# Behavior of cation vacancy in kenotetrahedral Cr-spinels from Albanian eastern belt ophiolites

FERDINANDO BOSI,* GIOVANNI B. ANDREOZZI, VINCENZO FERRINI, AND SERGIO LUCCHESI

Dipartimento di Scienze della Terra, Università di Roma "La Sapienza", P.le A.Moro 5, 00185 Roma, Italy

ABSTRACT

The crystal chemistry of 17 Cr-spinels from the Albanian eastern belt ophiolites was studied by a multi-analytical approach (EMPA, MS, SREF), processing the data with a tested optimization model to obtain site populations. The samples come from the three most important ultramafic massifs of Albania (Tropoja, Bulqiza, and Shebenik), and occur in ultramafic cumulates as well as in ultramafic mantle tectonites, associated with serpentinized olivine. All samples are characterized by $Cr \leftrightarrow Al$ and minor $Mg \leftrightarrow Fe^{2+}$ substitutions, and may be classified as magnesiochromite, except one, which is spinel s.s. Cation distributions showed that Cr and Al are ordered in M, and Fe^{2+} and Mg in the T site. Contents of Fe^{3+} measured by MS were always higher than those calculated from EMPA, and this non-stoichiometry reveals that the Albanian crystals underwent an increase in f_{O_2} conditions after mineral formation. Cation vacancies produced by Fe^{2+} oxidation occur in the T site, and the oxidation mechanism, is described by:

$$2\ ^TFe^{2+} + \tfrac{1}{2}\ O_2 \rightarrow 2\ ^TFe^{3+} + O^{2-} +\ ^T\square.$$
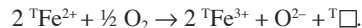
T-O variations show a non-linear regression with $^TFe^{2+}$, and this trend is due to both the cooperative effects of $^TMg \leftrightarrow\ ^TFe^{2+}$ substitution and $^TFe^{2+}$ oxidation. Cation vacancy in the T site does not impart rigidity to the polyhedron, because it cannot have chemical bonds with ligands: this feature, together with the spinel topology, makes the tetrahedron adopt "soft" behavior. In effect, the $^T\square$-O distance does not have a single value, but changes according to the population of the M site, as confirmed by comparison with literature data and also by application of the Bond Valence Model.