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Novel technique to control oxygen fugacity during high-pressure measurements of grain boundary conductivities of rocks

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This paper describes the development and application of a novel method for the measurement of grain boundary electrical conductivity of rock at high temperature and pressure. In this method, the metal electrodes, the corresponding metal shielding case, and the sleeves are altered in order to appropriately adjust and monitor the oxygen fugacity in a sample cavity in a high-pressure apparatus. As an example, a series of oxygen buffers including $Fe_3O_4+Fe_2O_3$, $Ni+NiO$, $Fe+Fe_3O_4$, $Fe+FeO$, and $Mo+MoO_2$ was selected and tested, and the oxygen fugacity was confirmed as adjusted during the process of electrical conductivity measurements. Application of this method provides a powerful means of restricting specific thermodynamic conditions at high temperature and pressure. © 2009 American Institute of Physics. [DOI: 10.1063/1.3097882]

I. INTRODUCTION

In high-pressure experiments, frequency, temperature, pressure, iron content, water content, and phase transitions are key parameters that must be closely monitored. Likewise, oxygen fugacity (f_{O_2}) is among the most important factors affecting the experimental results of electrical conductivity measurements of minerals and rocks that contain valence-variable elements. Currently, the issue of oxygen fugacity has become a central issue in the process of grain boundary electrical conductivity measurements of rock. Specifically, the ability to adjust the oxygen fugacity in multianvil apparatuses has become an area of intense research. For most traditional conductivity experiments, arbitrary adjustment of oxygen fugacity can be realized by adjusting the proportion of the gas buffer mixture (e.g., $CO+CO_2$) at high temperatures and ambient pressure.[1] However, it is often difficult to control f_{O_2} during high-pressure processes due to a number of prohibitive restrictions, including (i) the selected gas buffer pairs have a limited adjustment range of oxygen fugacity and (ii) the difficulty of implementing control in an actual high-pressure apparatus.

Cemič *et al.*[2] measured the electrical conductivity of the various chemical compositions of olivine (e.g., Fo100/Fa0, Fo90/Fa10, Fo80/Fa20, Fo60/Fa40, and Fo0/Fa100) at 1.0 GPa pressure, between 573 and 1348 K, and with three solid oxygen buffers [i.e., fayalite+quartz+magnetite, fayalite+quartz+iron, and iron+wüstite (IW)]. Although Cemič *et al.*[2] reported that chemical activities were appropriately controlled and the ac-bridge method was applied (f =1.6 KHz and V=0.1–1 V), their high-frequency range

resulted in data that neglected to consider the grain boundary influence on the electrical conductivity of the mineral at high pressure. As such, their results underestimated the electrical conductivity of synthetic olivine in the upper mantle. Xu and co-workers[3,4] applied the single buffer $Mo+MoO_2$ to control the oxygen partial pressures of the sample cavity using ac impedance spectroscopy to measure the electrical conductivity. Additionally, other similar single oxygen buffers such as Ni–NiO have been adopted in the measurement of electrical conductivity of single crystal olivine.[5]

To date, there is no experimental technique that can adequately adjust the oxygen fugacity in the measurement of grain boundary electrical conductivities at high pressure. Previous high-pressure electrical conductivity experiments were typically conducted under a fixed f_{O_2} in either an oxidative or a reductive environment. As such, the design of a new experimental method that is independent of pressure and temperature is of general interest.

In this study, a series of oxygen buffers [e.g., $Fe_3O_4+Fe_2O_3$ (MH), $Ni+NiO$ (NNO), $Fe+Fe_3O_4$ (IM), $Fe+FeO$ (IW), and $Mo+MoO_2$ (MMO)] was applied to control and adjust oxygen fugacity. Impedance spectroscopy was employed to measure the grain boundary electrical conductivity. Through systematic optimization of the metal and corresponding metal oxide types, the oxygen fugacity can be efficiently controlled.

