

Fe²⁺-Mg ORDERING IN ORTHOPYROXENE STUDIED AT A MICROSCOPIC SCALE USING PRECESSION ELECTRON DIFFRACTION. D. Jacob¹, L. Palatinus², P. Cuvillier¹, H. Leroux¹, C. Domeneghetti³, F. Cámara⁴ ¹UMET, CNRS-Université de Lille 1, 59655-Villeneuve d'Ascq, damien.jacob@univ-lille1.fr. ²Institute of Physics, 16200-Prague, Czech Republic, ³Dip.to di Scienze della Terra, Università di Pavia, 27100-Pavia, Italy, ⁴Dip.to di Scienze della Terra, Università di Torino, 10125-Torino, Italy.

Introduction: Fe²⁺ and Mg distribution on octahedral M1 and M2 sites of the orthopyroxene structure is an indicator of the cooling rate and closure temperature of the studied mineral [1]. These data are of great importance to retrieve the formation conditions, whatever the terrestrial or extra-terrestrial origin. The cationic distribution is generally obtained by X-ray diffraction (XRD) followed by structure refinement, leading to the atomic positions and sites occupancy with a good accuracy. Nevertheless, XRD is limited in spatial resolution. Contradictory results in cooling rate determination based on sites occupancy as determined by XRD have been explained by the occurrence of microstructural features such as local composition variations, exsolution lamellae and Guinier-Preston zones [2,3,4]. These features can only be revealed by imaging in a transmission electron microscope (TEM). XRD analysis then leads to averaged information, which may induce misinterpretation. In this work, we present results on site occupancy determination obtained at a microscopic scale in a TEM using precession electron diffraction. Studied samples, as study cases, are monocrystals of terrestrial metamorphic orthopyroxenes. Our analysis allows to distinguish unambiguously an ordered sample (natural, non-treated) from a disordered one (heat-treated).

Samples and experimental procedures: Studied specimens are monocrystals of natural (Mg_xFe_{1-x})Si₂O₆ orthopyroxenes (a few hundreds microns in size) from granulite rocks of the Wilson Terrane, North Victoria Land, Antarctica [5]. The average crystal composition as obtained by electron microprobe gives a Mg/(Fe+Mg) ratio close to 0.7. Small amounts of Ca and other minor elements such as Ti, Al, and Cr have also been detected. They are not considered in the present analysis. In order to get disordered structures, crystals of the same origin have been heated for 48 hours at 1000°C. The grains were sealed (after alternately washing with argon flux and evacuating) into a small silica tube together with an iron-wüstite buffer and then heated in a vertical furnace. Inside the silica tube the crystals and the buffer were put into two small separate Pt crucibles to avoid contact between them. Heating experiment was quenched by dropping the tube into cold water.

XRD has been used for structure refinement and site occupancy determination at the scale of the whole grains. Experimental conditions are described in [5]. In

plain natural state, the crystals are characterized by a high degree of Fe²⁺-Mg order with M2 sites mainly occupied by larger Fe²⁺ cations. After the high-temperature annealing, the structure is disordered with Fe²⁺ located on both M1 and M2 sites (Table 1).

	Ordered sample (plain natural)	Disordered sample (heat-treated)
X _{Fe} (M1)	0.029	0.155
X _{Fe} (M2)	0.554	0.438
Mg/(Fe+Mg)	0.7085	0.7035
Q=X _{Fe} (M2)-X _{Fe} (M1)	0.525	0.283

Table 1: Molar fractions of Fe on M1 and M2 sites as measured by XRD. *Q* is the ordering parameter.

TEM foils with thickness between 50 and 100 nm have been prepared from both natural and heated samples at the IEMN (Institute of Micro and Nano Electronic, University Lille 1) by focused ion beam technique using a FEI Strata DB 235 FIB-FESEM. TEM observations were performed at the University of Lille 1 on a FEI Tecnai G2-20 operated at 200 kV. Selected area electron diffraction patterns have been obtained using a defocused parallel beam and a circular aperture selecting an illuminated area of about 250 nm in diameter. The microscope is equipped with a DIGISTAR precession system supplied by the company Nanomegas. Applying the precession electron diffraction (PED) technique [6], dynamical interactions typical for electron diffraction are reduced and experimental intensities are less sensitive to experimental parameters such as the accurate orientation of the electron beam with respect to the sample. Comparison with simulated data is then more reliable. Dynamical calculations of diffracted intensities are obtained using various structure files with variable contents of Fe²⁺ and Mg on the M1 and M2 sites and for various values of the TEM sample thickness. Systematic comparison of simulated data with experimental ones has been undertaken and the best agreement is given by the lowest value of the weighted residual factor on intensities wR^2 .

