SPINELS RENAISSANCE: THE PAST, PRESENT, AND FUTURE OF THOSE UBQUITOUS MINERALS AND MATERIALS

CRYSTAL CHEMISTRY OF THE ULVÖSPINEL-QANDILITE SERIES†

FERDINANDO BOSI1,2,* , ULF HÅLENIUS2 AND HENRIK SKOGBY2

1Dipartimento di Scienze della Terra, Sapienza Università di Roma, Piazzale Aldo Moro 5, I-00185 Rome, Italy
2Department of Geosciences, Swedish Museum of Natural History, SE-10405 Stockholm, Sweden

ABSTRACT

Five spinel single-crystal samples within the ulvöspinel-qandilite series [(Fe2−xMgx)TiO4, 0.15 < x < 0.94] were synthesized and structurally and chemically characterized by X-ray diffraction and electron microprobe techniques. Site populations, derived from structural and chemical analysis, show that the tetrahedrally coordinated site (T) is exclusively populated by Mg2+ and Fe2+, while the octahedrally coordinated site (M) is populated by Ti4+, Mg2+, Fe2+, and minor amounts of Fe3+. The inverse cation distribution is characterized by parallel substitution of Mg2+ for Fe2+ at both the T and M sites along the series.

The variation in the unit-cell parameter from 8.527 to 8.495 Å is mainly related to the occurrence of Mg2+ at the M site rather than the T site. In fact, the substitution of Mg2+ for Fe2+ yields significant variations in M-O (from 2.045 to 2.034 Å) and only limited variation in T-O (from 2.007 to 2.002 Å). In conjunction with data from the literature, the present study provides a basis for quantitative analyses of the variation in 1/Mg-O bond distance from 1.966 Å for Mg-poor ulvöspinel to 1.990 Å for the qandilite end-member.

Keywords: Ulvöspinel, qandilite, electron microprobe, X-ray diffraction, cation ordering, crystal chemistry

INTRODUCTION

Several substances such as multiple oxides, sulfides (e.g., ZnAl2S4), selenides (e.g., CuCr2Se4), halides (e.g., Li2NiF4), and pseudohalides [e.g., ZnK(CN)4] crystallize in the spinel-type structure. Spinel oxides are defined by the general formula AB2O4, where A and B are usually cations of either 2+ and 3+ valence (A2B3O4, so-called 2-3 spinels), or of 4+ and 2+ valence (A4B2O4, so-called 4-2 spinels). The spinel structure, typically symmetry Fd3m, can be described as a slightly distorted cubic close packed array of oxygen anions, in which the A and B cations are distributed in one-eighth of all tetrahedrally coordinated sites (T) and half of all octahedrally coordinated sites (M) (e.g., Bragg 1919; Nishikawa 1919). The unit-cell parameters (a) and oxygen fractional coordinates (u, u, u) define the resulting tetrahedral (T-O) and octahedral (M-O) bond lengths (e.g., Lavina et al. 2002). The distribution of A and B cations over T and M sites leads to two different types of cation ordering: (1) normal spinel, where the A cation occupies T and the two B cations occupy M, and (2) inverse spinel, where one of the B cations occupies T and the remaining A and B cations occupy M. Disordered cation distributions are often encountered among the 2-3 spinels, and can be described by the general formula [(A⁺i B++)j](A2+j B3−j)O4, where i is defined as the inversion parameter. The value of the inversion parameter depends on the spinel composition and cation site preferences: for example, Cr³⁺ only occupies the M site, Al and Cu²⁺ exhibit preference for M, whereas Mg²⁺, Fe²⁺, Mn²⁺, Zn²⁺, and Co²⁺ exhibit preference for the T site (Andreozzi et al. 2001; Andreozzi and Lucchesi 2002; Lenaz et al. 2004; Bosi et al. 2010, 2012; Hålenius et al. 2011; Fregola et al. 2012; D’Ilipolito et al. 2012). In addition, the degree of inversion is strongly sensitive to temperature, and at high temperatures (around 1500 °C), the i-parameter may increase up to 0.35 for normal spinel and down to 0.70 for inverse spinel (Nell et al. 1989; O’Neill et al. 1992; Redfern et al. 1999; Andreozzi et al. 2000). The temperature dependence of cation ordering/disordering has petrological implications for cooling processes because it is strictly related to the closure temperature of spinel, i.e., the point where the ordering process is effectively quenched. Several studies have addressed this phenomenon (e.g., Princivalle et al. 1989, 1999, 2012; Della Giusta et al. 1996; Lucchesi and Della Giusta 1997; Lucchesi et al. 1998, 2010; Uchida et al. 2005; Lenaz et al. 2010; Lenaz and Princivalle 2011). Extensive solid-solution occurs between various spinel end-members, particularly among pairs with the same ordering type. For example, spinel (sensu stricto)-galaxite MgAl2O4-MnAl2O4 is a binary system consisting of two normal spinels (Hålenius et al. 2011), whereas ulvöspinel-qandilite Fe2TiO4-MgTiO4 is a binary system consisting of two inverse spinels (studied hereafter).

The ulvöspinel-qandilite series forms part of the Fe2TiO4-Mg2TiO4-FeF2O4-MgFe2O4 spinel quadrilateral, and spinels within this compositional field have been frequently utilized as petrogenic indicators of temperature and pressure for geological processes. Thermodynamic data and computational results related to order-disorder phenomena in qandilite and titanomagnetite have been reported in the literature (e.g., O’Neill and Scott 2005; Palin et al. 2008; Lilova et al. 2012; Harrison et al. 2013) as well as several crystal chemical studies (e.g., Wechsler et al. 1984; Wechsler and Von Dreele 1989; O’Neill et al. 2003; Bosi et al. 2009). However, no systematic investigation of the structural