Trioctahedral Fe-rich micas: Relationships between magnetic behavior and crystal chemistry

MARIA FRANCA BRIGATTI1*, MARCO AFFRONTE2, CHIARA ELMI1, DANIELE MALFERRARI1 AND ANGELA LAURORA1

1Dipartimento di Scienze Chimiche e Geologiche, Università di Modena e Reggio Emilia, Via G. Campi, 103, I-41125 Modena, Italy
2Dipartimento di Scienze Fisiche, Informatiche e Matematiche, Università di Modena e Reggio Emilia, Via G. Campi 213/a, I-41100 Modena, Italy

ABSTRACT

Six Fe-bearing mica samples with different Fe ordering, Fe2+/Fe3+ ratio, octahedral, and tetrahedral composition were studied. Four micas belong to the phlogopite-annite join (space group C2/m), two are Mg-rich annite and two are Fe-rich phlogopite, one is a tetra-ferriphlogopite (space group C2/m) and one is Li-rich siderophyllite (space group C2). Thus these samples had a different environment around the Fe cations and layer symmetry. These micas were characterized by chemical analyses, single-crystal X-ray diffraction, X-ray absorption spectroscopy, and magnetic measurements. In samples with Fe mostly in octahedral coordination, dominant magnetic interactions among Fe atoms are ferromagnetic, which reach a maximum at higher Fe2+/Fe3+ ratios. Samples with higher Fe2+/Fe3+ ratio are also characterized by higher values of the Curie-Weiss θ constant. Where Fe2+/Fe3+ ratios decrease, θ values also decrease. The Fe3+-rich phlogopite shows predominant Fe3+ in tetrahedral coordination and shows anti-ferromagnetic interactions with a negative value of the Curie-Weiss θ constant (i.e., θ = –25 K). Fe ordering in octahedral trans- and in one of the two cis-sites accounts for a greater θ value in Li-rich siderophyllite when compared to other samples showing similar octahedral Fe content. Our data suggest that Fe3+ cations and other non-ferromagnetic cations hinder long range magnetic ordering. This observation may produce for the different role of octahedral Fe magnetic interactions that can in principle develop along long Fe-rich octahedral chains, when compared to tetrahedral-octahedral interactions that are confined within the layer by the non-ferromagnetic cations of the interlayer. Spin glass behavior is indicated by the dependency of the temperature to produce maxima in the susceptibility curve. These maxima are related to the frequency of the applied AC magnetic field.

Keywords: Fe-rich micas, X-ray absorption spectroscopy, chemical analysis, single-crystal X-ray structure determination, magnetic measurements

INTRODUCTION

Magnetic techniques are powerful methods to understand electronic and thermodynamic properties of materials (Catalli et al. 2011; Hsu et al. 2010). When complex materials, such as minerals, are involved, magnetic investigations become extremely challenging. Iron is 40 times more abundant than any other magnetic element in the Earth’s crust, which is predominantly composed of silicates, thus suggesting why most magnetic studies on minerals are focused on iron silicates such as pyroxenes (Redhammer et al. 2011, 2012). These minerals represent model systems to study magnetic properties characterized by a competitive interaction within and between the quasi-one-dimensional (1D) infinite chains of transition metal bearing octahedral sites. Micas are typical examples of a layer structure, thus showing properties of quasi-two-dimensional (2D) infinite systems. The characterization of magnetic properties of natural Fe-rich trioctahedral micas was addressed by some authors (Anagnostopoulos et al. 1973; Marcelli et al. 2004; Dunlop et al. 2006; Pini et al. 2008, 2012), without however obtaining a full understanding of the role of local topology of Fe atoms on magnetic properties. Even if limited in number, studies devoted to magnetic properties of trioctahedral micas increased significantly in the few past years. These studies, in part were motivated by the abundance of these minerals in nature, but also because of the great variability in content, oxidation condition and local topology of Fe atoms present (Biedermann et al. 2014). The correlation between magnetic properties of natural trioctahedral micas and their crystal chemical and structural features have been explored previously to understand the origin of magnetic properties in minerals and to better characterize their structure, with particular reference for Fe coordination.

In trioctahedral micas, the Fe2+/Fe3+ ratio can vary significantly, together with its distribution within the layer. Fe3+ was found to occupy both tetrahedral (T) and octahedral (M) positions, whereas Fe2+ was located at M positions only (Brigatti and Guggenheim 2002). Fe2+ for Mg2+ octahedral substitution defines the trioctahedral mica join from phlogopite [KMg3AlSi3O10(OH)2] to annite [KFe3AlSi3O10(OH)2] (Bailey 1984). Tetrahedral substitution of Fe3+ for Si4+ gives tetra-ferriphlogopite [KMgFe3AlSi3O10(OH)2] from phlogopite, and tetra-ferri-annite [KFe3Al2Fe3Si3O10(OH)2] from annite. In trioctahedral lithian micas the [Si4+Li2][Al] vector* E-mail: mariafranca.brigatti@unimore.it