Results: For each specimen (ordered and disordered) PED patterns have been acquired along the [001] orientation on various areas of the TEM samples and for various precession angle (2.4 and 2.8°). Ex-

tracted diffracted intensities from each pattern have then been compared to simulated ones, obtained for various values of the sample thickness and for various cations distribution. For each pattern, estimations of the molar fractions of Fe on M1 and M2 sites $X_{\text{Fe}}(\text{M1})$ and $X_{\text{Fe}}(\text{M2})$ are obtained together with an estimation of the sample thickness as those resulting in the lowest wR^2 value (Fig. 1). The values of the wR^2 parameters for different experimental patterns range between 7 and 18%.

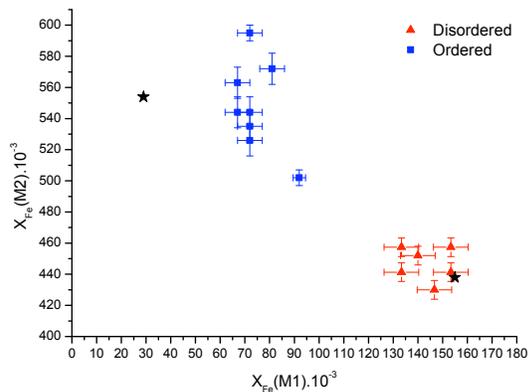


Fig. 1: $X_{\text{Fe}}(\text{M1})$ and $X_{\text{Fe}}(\text{M2})$ as determined by PED on the ordered and disordered samples. Each point (squares or triangles) corresponds to a single PED pattern. Patterns have been acquired on various places of the TEM thin foils. Stars correspond to values deduced from XRD.

The results show that:

- A distinction can be made between the two samples as a function of their ordering state. For the ordered sample (plain natural), $X_{\text{Fe}}(\text{M2})$ ranges around $550 \pm 50 \cdot 10^{-3}$ and $X_{\text{Fe}}(\text{M1})$ around $77 \pm 17 \cdot 10^{-3}$. For the disordered sample (heat-treated), $X_{\text{Fe}}(\text{M2})$ ranges around $442 \pm 17 \cdot 10^{-3}$ and $X_{\text{Fe}}(\text{M1})$ around $143 \pm 17 \cdot 10^{-3}$.
- The dispersion is larger for the ordered sample than for the disordered sample,
- A good agreement is observed between XRD and PED measurements for the disordered sample whereas a small, but significant discrepancy occurs for the ordered sample. In this case, XRD gives a lower value of $X_{\text{Fe}}(\text{M1})$ (around $30 \cdot 10^{-3}$) compared to PED.

Experimental conditions of acquisition being the same for the two samples, the results dispersion of results observed on the ordered sample may only come from the sample itself. Indeed, the disordered sample has been annealed at high temperature and thus thermally homogenized, whereas no treatment has been made on the natural sample. The natural sample may

then present some local composition and ordering heterogeneities. Composition heterogeneities in the natural sample may also explain the discrepancy between XRD and PED results. XRD leads to an average value of the composition and ordering at the grain scale that may differ from the local values obtained in TEM. To confirm this interpretation, some more local chemical analysis by TEM-EDX are in progress.

Conclusion: To our knowledge, a structure refinement including site occupancies at a submicronic scale using precession electron diffraction is demonstrated for the first time. Precision of the results is by far sufficient to distinguish between a crystal corresponding to a natural metamorphic ordered structure from a disordered one obtained after annealing at high temperature. Some intermediate state of ordering may even be characterized. Furthermore, our local measurements are sensitive enough to account for local heterogeneities in the natural sample. Coupled to local chemical analysis, application of this technique to the study of meteorites or cometary material containing orthopyroxene grains should be of great use to decipher the formation conditions (cooling rate and closure temperature) of the studied objects.

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