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ABSTRACT

A new "solid-state" oxygen buffering reaction (WC-COW), $WC + 1/2O_2 \rightleftharpoons CO + W$, is presented. At atmospheric pressure, the oxygen fugacity in equilibrium with this buffer is approximated in the range of 600–1200 °C by $\log f_{O_2} = 1.53 - \frac{21008}{T(K)} \pm 0.13$ bar. A simple method for maintaining oxygen fugacity in standard muffle furnaces using this buffer in off-the-shelf ceramic crucibles is described. The utility of the experimental arrangement in controlling oxygen fugacity during solid-state synthesis of iron-bearing silicates is demonstrated by rapid synthesis of fayalite, Fe_2SiO_4, from oxide starting mixtures at 1050 °C.

INTRODUCTION

High-temperature sample synthesis of transition-metal bearing oxide compounds often requires the control of redox conditions to ensure that the correct valence state is maintained. Oxygen fugacity, f_{O_2}, can be controlled using mixtures of gases such as carbon dioxide and carbon monoxide or water and hydrogen through their oxygen-producing reactions,
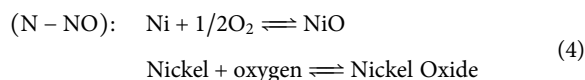
$$CO + 1/2O_2 \rightleftharpoons CO_2, \tag{1}$$

$$H_2 + 1/2O_2 \rightleftharpoons H_2O. \tag{2}$$
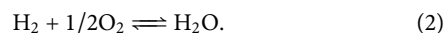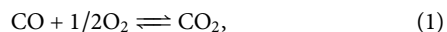
These gas mixtures allow, by variation of their proportions, the f_{O_2} to be controlled to any arbitrary value between the limits defined by the purity of the end-member gases, but they require careful control and monitoring. In addition, there are significant safety considerations in using flammable and toxic gases in high-temperature environments.

An alternative, solid-state method of control of f_{O_2} is required for experiments at high confining pressures. Here, metal–metal oxide mixtures are used as buffers (Eugster, 1957), which control the

f_{O_2} via reactions such as

$$(I - W): \quad Fe + 1/2O_2 \rightleftharpoons {}'FeO'$$
$$Iron + oxygen \rightleftharpoons Wüstite \tag{3}$$
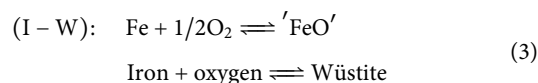
(Darken and Gurry, 1945) and

$$(N - NO): \quad Ni + 1/2O_2 \rightleftharpoons NiO$$
$$Nickel + oxygen \rightleftharpoons Nickel\ Oxide \tag{4}$$

(Huebner and Sato, 1970).

These metal–oxide mixtures are contained in an outer capsule, which surrounds a second capsule containing the sample, and f_{O_2} is communicated by diffusion of oxygen (or hydrogen produced by the dissociation of water in response to the changing fugacity conditions) through the wall of the inner capsule (see, for example, Holloway and Wood, 1988). The solid-state metal–oxide buffers constrain the oxygen fugacity to a particular value for a given metal–oxide pair, confining pressure and temperature. In order that the f_{O_2} is defined, both the metal and the oxide must be present, so solid-state buffered experiments tend to have a limited maximum duration defined by the rate of communication between the

outer capsule and surrounding pressure medium. In "un-buffered" experiments, the carbon–carbon monoxide (C–CO) (French and Eugster, 1965) buffer often defines the oxygen fugacity as graphite is a common component of furnaces and capsules in solid-state experiments at pressure up to about 5 GPa,

$$(C - CO): \quad C + 1/2O_2 \rightleftharpoons CO. \tag{5}$$
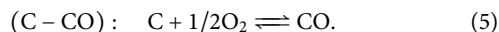
While solid-state buffers are not as versatile as gas mixtures in controlling the f_{O_2}, they do cover the important redox ranges occurring in the Earth and, hence, can be useful for synthesizing and performing reactions within important geological compositions. For example, the solid-state buffers involving reduction or oxidation of the iron-olivine endmember, fayalite, define the range of oxygen fugacities commonly encountered in the solid silicate portion of the Earth (Eugster, 1957),

