An alternative method of calculating cleavage energy: The effect of compositional domains in micas

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ABSTRACT

Cell parameters and atomic coordinates for the true micas are varied to simulate layer deformation along the [001]* direction by an external force. The resulting (deformed) structures are then used to determine bonding forces and to calculate a maximum force component along the [001]*. Bonding forces are compared to experimental observations of bond lengths of the interlayer, octahedral, and tetrahedral sites. Calculated bonding forces are consistent with experimental observations that locate the cleavage plane along the interlayer. Because many studies have shown that the chemical composition of the cleavage surface often differs from the structure of the bulk, compositional variations were considered in determining cleavage energy. The chemical composition of the cleavage surface may produce a reduction in cleavage energy. This reduction in energy depends on various elements occurring in greater number at the cleavage surface than in the bulk. A reduction in cleavage energy occurs if there is a reduction in the interlayer site size, as measured by the area defined by the first-coordination basal oxygen atoms. In addition, a reduction in lateral cell dimensions and an increase in the bonding force between the basal oxygen atoms and the interlayer cation also results in a reduction in cleavage energy in the direction normal to the layer.

Joins considered are phlogopite–annite, tetra-ferriphlogopite–tetra-ferri-annite, polythionite–siderophyllite, muscovite–celadonite, and muscovite–paragonite. A lack of homogeneity in composition may produce preferential cleavage locations within the family of (001) planes. The cleavage energy appears to be greater for homogeneous synthetic micas compared to natural micas.

Keywords: Micas, cleavage, electrostatic force, crystal chemistry, crystal structure

INTRODUCTION

Knowledge of the atomic arrangement of the topmost crystal surface of layer silicates is a requirement for the understanding of a large number of surface phenomena and the geochemical cycling of elements at the Earth’s crust (Hochella 1990). Micas are of special interest because they are common phases in metamorphic, sedimentary, and igneous rocks and are used in many technological applications. The planar basal (001) surface, readily produced by cleavage, is ideally suited for numerous applications such as catalysts, sensors, automotive paints, cosmetics, ceramic pigments, and many others (Hochella 1995; Kogel et al. 2006; Maurice 2009; Andrić et al. 2014). The cleavage of mica is believed to occur at the interlayer, parallel to (001), and results in the exposure of K atoms and is repulsed from other K atoms and the (OH) groups present in the ditrigonal cavity. Substitution of (OH) by F increases strength of the interlayer bonding (Giese 1977; Dahl and Dorais 1996). Some experimental studies (e.g., Poppa and Elliot 1971; Kogure 1997; Biino and Gröning 1998; Elmi et al. 2013, 2014a, 2014b) relating bulk and surface crystal chemistry of the micas showed relaxation and reconstruction phenomena at the mica surface (e.g., variation of coordination number for the interlayer cation, preferential coordination for Mg to F compared with Mg to OH). In addition, these studies showed compositional variation from the bulk, such as K depletion and Si reduction from its highly oxidized state to the elemental state. Potassium depletion at the cleavage surface has been observed in all micas studied and this result is consistent with cleavage occurring by failure of interlayer cation to basal oxygen atom bonds (González-Elipe et al. 1988; Biino and Gröning 1998; Kogure 1997; Elmi et al. 2013, 2014a, 2014b). In addition, for Li-rich micas, an increase in Li content was observed near the (001) cleavage surface, thus suggesting a preference for cleavage near Li-enriched regions. Similarly, in muscovite, Na was observed to significantly increase at the cleavage surface (Elmi et al. 2013). At the surface of phengitic muscovite, Biino and Gröning (1998) observed an increase in Al content and in minor octahedral cations, such as Mg, with respect to the bulk. The authors suggested that cleavage may involve regions enriched with chlorite-like domains. In phlogopite, Evans et al. (1979) observed, at the cleavage surface, an increase in Al content at the expense of Mg, which is consistent also with the hypothesis of Biino and Gröning (1998).