Equations of state, phase relations, and oxygen fugacity of the Ru-RuO₂ buffer at high pressures and temperatures

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ABSTRACT

Experimental studies and measurements of inclusions in diamonds show that ferric iron components are increasingly stabilized with depth in the mantle. To determine the thermodynamic stability of such components, their concentration needs to be measured at known oxygen fugacities. The metal-oxide pair Ru and RuO₂ are ideal as an internal oxygen fugacity buffer in high-pressure experiments. Both phases remain solid to high temperatures and react minimally with silicates, only exchanging oxygen. To calculate oxygen fugacities at high pressure and temperature, however, requires information on the phase relations and equation of state properties of the solid phases.

We have made in situ synchrotron X-ray diffraction measurements in a multi-anvil press on mixtures of Ru and RuO₂ to 19.4 GPa and 1473 K with which we have determined phase relations of the RuO₂ phases and derived thermal equations of state (EoS) parameters for both Ru and RuO₂. Rutile-structured RuO₂ was found to undergo two phase transformations, first at ~7 GPa to an orthorhombic structure and then above 12 GPa to a cubic structure. The phase boundary of the cubic phase was constrained for the first time at high pressure and temperature. We have derived a continuous Gibbs free energy expression for the tetragonal and orthorhombic phases of RuO₂ by fitting the second-order phase transition boundary and P-V-T data for both phases, using a model based on Landau theory. The transition between the orthorhombic and cubic phases was then used along with EoS terms derived for both phases to determine a Gibbs free energy expression for the cubic phase. We have used these data to calculate the oxygen fugacity of the Ru + O₂ = RuO₂ equilibrium, which we have parameterized as a single polynomial across the stability fields of all three phases of RuO₂. The expression is log fO₂(Ru – RuO₂) = (7.782 – 0.00996P + 0.001932P² – 3.76 × 10⁻⁸P³) + (–13.763 + 592P – 3.955P²)/T (+ –1.05 × 10⁸ – 4622P)/T², which should be valid from room pressure up to 25 GPa and 773–2500 K, with an estimated uncertainty of 0.2 log units. Our calculated fO₂ is shown to be up to 1 log unit lower than estimates that use previous expressions or ignore EoS terms.

Keywords: Oxygen fugacity, ruthenium/ruthenium dioxide, experimental petrology, phase relations, equation of state

INTRODUCTION

Knowledge of the redox conditions, or more specifically the oxygen fugacity (fO₂), at which rocks and melts formed is important for understanding a host of phenomena, such as the partitioning of variably valent elements, the speciation of volatiles, and the formation of accessory phases like sulfides, diamond, and metal alloys (Hirschmann et al. 2012; Gaillard et al. 2015; Smith et al. 2016; Davis and Cottrell 2018). Perhaps most importantly, the fO₂ of the mantle has controlled the nature of volcanically degassed species throughout Earth’s history (Hirschmann 2012). In addition, mantle fO₂ influences transport properties such as diffusion, creep, and electrical conductivity by controlling the Fe⁺/Fe³⁺ ratio and OH⁻ contents of minerals and melts (e.g., Pommier et al. 2010; Keefer et al. 2011; Yoshino and Katsura 2013). To place quantitative constraints on the effects of any redox or redox-influenced process at mantle conditions, experimental studies that either control or measure the fO₂ are necessary.

Recent studies on the speciation of ferric iron in minerals and melts at high pressure have further indicated the need for quite specific controls on oxygen fugacity (Zhang et al. 2017; Tao et al. 2018). Although the concentration of ferric iron in upper mantle rocks is relatively low (Canil and O’Neill 1996; Woodland et al. 2006), studies of sublithospheric diamonds (Kiseeva et al. 2018) and experimental studies at transition zone and lower mantle conditions indicate that the ferric iron components of minerals are increasingly stabilized with depth in the mantle (Lauterbach et al. 2000; Rohrbach et al. 2007). To explore this tendency, it is important to be able to determine the chemical potentials of ferric iron-bearing components in minerals and melts. One way to do this is to fix the oxygen fugacity of an experiment at conditions where measurable amounts of ferric iron components are present and then determining their concentration (O’Neill et al. 2006).

Standard methods that use redox buffering assemblages to fix fO₂ in experiments face major challenges when applied at pressures consistent with the deep mantle. They require too much space in the experimental apparatus to be practical, and uncertainties arise in both the activities and standard state properties of the components involved. The use of an outer capsule containing an H₂O-saturated...