II. EXPERIMENTAL SECTION

The detailed experimental setup is illustrated in Fig. 1. The oxygen buffers were prepared by combining the requisite metal and metal oxide (>99.99% purity), and the corresponding weight percentages of the metals and metal oxides for each prepared buffer were 97% Fe_3O_4+3% Fe_2O_3, 78% Ni+22% NiO, 72% Fe+28% Fe_3O_4, 78% Fe+22% FeO,

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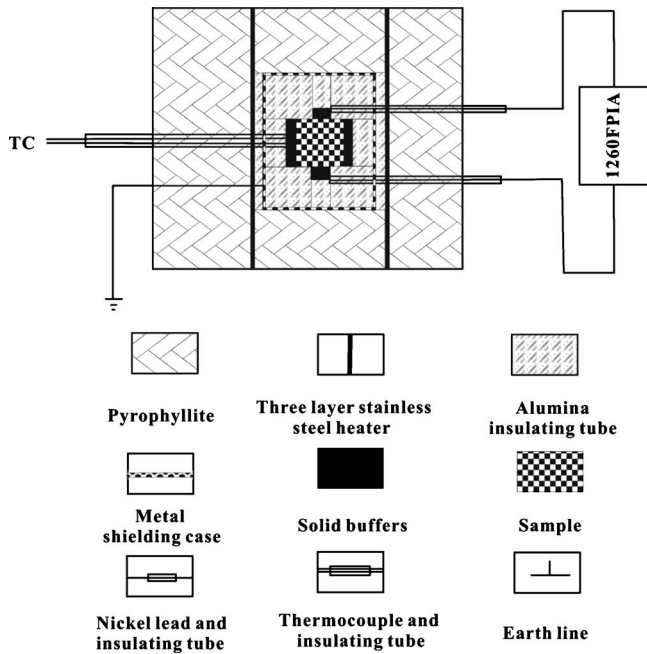
FIG. 1. Experimental assembly of controlling oxygen fugacity.

and 86% $Mo+14\%$ MoO_2. All buffers were pressed and sintered at the General Academy of Iron and Steel of China at 133 MPa and 1573 K under an argon atmosphere (equivalent time: 2.5 h). The sintered solid buffers were cut and polished into $\varphi 3.0 \times 1.45$ mm^2 disks as buffer electrodes and $\varphi 6.0 \times 5.0 \times 4.5$ mm^3 as sleeves using electric sparking discharge erosion at the Factory of the Chinese Aerospace and Aviation Administration.

All experiments were conducted in a YJ-3000t multianvil press at the Institute of Geochemistry, Chinese Academy of Sciences, Guiyang, China. The equipment was previously described in detail.[6] Six cubic tungsten carbide anvils were assembled and squeezed, providing pressures of up to 10 GPa. The maximum temperature reaches 2273 K only if a lanthanum chromate heater is applied. The experimental errors of the temperature and pressure gradients were measured at less than 10 K and 0.1 GPa, respectively. The electrical conductivity measurement errors were estimated at no more than 5%, and the principal source of error was determined to be dimensional changes in the sample, which are less than 8%.

The oxygen fugacity was monitored and adjusted by varying the selected metal type in the electrodes, corresponding sleeves, and shielding cases. The shielding case is made of metal foils such Ni, Fe, Mo, and so on, whose thickness is 25 μm. After the electrical conductivity measurements were completed, the recovered solid buffers were checked by x-ray diffraction analysis in order to confirm the coexistence of metal and metal oxide. If these two were found to coexist, the oxygen fugacity was successfully controlled and the resulting value was fixed in the sample chamber. Next, the metal type was changed in order to vary the oxygen fugacity.

III. RESULTS

Oxygen fugacity was successfully controlled by implementing the above described novel method when measuring

TABLE I. Theoretical calculations of log f_{O_2} (f_{O_2}: bar) at high temperature and 2.0 GPa pressure. [Log $(f_{O_2})_{P,T} = -A/T + B + C$ $(P-1)/T$, where T is the absolute temperature (Kelvin, <2273 K), P is the pressure (bar), $C = -\Delta V_S/2.303R$, where ΔV_S stands for the bulk variation in mol volume of solid components before and after experimental reaction (cm^3/mol), and R is the gas state constant (cm^3 atm/mol K^{-1}).]

Oxygen buffer	A	B	C	According to references
WH	24 634	13.966	0.019	Present work
NNO	24 930	9.36	0.046	6
IM	29 260	8.99	0.061	Present work
IW	27 215	6.57	0.052	Present work
MMO	30 650	8.92	0.054	3 and 4

the grain boundary electrical conductivity of rocks at high temperature and pressure. We subsequently demonstrate control of oxygen fugacity by using MMO, IW, IM, NNO, and MH buffers in the grain boundary electrical conductivity measurement process. By changing the different oxygen buffers, the oxygen fugacity was adjusted independently of temperature and pressure, which were set at 1173 K and 2.0 GPa, respectively. Five types of oxygen fugacity values are shown in Table I, indicating that these values increase with buffer in the following order: MMO, IW, IM, NNO, and MH. Figure 2 shows representative impedance spectroscopy data. The parameters for the WH, IM, and IW buffer systems that are attributed to "present work" have been determined using the method in Ref. 6.