$$(F - MQ) \quad 3Fe_2SiO_4 + O_2 \rightleftharpoons 2Fe_3O_4 + 3SiO_2$$
$$\text{Fayalite} + \text{oxygen} \rightleftharpoons \text{Magnetite} + \text{Quartz}, \tag{6}$$

$$(QI - F) \quad SiO_2 + 2Fe + O_2 \rightleftharpoons Fe_2SiO_4$$
$$\text{Quartz} + \text{Iron} + \text{oxygen} \rightleftharpoons \text{Fayalite}. \tag{7}$$
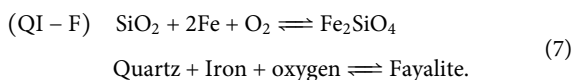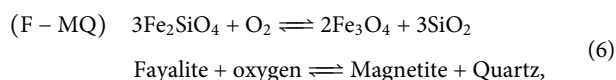
Iron is the most common transition element on Earth (e.g., McDonough and Sun, 1995), and so, within experimental petrology, the control of the iron valence state and stable iron-bearing compounds is often the main objective. Most of the solid-state buffer reactions are sub-parallel in P–T space, having similar negative entropies and volumes of the reaction [as written in Eqs. (3)–(7)], dominated by the formation of oxygen gas on the reduced side of the reaction. For a discussion of oxygen fugacity, see Lewis (1901), and for its control in petrology experiments, see Holloway and Wood (1988) and Frost (1991).

The C–CO buffer, by contrast, has a positive entropy and volume of the reaction, and as a consequence, C–CO becomes progressively oxidizing with increasing confining pressure and decreasing temperature compared to the metal–metal oxide buffers (Fig. 1). Simple use can be made of the positive volume change of the reaction to maintain redox conditions close to the C–CO buffer in muffle furnaces, which are open to air using crucibles with closely fitting, but not sealed, lids and which contain sacrificial graphite. At high temperatures where reaction rates are sufficiently fast, graphite will react with any excess oxygen that might be present in the crucible, for example, in air that might have been included at the start of the experiment, to produce a small positive pressure of carbon monoxide. This carbon monoxide leaks out of the crucible providing a constant flow of gas, which effectively excludes ingress of further oxygen and maintains the oxygen fugacity at or close to the equilibrium values defined by Eqs. (1) and (5). Unfortunately, at the temperatures where reactions are sufficiently fast for synthesis of silicate minerals (>1000 °C), the C–CO buffer is more reduced than QI-F, resulting in the exsolution of metallic iron from iron silicate samples. Indeed, it is these properties of the C–CO buffer which make it such an important component in foundry crucibles and casting sands, and it underpins the refinement of iron in blast furnaces (Harvey, 1945; Jarfors and Seifeddine, 2015).
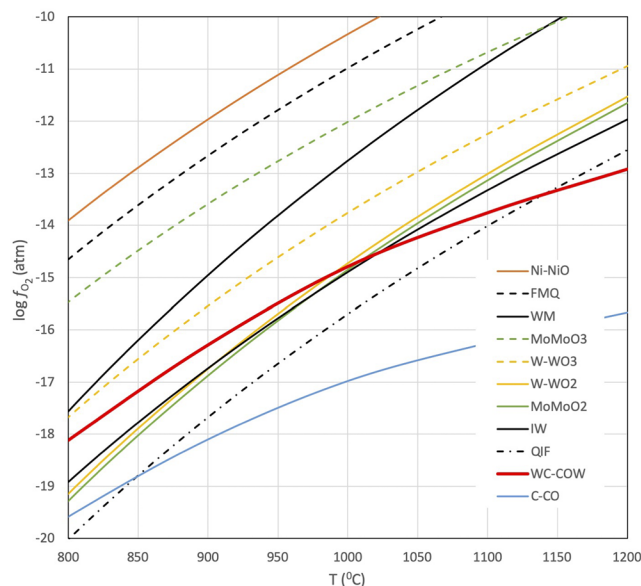

FIG. 1. Some common solid-state oxygen buffers plotted in a common temperature range of interest for experimental petrology and solid-state synthesis. The WC-COW buffer is sub-parallel to CCO, having a similar positive volume change of the reaction but is more oxidizing than QIF at temperatures below ~1100 °C.

