American Mineralogist, Volume 97, pages 1726–1740, 2012

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. Woodland[6]

[1]Department of Astronomy, Mount Holyoke College, 50 College Street, South Hadley, Massachusetts 01075, U.S.A.
[2]Department of Computer Science, University of Massachusetts, 140 Governor's Drive, Amherst, Massachusetts 01003, U.S.A.
[3]Department of Geological Sciences, University of Idaho, Moscow, Idaho 83844, U.S.A.
[4]Department of Earth and Planetary Sciences, Rutgers University, 610 Taylor Road, Piscataway, New Jersey 08854, U.S.A.
[5]University of Chicago, Center for Advanced Radiation Sources, 5640 S. Ellis Avenue, Chicago, Illinois 60637, U.S.A.
[6]Institute für Geowissenschaften, Universität Frankfurt, Altenhöferallee 1, 60438 Frankfurt, Germany

Abstract

Measurements of $Fe^{3+}/\Sigma Fe$ 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 $Fe^{3+}/\Sigma Fe$. 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 $Fe^{3+}/\Sigma Fe$ 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 $Fe^{3+}/\Sigma Fe$ 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