American Mineralogist, Volume 101, pages 2677–2688, 2016

Submicrometer-scale spatial heterogeneity in silicate glasses using aberration-corrected scanning transmission electron microscopy

Katherine D. Burgess[1,*], Rhonda M. Stroud[2], M. Darby Dyar[3], and Molly C. McCanta[4]

[1]ASEE Postdoctoral Fellow, U.S. Naval Research Laboratory, Washington, D.C. 20375, U.S.A.
[2]U.S. Naval Research Laboratory, Washington, D.C. 20375, U.S.A.
[3]Mount Holyoke College, South Hadley, Massachusetts 01075, U.S.A.
[4]Tufts University, Medford, Massachusetts 02155, U.S.A.

Abstract

Experimental silicate glasses are often used as analog and calibration material for terrestrial and planetary materials. Measurements of Fe oxidation state using electron energy loss spectroscopy (EELS) in an aberration-corrected scanning transmission electron microscope (ac-STEM) show that a suite of experimental silicate (e.g., basaltic, andesitic, rhyolitic) glasses have spatially heterogeneous oxidation states at scales of tens of nanometers. Nano-crystals are observed in several of the glasses, indicating nucleation and incipient crystallization not seen at the scale of electron microprobe analysis (EMPA). Glasses prepared in air are uniformly oxidized while glasses prepared at the iron-wustite (IW) or quartz-fayalite-magnetite (QFM) buffers range from reduced to highly oxidized. EELS spectral shapes indicate that oxidized glasses have tetrahedral Fe^{3+}. The nanoscale compositional and structural heterogeneities present in the experimental glasses mean that the suitability of such glasses as analogs for natural materials and calibration standards depends strongly on the scale of the measurements being done. The electron beam quickly damages silicate glass, but data showing changes in oxidation state among and within samples can be obtained with careful control of the beam current and dwell time. Determination of oxidation state in silicate glasses via STEM-EELS is very challenging, and accurate and reliable measurements of $Fe^{3+}/\Sigma Fe$ require careful sample preparation and control of microscope conditions and benefit from comparison to complementary techniques.

Keywords: Iron oxidation, silicate glass, transmission electron microscopy (TEM), electron energy loss spectroscopy (EELS), beam damage