A convenient method for measuring ferric iron in magnesiowüstite (MgO-Fe$_{1-x}$O)

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ABSTRACT

We present a new oxybarometer for magnesiowüstite-bearing systems, which is easily applied using widely available techniques. A scale relating the proportion of Fe$^{3+}$ [$\alpha = \text{Fe}^{3+}/(\text{Fe}^{3+} + \text{Fe}^{2+})$] to the position of the (220) reflection and total Fe (y) in magnesiowüstites (Mg$_{(1-x)}$,Fe$_x$)$_2$O has been derived from measured values in samples equilibrated at various oxygen fugacities:

$$\alpha = 13.0047 - 39.4829f + 40.0540t^2 - 13.5701t^3(\pm 0.007 + 0.09\alpha),$$

$$f = (d_{220} - 1.4890)/(0.0510y + 0.0206y^2)(\pm 0.0001).$$

Previously established partition coefficients can then be used to relate estimated Fe$^{3+}$ content to equilibrium oxygen fugacity ($f_o$) in the composition range 0 < y < 0.2. Equilibrium oxygen fugacities of log $f_o$ ≤ −1.7 can be estimated to ±0.5 log units using just X-ray powder diffraction and electron microprobe analytical techniques.

INTRODUCTION

Accurate characterization of the equilibrium oxygen environment is fundamental to understanding the petrogenesis of many rocks. High-pressure experiments, however, commonly have poor control of the oxygen environment, which leads to uncertainties in the application of those results to natural systems. Although Mössbauer spectroscopy has proven extremely successful in measuring Fe$^{3+}$ contents of non-stoichiometric minerals, this technique normally requires large sample volumes or synthetic samples enriched in the Mössbauer isotope $^{57}$Fe. It would be convenient, therefore, to have a simple analytical technique to estimate the equilibrium oxygen fugacity of experimental and natural samples as an oxybarometer.

The wüstite family of oxides accommodates significant non-stoichiometry, and the solid-solution phase magnesiowüstite is present in some natural and synthetic assemblages. Magnesiowüstite is formed in the shallow crust by contact metamorphism of limestones or during emplacement and eruption of carbonatites. Additionally, magnesiowüstite is thought to be a major constituent of the lower mantle. Magnesiowüstite inclusions found in diamonds, which are thought to have originated in the lower mantle, were analyzed for Fe$^{3+}$ by micro-Mössbauer spectroscopy (McCammon et al. 1995). Dobson et al. (1997) and Wood and Nell (1991) demonstrated that Fe$^{3+}$ greatly affects the electrical conductivity of magnesiowüstite at the elevated T of the lower mantle. Biggar (1974) demonstrated that non-stoichiometry in magnesiowüstite causes significant lattice relaxation and suggested that the systematic variation of cell parameter with oxygen fugacity can be used as a standard for calibrating gas-mixing furnaces. The defect-structure and redox equilibria of magnesiowüstite were studied extensively (Brynestad and Flood 1958; Speidel 1967; Valet et al. 1975; Gourdin et al. 1979) and the formulation of Valet et al. (1975) accurately predicts the T-P$_o$-[Fe/(Fe+Mg)] dependence of Fe$^{3+}$ content. We have used the data of Biggar (1974) along with new experimental data from the present study to quantify the dependence of cell parameter on Fe$^{3+}$ in magnesiowüstite. We find that this produces an oxybarometer accurate to ±0.5 log units at values of oxygen fugacity relevant to the Earth.

EXPERIMENTAL AND ANALYTICAL METHODS

Polycrystalline magnesiowüstite samples of 4.6, 10.0, 14.9, and 20.0 ± 0.1 mol% wüstite were synthesized by sintering stoichiometric mixtures of MgO, Fe$_2$O$_3$, and Fe at 1100 °C. After three to five 15 h cycles of grinding and sintering under the CO-CO$_2$ oxygen buffer, starting samples were homogeneous with Fe$^{3+}$ below the detection limit by Mössbauer spectroscopy. Small aliquots (0.1 g) of these samples were then suspended on platinum wires and equilibrated with CO-CO$_2$ mixtures at 1 atm total P and 1300 °C for 4 h before quenching by withdrawing the wire to the top of the gas-mixing furnace. Quench rates thus obtained, of up to 400 °C/min, allowed monophase samples with up to 33% Fe$^{3+}$ to be synthesized. To obtain higher Fe$^{3+}$/Fe, samples were synthesized in a Walker-type multi-anvil press at 50 kbar and 1300 °C. A 14 mm edge length octahedron of Armeco 584 castable ceramic was compressed using 8 mm truncation edge length WC anvils. Pressure was calibrated at room temperature using the transitions of Bi (2.5,7.7...