

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 O₂-specific solid electrolytes. Repetitive calibrations of the experimental apparatus with the iron-wüstite (IW) buffer indicate that the precision of the measured fO₂'s at 1312 ± 1 K is 2.37% (±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 Al₂O₃ elements (SIRO₂) are reactive to free oxygen. They also indicate that the fO₂ of equilibration of an Ar-filled SIRO₂ sensor depends, among other factors, on the fO₂ of the previous run.

Results from some natural samples indicate that: (a) the fO₂ 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 fO₂'s are not sufficient to demonstrate equilibrium. To circumvent these problems, an experimental procedure was developed to reverse and bracket the equilibrium fO₂'s.

Good agreement was obtained between electrochemically derived fO₂'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 ilmenite₈₈.

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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