

Accurate determination of ferric iron in garnets by bulk Mössbauer spectroscopy and synchrotron micro-XANES

M. DARBY DYAR,^{1,*} ELLY A. BREVES,¹ ERICA EMERSON,¹ SAMUEL W. BELL,¹ MELISSA NELMS,¹ MARIE V. OZANNE,¹ SAMANTHA E. PEEL,¹ MARCO L. CARMOSINO,² JONATHAN M. TUCKER,¹ MICKEY E. GUNTER,³ JEREMY S. DELANEY,⁴ ANTONIO LANZIROTTI,⁵ AND ALAN B. WOODLAND⁶

¹Department of Astronomy, Mount Holyoke College, 50 College Street, South Hadley, Massachusetts 01075, U.S.A.

²Department of Computer Science, University of Massachusetts, 140 Governor's Drive, Amherst, Massachusetts 01003, U.S.A.

³Department of Geological Sciences, University of Idaho, Moscow, Idaho 83844, U.S.A.

⁴Department of Earth and Planetary Sciences, Rutgers University, 610 Taylor Road, Piscataway, New Jersey 08854, U.S.A.

⁵University of Chicago, Center for Advanced Radiation Sources, 5640 S. Ellis Avenue, Chicago, Illinois 60637, U.S.A.

⁶Institute für Geowissenschaften, Universität Frankfurt, Altenhöferallee 1, 60438 Frankfurt, Germany

ABSTRACT

Measurements of $\text{Fe}^{3+}/\Sigma\text{Fe}$ in geological materials have been intractable because of lack of access to appropriate facilities, the time-consuming nature of most analyses, and the lack of precision and reproducibility in most techniques. Accurate use of bulk Mössbauer spectroscopy is limited by largely unconstrained recoilless fraction (f), which is used to convert spectral peak area ratios into valid estimates of species concentrations and is unique to different mineral groups and compositions. Use of petrographic-scale synchrotron micro-XANES has been handicapped by the lack of a consistent model to relate spectral features to $\text{Fe}^{3+}/\Sigma\text{Fe}$. This paper addresses these two deficiencies, focusing specifically on a set of garnet group minerals. Variable-temperature Mössbauer spectra of the Fe^{2+} -bearing almandine and Fe^{3+} -bearing andradite end-members are used to characterize f in garnets, allowing $\text{Fe}^{3+}/\Sigma\text{Fe}$ to be measured accurately. Mössbauer spectra of 19 garnets with varying composition were acquired and fit, producing a set of garnet-specific standards for Fe^{3+} analyses. High-resolution XANES data were then acquired from these and 15 additional previously studied samples to create a calibration suite representing a broad range of Fe^{3+} and garnet composition. Several previously proposed techniques for using simple linear regression methods to predict $\text{Fe}^{3+}/\Sigma\text{Fe}$ were evaluated, along with the multivariate analysis technique of partial least-squares regression (PLS). Results show that PLS analysis of the entire XANES spectral region yields the most accurate predictions of Fe^{3+} in garnets with both robustness and generalizability. Together, these two techniques present reliable choices for bulk and microanalysis of garnet group minerals.

Keywords: Garnet, almandine, andradite, grossular, Mössbauer spectroscopy, XANES, ferric iron