In contrast, while several metal–metal oxide buffers fall in the appropriate f_{O_2} range, the negative volume change of oxidation causes more air to be drawn into the crucible, resulting in poor buffering and rapid consumption of the buffer. The present paper describes an inexpensive arrangement of nested ground alumina crucibles, combined with a new positive-volume change oxygen buffer (WC-COW), which minimizes the exchange between the sample environment and the furnace. Using this technique, pure fayalite can be produced after six days of sintering at 1050 °C. A typical muffle furnace with a 5 l capacity can readily hold multiple crucible sets, each capable of containing 10–20 g of sample and so this simple method allows efficient, cost-effective processing of several redox-sensitive samples at once.

The WC-COW buffer

The new buffer relies on the reaction of tungsten carbide with oxygen to produce tungsten metal and carbon monoxide,

$$(WC - COW): \quad WC + 1/2O_2 \rightleftharpoons CO + W. \tag{8}$$
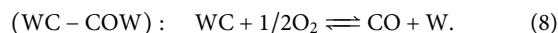
This new oxygen buffer is sub-parallel to the C–CO buffer in $P–T–f_{O_2}$ space, having a similar volume and entropy of the reaction. It is, however, significantly more oxidizing, being on the oxidizing side of QIF at temperatures below ~1130 °C. The equilibrium oxygen fugacity is calculated from reactions (1), (8), and (9),

$$WC + CO_2 \rightleftharpoons 2CO + W, \tag{9}$$
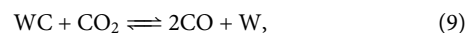
following the procedure of French and Eugster (1965) and is plotted in Fig. 1, along with some common solid-state buffers, for a total pressure of 1 bar. Gasses are assumed to be ideal for the

present calculations. In the temperature range of 600–1200 °C, at 1 bar total pressure, the oxygen fugacity of the WC-COW buffer can be approximated (following Frost, 1991) as

$$\log f_{O_2} = 1.53 - \frac{21008}{T(K)} \pm 0.13 \, \text{bar}. \quad (10)$$

At temperatures below ~980 °C, the WC-COW equilibrium curve becomes more oxidizing than W-WO$_2$ and reaction (8) should be modified to

$$WC + 1.5O_2 \rightleftharpoons CO + WO_2. \quad (11)$$

Under these conditions, the volume change of the reaction is negative and there is little advantage over the traditional metal–metal oxide buffers.

Nested crucibles

The WC-COW buffer is implemented here in an arrangement that is designed for use in 1 atm muffle furnaces. Samples that are not sensitive to f_{O_2} can be placed in a crucible with a loose-fitting lid so that no overpressure is generated in the crucible as it heats up in the furnace. For f_{O_2}-sensitive samples, ingress of atmospheric oxygen is a significant problem requiring f_{O_2} buffering when using muffle furnaces, but oxygen ingress can be sufficiently rapid with loose-fitting lids that the buffer material is entirely consumed during the experiment. This section describes a simply prepared arrangement of nested alumina crucibles, which slow down oxygen ingress sufficiently for buffered synthesis experiments lasting several days using the WC-COW buffer. The arrangement is shown in Fig. 2.

Cylindrical alumina crucibles (Alsint 23) with nominal dimensions of (part A in Fig. 2) 30 mm inner diameter, 35 mm outer diameter, and 50 mm height and (part B in Fig. 2) 26 mm inner
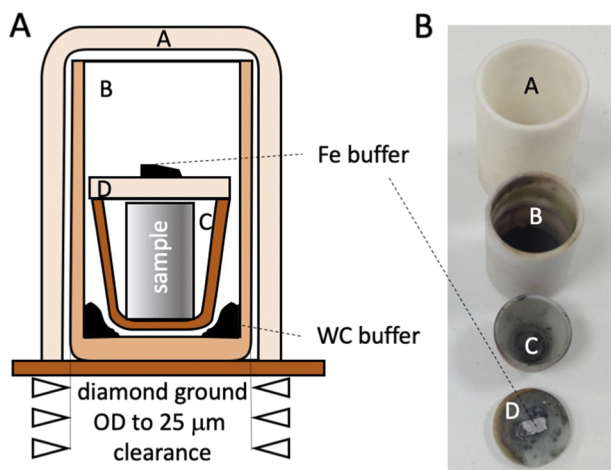

