their IR spectroscopic study, Papin et al. (1997) demonstrated that the OH/F distribution in Al-rich phlogopite is not statistically random: the hydroxyl groups prefer Mg\(^{II}\)Al coordination and the fluorine atoms prefer Mg\(^{III}\) coordination. This is in agreement with our recent \(^{19}F\), \(^{1}H\), and \(^{29}Si\) MAS NMR study (Fechtelkord et al. 2003a), and IR study (Fechtelkord et al. 2003b), which found the same kind of non-statistical distribution of cations and anions in the octahedral sheets. In addition, it was shown that samples with hydroxyl-rich compositions exhibit an increased Al content in the tetrahedral sheets, suggesting a stabilizing effect on the formation of Al-rich