Figure 3 plots the relationship between the logarithm of the grain boundary electrical conductivity of peridotite in the upper mantle and the logarithm of oxygen fugacity, and the fitting result is shown in formula (1). A model of grain boundary electrical conductivity and oxygen fugacity at high pressure was constructed and was consistent with the
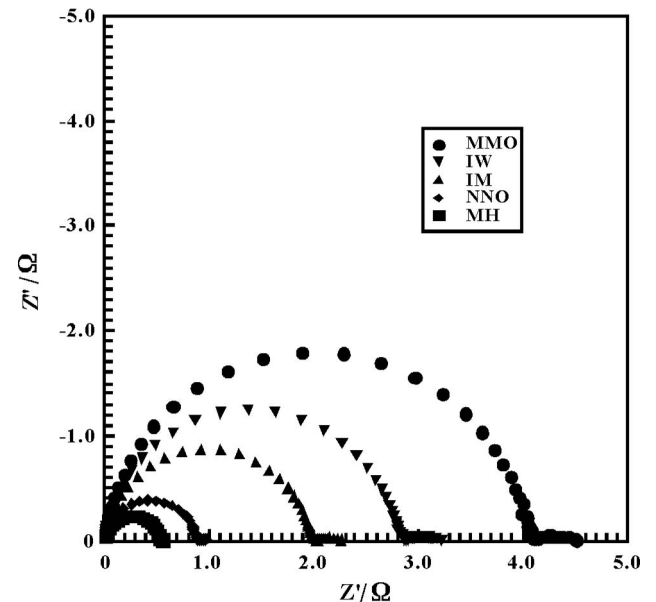

FIG. 2. Z' vs Z'' plot of complex impedance of peridotite from $10^{-2}-10^6$ Hz (right to left) obtained under conditions of 2.0 GPa and 1173 K and MMO, IW, IM, NNO, and MH buffers. Z' and Z'': real and imaginary parts of complex impedance.
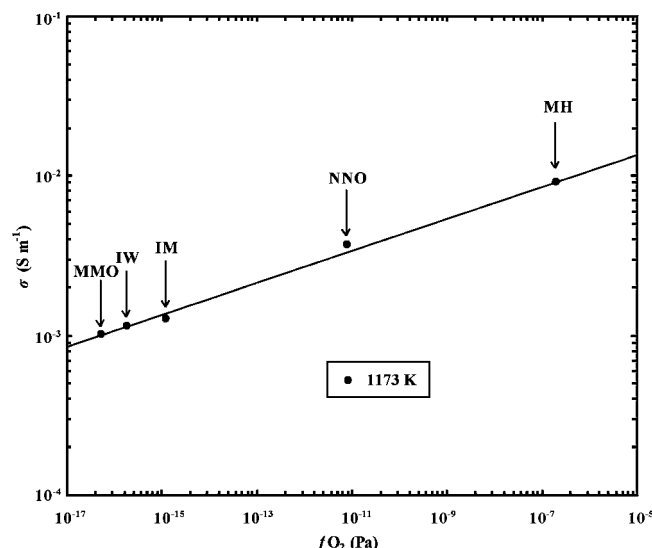
FIG. 3. Logarithm of grain boundary electrical conductivity vs logarithm of oxygen fugacity for peridotite under conditions of 2.0 GPa and 1173 K.

previously reported results of Roberts and Tyburczy[7] (1993), who used $CO+CO_2$ to control oxygen fugacity at ambient pressure.

$$\log_{10}(\sigma) = 0.1022 \times \log_{10}(f_{O_2}) - 1.332. \qquad (1)$$

The x-ray diffraction of each recovery buffer was analyzed, and two phases were determined to coexist. As such, this novel technique to control oxygen fugacity in the process of grain boundary conductivity measurement was confirmed to be successful at high temperature and pressure. Additional details of this work will be reported elsewhere.[8]

Although the experiments on oxygen fugacity control were designed and applied exclusively in an anhydrous peridotite system in the upper mantle, this technique should also be applicable for the hydrous wadsleyite system in the transition zone using the KAWAI-type 1000t multianvil press.[9]

ACKNOWLEDGMENTS

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