FIG. 2. The nested crucible arrangement for maintaining a controlled oxygen-fugacity environment during high-temperature sintering experiments. (a) Cross section of the assembled crucibles; the coloring of alumina components is for clarity only. (b) Photograph of the main components labeled (A) through (D) in panel A.

diameter, 30 mm outer diameter, and 40 mm height were purchased from Alfa Aesar. The outer diameters of the smaller, part B, crucibles were diamond-ground so that they just smoothly slide inside a larger crucible to create matched pairs of nested crucibles. The clearance between the inner and outer crucibles, estimated from the speed with which a small crucible settled into its paired outer crucible under gravity, was typically between 20 and 40 μm. Manufacturing imperfections of the inner surfaces of crucibles meant that it was not possible to surface grind fits to any finer tolerance than this, but, as shown below, this is quite sufficient to maintain adequate buffering of samples. Samples and buffers can be placed directly inside the inner crucible, but to avoid cross contamination, a third shallow conical crucible (Alsint 23, with an outer diameter of 22 and a height of 25 mm; part C) was placed inside the small part B crucible of the matched pair. Starting oxide mixtures were ground together to a <10 μm grain size under isopropanol, with the addition of 0.5% polyvinyl alcohol binder at the end of grinding. In addition to significantly increasing the cohesive strength of cold-pressed pellets, the PVA binder causes strong flocculation of the powder mixture, forming a gel-like consistency when added to the propanol. This inhibits unmixing of the different powder components, which can occur through differential gravitational settling in oxides with very differing densities. The binder decomposes during sintering, leaving no solid residue or contamination of the sample. Once the alcohol had completely evaporated, the oxide mixture was pressed in a 13-mm-diameter pelleting press under 3 tons load.

The buffer material was placed either between the small crucible of the matched pair and the conical sample-containing crucible or on top of an alumina disk, which acted as a loose-fitting lid. Buffers that produce a positive volume change on oxidation, such as WC-COW, are placed at the bottom of the assembly, between the sample crucible and inner crucible of the matched pair, in order that the CO produced by the reaction provides a gas purge for the entire crucible assembly. For buffers with a negative volume change, such as I–W, it is advantageous to place them closer to the source of gas ingress (i.e., on top of the lid—part D in Fig. 2) to avoid fresh oxygen being drawn over the sample as the redox reaction progresses.

The inner crucible of the matched pair containing the sample crucible and buffer was then placed on a ceramic plate and the outer nesting crucible allowed to settle over its matched inner crucible under gravity to complete the assembly as indicated in Fig. 2(a). A carbolite muffle furnace was pre-heated to the temperature of interest, and the nested crucible set was placed in the furnace still on its ceramic tile base. After the required time at temperature, the assembly was quenched by removing from the still hot furnace. Just the reduced part of buffer assemblages was added to the crucible since oxygen is present in the air filling the space inside the crucibles, so the oxidized component of the buffer is produced on the initial reaction between this air and the reduced component of the buffer. The nested crucibles described above can be used repeatedly for many synthesis experiments, provided care is made to avoid dust or grit contaminating the interface between the matched crucible pair. For the proof of concept tests here, 5–15 g samples of fayalite were prepared from starting powders of SiO$_2$, Fe, and Fe$_2$O$_3$, all greater than 99.99% purity, mixed in stoichiometric proportion.

