Spinels Renaissance: The Past, Present, and Future of Those Ubiquitous Minerals and Materials

Geothermometric study of Cr-spinels of peridotite mantle xenoliths from northern Victoria Land (Antarctica)†

Cristina Perinelli1,*, Ferdinando Bosi2,4, Giovanni B. Andreozzi2, Aida M. Conte3 and Pietro Armienti1

1Dipartimento di Scienze della Terra, Università di Pisa, via S. Maria 53, 56100 Pisa, Italy
2Dipartimento di Scienze della Terra, Sapienza Università di Roma, P.le Aldo Moro 5, 00185 Roma, Italy
3CNR-Istituto di Geoscienze e Georisorse, UOS Roma, P.le Aldo Moro 5, 00185 Roma, Italy
4Department of Geosciences, Swedish Museum of Natural History, SE-0405 Stockholm, Sweden

ABSTRACT

The crystal chemistry of Cr-spinels included in spinel peridotite mantle xenoliths from Baker Rocks and Greene Point (northern Victoria Land, Antarctica) has been studied by single-crystal structure refinement and electron microprobe analysis. All crystals are characterized by a dominance of Al ↔ Cr substitution with minor evidences of Mg ↔ Fe2+ substitution and pertain to the Mg-rich portion of the spinel sensu stricto-chromite join. The two groups of samples, Baker Rocks (BR) and Greene Point (GP), show distinct degree of cation order with the inversion parameter ranging from 0.17 to 0.20 for BR spinels and from 0.06 to 0.13 for GP crystals. Closure temperatures, computed by a geothermometer based on the 8Al+7Mg ↔ 7Al+3Mg intracrystalline exchange, range from 883 to 911 °C for BR spinels and from 592 to 675 °C for GP spinels. We show that this difference is due to the higher concentration in Fe3+ in GP spinels that enabled a faster kinetics of the intracrystalline cation ordering reaction, allowing the GP spinels to reach a higher degree of cation ordering and then lower closure temperatures.

Keywords: Cr-spinel, crystal structure, crystal chemistry, geothermometer, order-disorder kinetics, mantle xenoliths, Antarctica

INTRODUCTION

Spinel-group minerals (Mg,Fe2+)2(Cr,Al,Fe3+)2O4 are common accessory phases of basic and ultrabasic rocks both in the Earth’s upper mantle and the crust. It is widely recognized that the structure and physical properties of spinels are governed by their formation conditions (temperature, pressure, and chemical characteristics of the system), therefore spinels are widely exploited to reconstruct the physical parameters of their environment of origin (see, e.g., Irvine 1965, 1967; Dick and Bullen 1984; Barnes and Roeder 2001). The importance of this group of minerals has prompted extensive studies, many of which are aimed at defining intracrystalline order-disorder relationships and their dependence on equilibrium temperature, cooling history, and composition (e.g., Della Giusta et al. 1996; Princivalle et al. 1999; Andreozzi et al. 2000, 2001; Andreozzi and Princivalle 2002; Bosi et al. 2008; Lucchesi et al. 2010).

The general formula of spinel may be defined as AB2O4, where A and B are usually divalent and trivalent cations (respectively), although tetravalent cations can often occur (e.g., FeTi2O4). The spinel structure (space group 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). With origin at 3m, T and M sites have fixed coordinates (½, ½, ½ and ½, ½, ½) of the cell edge, respectively, and oxygen occupies a 3m point symmetry site with variable (u u u) coordinates. Modifications of T-O and M-O bond distances to accommodate various chemical compositions and/or cation ordering determine variations in the oxygen positional parameter u and the cell edge a. Two extreme site populations are possible: normal i(A)(B)2O4 and inverse i(B)2(A)O4, both being ordered. However, natural spinels are commonly disordered and their cation distributions lie between these two extremes. The general formula defining the disordered cation distributions is i(Ai)(Bi)(AB)2O4 where the letter i represents the inversion parameter that is the number of divalent cations at the M site. This parameter is strongly sensitive to temperature, and the inspection of literature reveals that for temperature increasing up to 1500 °C the value of i increases in normal spinels, from ca. 0 to ca. 0.35, and decreases in inverse spinels, from ca. 1 to ca. 0.70 (Nell et al. 1989; O’Neill et al. 1992; Redfern et al. 1999; Andreozzi et al. 2000). In addition to temperature, the value of i is strongly dependent on spinel chemical composition and cation site preference. As for example, it is recognized that Cr3+ only occupies the spinel M site; Al and Cu2+ exhibit preference for the M site but are available to partly invert into the T site at high temperature; Fe3+ has no preference; Mg, Fe2+, Mn2+, and Co2+ exhibit preference for the T site but are available to partly invert into the M site at high temperature; Zn only occupies the

* E-mail: cperinelli@tiscali.it
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