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

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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 Fe3+/ΣFe 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 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, Fe3+/ΣFe 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 Fe3+ (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

INTRODUCTION

The oxidation state of the Earth’s upper mantle is still a matter of debate, mainly because rock samples from depths >250 km are virtually absent except for rare ultradepth xenoliths (Haggerty and Sautter 1990; Sautter et al. 1991) and mineral inclusions in diamond (e.g., Pearson et al. 2014). However, the oxidation state of the Earth’s mantle exerts a significant influence on the stability of C-O-H-volatiles and therefore has important implications for the phase relations and melting behavior (Kushiro et al. 1968; Taylor and Green 1988; Ballhaus and Frost 1994; Gaetani and Grove 1998; Dasgupta and Hirschmann 2006; Foley 2011; Tumiati et al. 2012; Stagno et al. 2013). Hydrogen incorporation (e.g., Kohlstedt et al. 1996), and the rheology of the mantle (Mackwell et al. 1985) as well as for diamond/graphite vs. carbonate stability (Dasgupta and Hirschmann 2010; Stagno and Frost 2010; Rohrbach and Schmidt 2011; Stagno et al. 2013; Luth and Stachel 2014; Yaxley et al. 2017). The oxidation state of the upper mantle can be determined by the Fe3+/ΣFe content of mantle minerals since iron is a major element in Earth’s mantle and is incorporated into every mantle mineral (e.g., O’Neill et al. 1993b; Luth and Canil 1993; Canil and O’Neill 1996). The oxygen fugacity (f02) of the uppermost mantle predominantly lies between FMQ+2 and FMQ-2 as indicated by xenoliths and samples of basaltic melts and peridotite massifs (Luth et al. 1990; Ballhaus 1993; Frost and McCammon 2008). With increasing depth, the upper mantle becomes more reduced, approaching Δlog f02 values of FMQ-4 at 220 km depth (Woodland and Koch 2003; McCammon and Kopylova 2004; Frost and McCammon 2008; Stagno and Frost 2010; Yaxley et al. 2012). In the upper mantle, the f02 correlates with the ferric iron content of minerals, so that spinels in harzburgite and lherzolite at pressures up to 2.7 GPa show a decrease of ferric iron with decreasing f02 tending toward zero when metallic iron is a stable phase (Ballhaus et al. 1991). This linear relationship between f02 and Fe3+/ΣFe is not observed in experimental phase assemblages at pressures corresponding to the lowermost upper mantle, the transition zone or the lower mantle, where majoritic garnet and bridgmanite with high ferric iron contents coexist with metallic iron (O’Neill et al. 1993a; McCammon 1997; McCammon and Ross 2003; Frost et al. 2004; Rohrbach et al. 2007, 2011). In a typical upper mantle assemblage, ferric iron is concentrated in modally minor phases like clinopyroxene and spinel since olivine incorporates negligible ferric iron and orthopyroxene incorporates only between 0.2 and 0.6 wt% FeO at low Fe3+/ΣFe between 0.03 and 0.10 (O’Neill et al. 1993b; Canil and O’Neill 1996; Woodland and Koch 2003; Yaxley et al. 2012). Above