CONTRIBUTION TO THE Fe₂O₃/FeO DETERMINATION IN BASALTIC ROCKS

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The relationship between the oxidation state of iron and the fo₂ as a function of temperature has been used to determine the Fe₂O₃/FeO ratio in basaltic rocks as follows:

\[
\log (\text{FeO}/\text{Fe₂O₃}) = 56419 \left( -\log f_{O2} \right)^{-1.544}
\]

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In recent years it has become a standard method to adjust the Fe₂O₃/FeO ratio before the norm calculations. This is done mainly to minimize the effects of secondary oxidation, which occurs in almost all basaltic rocks.

In most of the experimental works the ratio is uncertain because it cannot be measured directly because of the small amount of run product. However, the knowledge of the oxidation state is of primary importance.

In attempt to eliminate the effects of secondary oxidation there are many different methods in the literature. For example Brooks (1976) and Green et al. (1974) adopted a value for Fe₂O₃/FeO of 0.15, Stice (1968) of 0.25 etc.

Considering the chemical variation between the olivine basalts and e.g. quartz normative basalts it is, however, incorrect to use any fixed ratio of Fe₂O₃/FeO for both types of rocks. In an attempt to take the compositional effect into consideration, Irvine and Baragar adopted the method of making Fe₂O₃ equal to 1.5 % + TiO₂ (wt-%).

Thus, the method of fixed ratio of 0.15 might be true for basic rocks but is substantially too low for more silicic rocks. Further, the use of the method of Irvine and Baragar gives too high oxidation state especially for high TiO₂ basalts.

The fact that the oxidation state is a function of oxygen fugacity might provide a convenient method to resolve this Fe₂O₃/FeO ratio problem. In the nature the oxygen fugacity is a function of temperature,

\[
\log f_{O2} = - \frac{27300}{T(°K)} + 10.30
\]

for basaltic rocks. This QFM-buffer equation is discussed by Eugster and Wones (1962).

In the light of primary oxidation the liquidus temperature required for the fugacity equation can be calculated using the experimental data of several authors for

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basalts, ranging the composition from olivine
basalt to quartz normative tholeiite.

The best fitting of the least square method
gives the following equations for the experi-
ments plotted in Fig. 1.

1. \( T (\degree C) = 1947 - 1373 \left[ \text{FeO}^t/(\text{FeO}^t + \text{MgO}) \right] \)
   for \( \text{FeO}^t/(\text{FeO}^t + \text{MgO}) \leq 0.50 \)

2. \( T (\degree C) = 1497 - 479 \left[ \text{FeO}^t/(\text{FeO}^t + \text{MgO}) \right] \)
   for \( 0.50 < \text{FeO}^t/(\text{FeO}^t + \text{MgO}) \leq 0.70 \)

3. \( T (\degree C) = 1713 - 279 \log \left[ \text{SiO}_2/(\text{MgO}/\text{CaO}) \right] \)
   for more silicic rocks.

The relationship between the oxidation
state of iron and the \( f_{O_2} \) was primarily
studied by Fudali (1965). However, he does
not give any universal method because the
relationship is a function of the \( f_{O_2} \) and tem-
perature both. Roeder and Emslie (1970) ap-
proximated the problem by representing an
equation at known (1200 \( \degree C \)) temperature:
Contribution to the FeO/Fe2O3 determination in basaltic rocks

1.4
1.0
0.6
0.2
-0.2
-0.6
-1.0
-16 -14 -12 -10 -8 -6 -4

Log fo2

Fig. 2. Oxidation state of iron as a function of oxygen fugacity.
2. Basalts
3. Acid rocks (andesite, tonalite, granite, rhyolite, diorite, pitchstones)
4. Some representative diorite-granite averages
5. Nepheline-syenites, ignimbrites, riebeckite granites
6. Ultrabasic rocks
7. Best fitting curve for acid rocks
8. Best fitting curve for basaltic rocks


\[
\log \frac{X_{FeO}}{X_{FeO_{1.5}}} = -0.20 \log f_{O2} - 1.04
\]

In attempt to take account both temperature and \( f_{O2} \), the author has plotted the relationship between the oxidation state of iron and the \( f_{O2} \) as a function of the calculated temperature using the equations 1—3 (Fig. 2).

All the experimental data by several au-
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authors form an reasonably well correlating curve between these parameters. The best fitting by the method of least squares for this experimental data gives rather complicated equation:

$$\log \left( \frac{\text{FeO}}{\text{Fe}_2\text{O}_3} \right) = 56419 \left( -\log f_{O_2} \right)^{-5.44}$$

for basaltic rocks.

To test the feasibility of the method several analyses from the literature have been plotted on Fig. 2. All these analyses follow well the fitted experimental curve. However, most of the points show lower $f_{O_2}$ or by other words higher oxidation state. This is caused just by the secondary oxidation.

References


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