Performance of the WC-COW buffer and nested crucibles

In order to test the performance of the new buffer system in the nested crucible arrangement, fayalite was synthesized as described above using either 5.6 μm powder of WC (1 g per experiment) or Fe (powder and lumps were tested; 1–5 g per experiment) as buffers at 950 and 1050 °C. The larger mass of Fe was required to provide sufficient surface area for the buffering reaction to proceed at a reasonable rate. Each sintering cycle lasted for 1–2 days, and the fayalite was re-ground and pelleted between cycles. The buffer materials recovered from WC-buffered experiments were loose, or very poorly sintered, powders. In the case of the I–W buffer, iron oxides formed a solid coherent coating around the metallic iron regardless of whether iron was added as loose powder or solid lumps, significantly reducing the effective surface area available for the reaction of the powdered iron buffer. Figure 3 shows x-ray diffraction patterns of the recovered buffer materials after one cycle of 24 h. X-ray
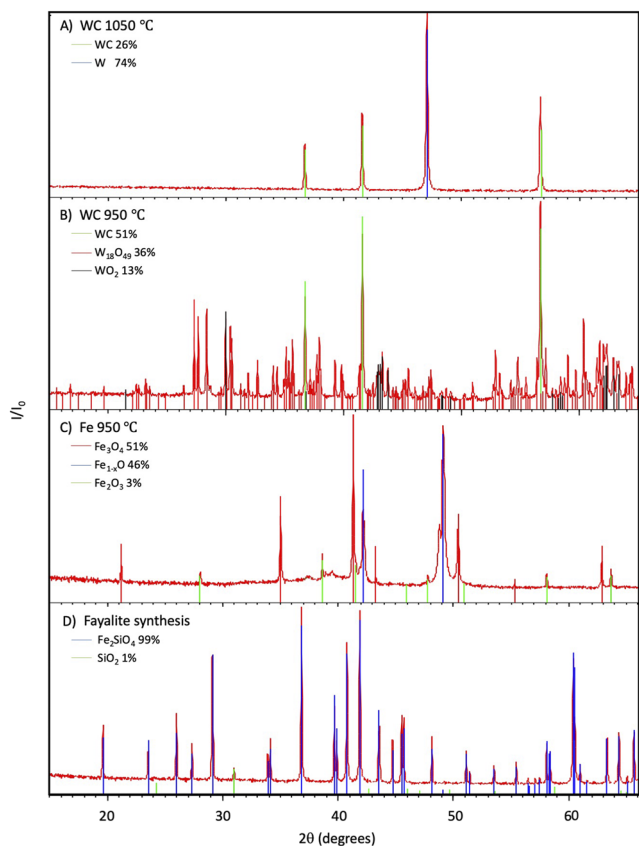

FIG. 3. X-ray diffraction patterns (Co Kα_1 radiation) of samples and buffer materials recovered from sintering experiments in nested crucibles. Intensities are plotted on a square-root scale. WC buffer recovered from (a) 1050 and (b) 950 °C; (c) oxide coating from Fe buffer recovered from 950 °C; and (d) fayalite synthesized under oxygen fugacity buffered by WC-COW at 1050 °C. Phase assignment and weight percentages from PANalytical HighScore Plus software and ICDD PDF2 database.

diffraction analysis is described elsewhere (Dobson et al., 2011). The WC buffer [Figs. 3(a) and 3(b)] reacted at 1050 °C to form metallic tungsten, consistent with reaction (8), and at 950 °C, it reacted to form mixed tungsten oxides, suggesting that the WC-COW buffer is more oxidizing than W-WO$_2$ at this temperature. Iron oxides removed from the surface of the metallic iron buffer material contained a mixture of wüstite (Fe$_{1-x}$O), Fe$_2$O$_3$, and Fe$_3$O$_4$ [see Fig. 3(c)]. This implies that the iron did not effectively buffer the f_{O_2} in these experiments and that the oxygen fugacity in the crucibles might have been closer to the wüstite–magnetite (W–M) buffer. Given that the oxide formed a solid coating surrounding the metallic iron, this suggests that iron oxidation was rate limited by diffusion of oxygen through the oxide layer, resulting in a fugacity gradient through the layer with local equilibria of I–W maintained at the surface of the iron and W–M further out in the oxide layer (as discussed, for example, by Slattery et al., 1995). This variation in oxygen fugacity through the oxide layer explains the splitting of the wüstite reflections in the diffraction patterns, which is ubiquitous in recovered iron oxide–buffer samples (e.g., Chen and Yuen, 2002). Wüstite is well known for accommodating significant non-stoichiometry, with the iron deficit being a positive function of f_{O_2}. This non-stoichiometry produces a measurable effect on the lattice parameters of wüstite solid solutions (see, for example, Dobson et al., 1998), and hence, the splitting of the wüstite reflections in the diffraction pattern presented here is likely to represent varying degrees of non-stoichiometry (and hence varying f_{O_2}) across the oxide layer rather than a deviation from cubic crystal symmetry in the wüstite.

