American Mineralogist, Volume 98, pages 110–119, 2013

Microbeam X-ray analysis of Ce^{3+}/Ce^{4+} in Ti-rich minerals: A case study with titanite (sphene) with implications for multivalent trace element substitution in minerals

Penelope L. King,[1,2,3,*] Tsun-Kong Sham,[4] Robert A. Gordon,[5] and M. Darby Dyar[6]

[1]Department of Earth Sciences, The University of Western Ontario, London, Ontario N6A 5B7, Canada
[2]Institute of Meteoritics, University of New Mexico, Albuquerque, New Mexico 87109, U.S.A.
[3]Research School of Earth Sciences, Australian National University, Canberra ACT 0200, Australia
[4]Department of Chemistry, The University of Western Ontario, London, Ontario N6A 5B7, Canada
[5]Pacific Northwest Consortium, Department of Physics, Simon Fraser University, Burnaby, British Columbia, Canada and the University of Washington, Seattle, Washington, U.S.A.
[6]Department of Earth and Environment, 50 College St, Mount Holyoke College, South Hadley, Massachusetts, 01075 U.S.A.

Abstract

Cerium L_3 absorption edge (L_3-edge) X-ray absorption near edge structure (XANES) spectra were obtained from ~7 × 5 μm areas on green titanite and brown titanite (both with total Ce ~ 0.6 wt%) using the X-ray microprobe at the Pacific Northwest Consortium–X-ray Science Division (PNC-XSD) Insertion Device (ID) line of the Advanced Photon Source (APS). Using a wavelength-dispersive X-ray (WDX) fluorescence detector with a bent LiF (220) crystal monochromator ($E/\Delta E$ ~ 1000), we have overcome the challenge of having to measure trace amounts of Ce in a Ti-rich sample of which the energy of the fluorescence X-rays from Ce L_3-edge and Ti K-edge excitation cannot be resolved with solid-state detectors. We show that both Ce^{3+} and Ce^{4+} are present in our titanite samples by examining the Ce L_3-edge XANES spectra.

Our results show that to correctly determine trace element substitution mechanisms in titanite (and other minerals), it is necessary to determine multivalent element concentrations, including Ce^{3+}/Ce^{4+}. We present a new approach for predicting and evaluating multivalent trace element substitution in titanite and other minerals.

Keywords: Multivalent elements, XANES, trace element substitution