American Mineralogist, Volume 105, pages 1866–1874, 2020

Ferric-ferrous iron ratios of experimental majoritic garnet and clinopyroxene as a function of oxygen fugacity

Laura J.A. Rzehak[1,2,*], Arno Rohrbach[2], Christian Vollmer[2], Heidi E. Höfer[3], Jasper Berndt[2], and Stephan Klemme[2]

[1]Ruhr Universität Bochum, Institut für Geologie, Mineralogie und Geophysik, Universitätsstrasse 150, 44780 Bochum, Germany
[2]Westfälische Wilhelms-Universität Münster, Institut für Mineralogie, Corrensstrasse 24, 48149 Münster, Germany
[3]Goethe Universität Frankfurt am Main, Institut für Geowissenschaften, Altenhöferallee 1, 60438 Frankfurt am Main, Germany

Abstract

The oxidation state of iron in upper mantle minerals is widely used to constrain the Earth mantle's oxidation state. Previous studies showed high levels of ferric iron in high-pressure majoritic garnets and pyroxenes despite reducing conditions. To disentangle the effects of pressure and increasing oxygen fugacity on the $Fe^{3+}/\Sigma Fe$ ratios of garnet and clinopyroxene, we performed high-pressure experiments at a pressure of 10 GPa in a 1000-ton Walker-type multi-anvil apparatus at the University of Münster. We synthesized majoritic garnets and clinopyroxenes with a total iron content close to natural mantle values at different oxygen fugacities, ranging from IW+4.7 to metal saturation at IW+0.9. We analyzed the iron oxidation state in garnets with the electron microprobe "flank method." Furthermore, we investigated the oxidation state of iron in garnets and clinopyroxenes with transmission electron microscopy (TEM) electron energy loss spectroscopy (EELS). Although the flank method measurements are systematically lower than the EELS measurements, $Fe^{3+}/\Sigma Fe$ obtained with both methods agree well within 2σ errors. The "flank method" has the advantage of being much faster and more easily to set up, whereas TEM-EELS has a much higher spatial resolution and can be applied to various non-cubic minerals such as orthopyroxenes and clinopyroxenes. We used our experimental results to compare two geobarometers that contain a term for ferric iron in garnet (Beyer and Frost 2017; Tao et al. 2018) with two geobarometers that do not account for ferric iron (Collerson et al. 2010; Wijbrans et al. 2016). We found that for garnets with low total Fe and Fe^{3+} (like many natural garnets), the pressures can be calculated without including the ferric iron content.

Keywords: Majorite, multi-anvil apparatus, electron energy loss spectroscopy, transmission electron microscopy, flank method, ferric iron, oxygen fugacity, Earth mantle