# ELECTROCHEMICAL DETERMINATION OF THE OXYGEN FUGACITY OF MANTLE-DERIVED ILMENITE MEGACRYSTS

by

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## ABSTRACT

The oxidation state of eleven mantle-derived ilmenite-bearing xenoliths from four different localities was studied using $O_2$-specific solid electrolytes. Repetitive calibrations of the experimental apparatus with the iron-wüstite (IW) buffer indicate that the precision of the measured $fO_2$'s at 1312 $\pm$ 1 K is 2.37% ($\pm$0.01 log units). Results obtained with the IW and Ni-NiO buffers agree with values reported by other investigators (e.g., Darken and Gurry, 1945; Kemori et al., 1979).

Experiments on blank systems (no sample) demonstrated that the oxygen sensors that include $Al_2O_3$ elements ($SIRO_2$) are reactive to free oxygen. They also indicate that the $fO_2$ of equilibration of an Ar-filled $SIRO_2$ sensor depends, among other factors, on the $fO_2$ of the previous run.

Results from some natural samples indicate that: (a) the $fO_2$ developed by the blank system can modify the composition of the sample during the experiments; and (b) the criteria of stability of the Emf with time, and thermal reproducibility of the measured $fO_2$'s are not sufficient to demonstrate equilibrium. To circumvent these problems, an experimental procedure was developed to reverse and bracket the equilibrium $fO_2$'s.

Good agreement was obtained between electrochemically derived $fO_2$'s on Mg-ilmenite-titanomagnetite intergrowths and values calculated using the iron-titanium oxide geothermometer-oxybarometer. However, the electrochemical determinations are systematically about

0.6 log $fO_2$-units more oxidized. This bias may be ascribed to the effects of the geikielite component of the ilmenite$_{ss}$.

Auto-oxidation was observed in clinopyroxene-ilmenite intergrowths. Whether this behavior is observed, however, depends on the thermal treatment given to the sample during the experiment.

All of the results are characterized by redox conditions at or above the FMQ (or EMOG) buffer at one bar and are in agreement with those of Haggerty and Tompkins (1983) and Arculus et al. (1984) for similar samples. The measured intrinsic $fO_2$'s of a homogeneous Mg-ilmenite from Monastery Mine, which showed good reversibility and a continuous log $fO_2$ - 1/T pattern from 800°C to 1150°C during slow heating, agree very well with data obtained independently by McMahon (1984) using gas equilibration techniques at 1 atm. The agreement indicates that electrochemically derived $fO_2$'s are not high pressure relicts but rather are equilibrium values at 1 atm.

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COLLEGE OF SCIENCE AND MATHEMATICS

The dissertation submitted by

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has been read by the undersigned. It is hereby recommended for acceptance to the Faculty of the University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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TABLE OF CONTENTS

## LIST OF FIGURES

# LIST OF TABLES