The relative efficacy of the WC-COW and I–W buffers in controlling the oxygen fugacity in the current experimental arrangement can be judged from the fayalite synthesis experiments. Pure fayalite was produced after four cycles of sintering with the WC buffer at 1050 °C [Fig. 3(d)], whereas fayalite synthesized using the Fe buffer was not completely reacted after six cycles, containing traces of FeO, Fe$_2$O$_3$, and SiO$_2$. Indeed, fayalite pellets recovered from iron-buffered experiments invariably showed a dark brown surface discoloration due to the presence of high-valent iron oxides. As noted previously, the positive volume change on oxidation of the WC-COW buffer system provides an effective gas purge in the nested crucible system, but this self-purging might not be the only reason for its efficacy in controlling oxygen fugacity. The recovered WC buffer material was qualitatively different in form from that recovered from iron-buffered experiments, being a loose powder mixture of the reduced and oxidized components rather than metal surrounded by sintered oxides. Early experiments on kinetics of oxidation of carbides (e.g., Webb et al., 1956) attributed the rapid oxidation of WC at elevated temperatures to the formation of CO gas at the oxidizing front, causing delamination of the oxide layer from the carbide matrix. A similar delamination process might be active here during partial (WC-buffered) oxidation: this would then provide exposed surfaces of WC for rapid continued re-equilibration of the oxygen-bearing atmosphere with the WC buffer.

The WC-COW buffered syntheses presented here are relatively simple and rapid compared with other methods in the literature for solid-state fayalite synthesis at similar temperatures (Brinkman and Laqua, 1985; Barkmann and Cemič, 1996; Dachs et al., 2007; and Lilova et al., 2018).

Implementation of the WC-COW buffer in high-pressure devices

The WC-COW buffer as described here relies on ingress of oxygen from the surrounding environment to provide the oxidized component of the buffering reaction, and it was designed to combat the deleterious effects of oxygen ingress during sintering in 1 atm muffle furnaces. There are two possibilities for its implementation in high-pressure solid-media devices:

(1) Oxygen can be derived from the gas filling any initial porosity in the ceramic pressure medium. This is the means by which graphite furnaces in piston–cylinder and multi-anvil cells are assumed to buffer the oxygen fugacity in the absence of any other buffering reaction.

(2) Oxygen can be supplied by reaction with an initially oxidized component in the sample or buffer mix. It is, for example, common practice during high-pressure synthesis experiments to use glass starting materials due to their high reactivity. These glasses are often produced by fusion in muffle furnaces and water quenching, with the resulting glass being in an oxidation state in equilibrium with air. On annealing at high-pressure buffered by WC, the glass will be reduced to produce CO and W in the buffer. In the case where starting materials in the sample are not oxidized, the addition of a small amount of WO_2 to the starting WC buffer would have a similar effect.

A final note of caution is required. Once the WC is fully consumed, the production of high-valent tungsten oxides on subsequent reaction with air has a strongly negative volume change of the reaction, causing the sample environment to rapidly oxidize. Care should be taken, therefore, to ensure that sufficient buffer is used for the duration of the experiment. Due to the machining imperfections of the alumina crucibles, each nested pair requires some calibration experiments to determine how quickly buffers are consumed. The complete consumption of the WC buffer is readily identified by the presence of bright green WO_3 or by x-ray diffraction of the buffer material *post hoc* to identify the presence of WO_2. The worst effects of completely consuming the WC buffer can be avoided by adding a small (<0.5 g is sufficient) chip of metallic iron to buffer the oxygen fugacity below $W-WO_2$ in the event that the carbide is fully consumed. This iron should be placed on the sample crucible lid (as shown in Fig. 2) for the reasons discussed above.

CONCLUSION

The WC-COW buffer is effective at maintaining oxygen fugacity in the range necessary for synthesis of iron-bearing silicate minerals in 1 atm furnaces in the temperature range of 1000–1100 °C. The use of this buffer for rapid synthesis of fayalite at 1050 °C demonstrates its effectiveness in this temperature range.

ACKNOWLEDGMENTS

DATA AVAILABILITY

The data that support the findings of this study are available within the article.

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