

Quantitative analysis of precession electron diffraction: application to the determination of ordering state in pyroxene

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Precession electron diffraction (PED) has recently renewed the interest in electron diffraction for structural and microstructural analysis [1]. The main advantage is that, being sequentially acquired out of a zone-axis orientation, diffracted intensities are less affected by dynamical interactions. This has already been proved to be useful for microstructures characterization in cases where crystal exhibits low symmetry departure [2]. For quantitative analysis of intensities and comparison with calculated values, dynamical interactions have to be considered [3]. In this work, we address the sensitivity of PED intensities to determine cation ordering in complex mineral structures such as orthopyroxene [OPX; $(\text{Mg}_x\text{Fe}_{2-x})\text{Si}_2\text{O}_6$] from igneous origin. In this structure, the Mg and Fe^{2+} ordering process among two non-equivalent crystallographic sites is related to the kinetics of diffusion process, making the mineral a potential geo-thermometer for deciphering the formation conditions of terrestrial or extra-terrestrial rocks. The gain in spatial resolution associated with the use of electron beam instead of X-rays for diffraction experiments open access to mineral samples of limited size of with complicated microtextures.

The two studied samples are monocrystals of natural OPX from granulite rocks of the Wilson Terrane in Antarctica [4]. Composition as measured by microprobe analysis is close to $\text{Mg}_{1.4}\text{Fe}_{0.6}\text{Si}_2\text{O}_6$, giving a Mg/(Mg+Fe) ratio close to 0.7. One crystal has been kept untreated (plain natural), and shows an ordered structure. The other one has been heated for 48h at 1000°C and then quenched, thus obtaining a disordered structure. The degree of order of both single crystal grains have been characterized by XRD structure refinement. TEM samples have been extracted using Focused Ion Beam from mono-crystalline grains previously studied by XRD. The space group is orthorhombic *Pbca* with $a=1.8337$, $b=0.8971$ and $c=0.5232$ nm for the untreated crystal and $a=1.8291$, $b=0.888$ and $c=0.5207$ nm for the heat-treated one. According to the structure refinement against single-crystal x-ray diffraction data, the order parameter, defined as $Q=X_{\text{Fe}}(\text{M}2)-X_{\text{Fe}}(\text{M}1)$, is 0.525 for the untreated sample (ordered) and $Q=0.283$ for the heat-treated sample (disordered), where $X_{\text{Fe}}(\text{M}1)$ and $X_{\text{Fe}}(\text{M}2)$ are the atomic fractions of Fe^{2+} occupying the M1 and M2 sites of the OPX structure, respectively. TEM experiments have been carried out using a LaB₆ FEI Tecnai G20 equipped with Nanomegas Digistar precession module. Selected Area Electron Diffraction (SAED) and microdiffraction patterns have been collected with precession semi-angles between 1 and 3 degrees. Subsequent data analysis showed that the sample thickness was less than 60 nm.

By using precession, experimental intensities are less sensitive to experimental parameters such as orientation of the electron beam with respect to the sample. Moreover, due to the reduction of dynamical interactions between diffracted intensities, strong intensity modulations appear associated to structure factors and kinematically forbidden reflections tend to disappear (Figure 1).

Dynamical simulations, obtained on OPX structure files using various values of the molar fractions $X_{\text{Fe}}(\text{M}1)$ and $X_{\text{Fe}}(\text{M}2)$, reveal the sensitivity of PED intensities to the order parameter Q . Thus, the comparison of simulated and experimental intensities gives access to the actual molar fraction [$X_{\text{Fe}}(\text{M}1)$, $X_{\text{Fe}}(\text{M}2)$] of the samples by minimizing the weighted residual factor wR^2 between the two data sets. Dynamical simulations are calculated with the software INBLOCH and compared with experimental intensities extracted from the experimental diffraction patterns using the software PETS. Both softwares have been developed by L. Palatinus [5].

For both samples, the observed values for $X_{\text{Fe}}(\text{M}1)$ and $X_{\text{Fe}}(\text{M}2)$ are in good agreement with those obtained by XRD (Fig. 2). A larger dispersion is observed for the ordered sample, probably

due to the chemical thermal homogenization of the disordered sample during heating. On the contrary, local composition and structural heterogeneities may be present in the natural untreated sample, thus possibly explaining the larger discrepancy between $X_{\text{Fe}}(\text{M1})$ and $X_{\text{Fe}}(\text{M2})$ on the ordered sample and the XRD values, which represent an average value of the ordering state at the micrometric scale, while PED gives values at nanometric scale.

Therefore, PED allows the quantitative analysis of diffracted intensities for structure refinement including site occupancy determination of complex structures by comparison with dynamical simulations. In the present work we distinguish two crystals with different ordering state and an intermediate state may even be characterized. This opens a path to the retrieval of fine structural data such as the order parameter at a very local scale, which is of great use for determining the sample thermal history. To achieve such an analysis, dynamical simulations as well as precise acquisition of experimental data are required.

References

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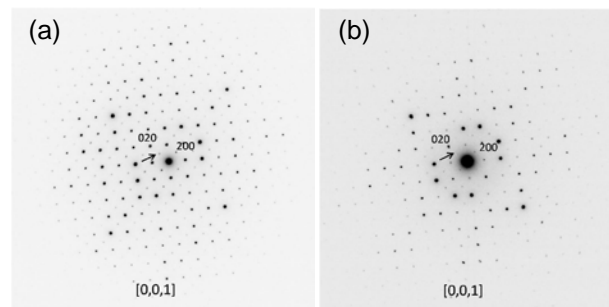


Figure 1. SAED patterns taken along the $[001]$ zone-axis. The arrow indicates the kinematical forbidden 010 reflection, which tends to disappear with increasing precession angle. Precession semi-angles: (a) 0.8° and (b) 2.8° .

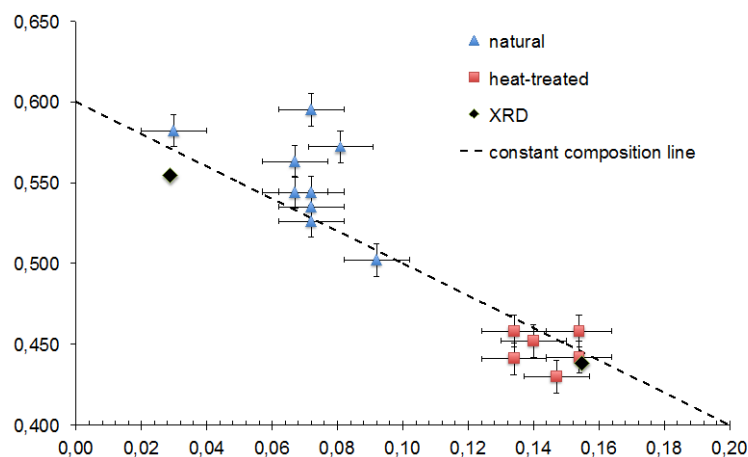


Figure 2. $X_{\text{Fe}}(\text{M1})$ and $X_{\text{Fe}}(\text{M2})$ as determined by PED on the ordered (triangles) and disordered samples (square). Each point corresponds to a single PED pattern. Data have been taken at various places of the TEM samples and for various precession angles (2.4° and 2.8°). Diamonds correspond to the XRD values. The dashed line corresponds to the line of constant composition for a stoichiometric OPX with $\text{Mg}/(\text{Mg}+\text{Fe})=0.70$.