Iron distribution in orthopyroxene:
A comparison of Mössbauer spectroscopy
and X-ray refinement results

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Abstract: The Fe-Mg distribution over the M1 and M2 octahedral sites in five natural orthopyroxenes has been
determined by single-crystal X-ray diffraction (XRD) and Mössbauer spectroscopy (MS). The results from the two
methods are in good agreement for two Fe/Mg intermediate composition samples, provided that the MS data are
thickness-corrected. For two Fe-poor and one Al-rich sample, the results diverge; XRD gives a more ordered
Fe-Mg distribution than MS, with up to 0.05 more Fe atoms per formula unit in the M2 position.
The thickness effect on MS for ordered orthopyroxene is shown to cause considerable distortion of the spectra,
resulting in an underestimate of the degree of ordering. For normally thick absorbers (5 mg Fe/cm²), MS data will
allocate approximately 2% too much of total Fe to the M1 position. However, the Fe distribution obtained from
MS data can be corrected by extrapolation to zero thickness according to the formula
\[ \text{Fe(M1) / Fe(tot)correct} = \text{[Fe(M1)/Fe(tot)meas - 0.004085t]}/(1 - 0.00303 t) \]
where \( t \) is the Fe « thickness » of the absorber in mg Fe/cm².

Key-words: X-ray diffraction, Mössbauer spectroscopy, thickness effect, orthopyroxene, order-disorder.

Introduction

The order-disorder exchange reaction in orthopyroxene and its temperature-dependent kinetics have been studied extensively (see review by Ganguly, 1982). The interest in this reaction stems from the possibility of estimating natural cooling rates for the rocks in which orthopyroxenes occur. The ordering reaction, that takes place during cooling, can be expressed as:

\[ \text{Fe(M1)} + \text{Mg(M2)} = \text{Fe(M2)} + \text{Mg(M1)} \] (1)

where Fe orders at the M2 position at lower temperatures. At some point during the cooling process, the kinetics of the reaction become too sluggish to maintain equilibrium, and at lower temperatures, Fe-Mg exchange is quenched. The degree of ordering achieved is thus a function of the cooling rate. Extremely high precision and accuracy in the determination of site occupancies is required if accurate cooling rates are to be established; so far, estimated cooling rates have errors of up to two orders of magnitude (Gan-