(Fe, Mg) distribution in olivine: 
effects of data collection and refinement strategies

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Abstract: Determination of cation distributions in minerals is crucial for any thermodynamic application. In order to explore to what extent the choice of X-ray data collection, reduction, and structure refinement procedures might influence obtained site occupancies, a methodological and interlaboratory study was undertaken. Two single crystals of olivine (Fo90 and Fo45) were used to collect diffraction data up to θ = 110° (MoKα) in three Italian laboratories with different single-crystal diffractometers (SIEMENS AEDII, PHILIPS PW1100, KUMA KM4). In each laboratory, several data collections (12 and 10 for samples Fo90 and Fo45, respectively) were carried out for each crystal, changing crystal mounting and measurement strategies for every experiment. All data were refined using the Strucy, Orfls and Shelx-93 programs with various refinement models, refinement strategies and weighting schemes, for a total number of 240 and 204 refinements for samples Fo90 and Fo45, respectively. The main results are as follows.

a) Atomic coordinates obtained by refining data sets at various resolutions with different refinement programs and crystal mountings do not change significantly. The structural geometry is therefore not affected by either resolution or refinement strategy.

b) When refining a single set of data with different programs, the differences obtained for M1 and M2 site occupancies are up to 0.02 and 0.03 for both Fo90 and Fo45 crystals due to changing refinement models (valence states, extinction correction) and refinement strategy.

c) When all the data sets collected in the three laboratories were refined with the same program (Shelx-93), the results only suffered from different crystal mountings and experimental apparatus, and showed differences in M1 and M2 site occupancies up to 0.017. Considering both cases b and c, we observed differences which are approximately ten times the e.s.d.’s of the single values.

d) The use of scattering curves with no pre-established ionization for Si and O led to better agreement between crystallographic site occupancies and chemical data.

Key-words: olivine, single-crystal X-ray diffraction, site refinement, cation distribution.

Introduction

The determination of the Fe²⁺ and Mg distribution between the two non-equivalent M1 and M2 octahedral sites of olivine and orthopyroxene is crucial for thermometric applications, and has been the object of several works in the last few years (Kirkel, 1996; Kroll et al., 1997; Heinemann et al., 1999; Stimpfl et al., 1999). The major difficulty is to define the reliability of Fe²⁺-Mg intracrystalline distribution in terms of both precision and accuracy. Obtained results are only accurate within the indicated precision if the data quality dominates that precision, i.e. if data quality is poor; in this case precision cannot easily be used for thermometric purposes.

Considering that any experimental method is affected by some kind of systematic error, the reliability of X-ray results (intensities collected and refined parameters) suffers from uncertainties due to data collection strategy (e.g. part of the reciprocal space from which observations are collected, counting statistics, number of equivalent reflections measured). In addition, refined M1-M2 site