American Mineralogist, Volume 98, pages 1172–1186, 2013

Fundamental Mössbauer parameters of synthetic Ca-Mg-Fe pyroxenes

M. Darby Dyar,[1,*] Rachel L. Klima,[2] Alexandra Fleagle,[1] and Samantha E. Peel[1]

[1]Department of Astronomy, Mount Holyoke College, 50 College Street, South Hadley, Massachusetts 01075, U.S.A.
[2]Johns Hopkins University, Applied Physics Laboratory, Laurel, Maryland 20723, U.S.A.

ABSTRACT

Understanding of Fe site occupancy across the Ca-Fe-Mg pyroxene quadrilateral requires knowledge of space groups and appreciation of the diversity of site geometries across Ca-Mg-Fe composition space. Most commonly, site occupancies are measured using some combination of single-crystal structure refinements (SREF) from X-ray diffraction data and Mössbauer spectroscopy for bulk measurements. The vast majority of previous Mössbauer studies have been hampered by the lack of differential recoil-free fraction data that describe how the Fe^{2+} and Fe^{3+} cations are bonded in the M1 and M2 sites in pyroxene. To remedy this situation, this paper examines 658 Mössbauer spectra acquired from 64 synthetic samples covering the pyroxene quadrilateral in roughly 10 mol% increments, and determines their fundamental Mössbauer parameters as a function of composition. Results show variations in all the Mössbauer parameters studied: center shift (δ), quadrupole splitting (Δ), area, recoil-free fraction (f), Mössbauer temperature (Θ_M), and intrinsic isomer shift (δ_I). The most systematic variations with composition are seen for δ and f, while small variations are seen for Δ, Θ_M, and δ_I. These data are then related to characteristics of the pyroxene crystal structure to examine the relationship between site geometry and recoil-free fraction. In general, smaller bond lengths (e.g., in the M1 site along the enstatite-ferrosilite join) result in higher f values. As Ca is added to the structure and Mg is removed, the f value for M1 increases as the site becomes larger and more regular. Larger sites with lower bond strengths result in lower values of f because the cation is less tightly bound in the crystal structure and thus encounters more recoil. This result is in keeping with theoretical expectations, but has not previously been clearly demonstrated for minerals with experimental data. Values of recoil-free fraction determined in this study will facilitate more accurate determinations of cation site occupancies in pyroxenes from Mössbauer data and lend insights into the geometries of the M1 and M2 sites.

Keywords: Mössbauer, recoil-free fraction, orthopyroxene, clinopyroxene, hedenbergite, diopside, pigeonite, enstatite, ferrosilite, augite