

# CONTRIBUTION TO THE $\text{Fe}_2\text{O}_3/\text{FeO}$ DETERMINATION IN BASALTIC ROCKS

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The relationship between the oxidation state of iron and the  $f_{\text{O}_2}$  as a function of temperature has been used to determine the  $\text{Fe}_2\text{O}_3/\text{FeO}$  ratio in basaltic rocks as follows:

$$\log (\text{FeO}/\text{Fe}_2\text{O}_3) = 56419 (-\log f_{\text{O}_2}) - 5.44$$

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In recent years it has become a standard method to adjust the  $\text{Fe}_2\text{O}_3/\text{FeO}$  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 can not 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  $\text{Fe}_2\text{O}_3/\text{FeO}$  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, uncorrect to use any fixed ratio of  $\text{Fe}_2\text{O}_3/\text{FeO}$  for both types of rocks. In an attempt to take the compositional

effect into consideration, Irvine and Baragar adopted the method of making  $\text{Fe}_2\text{O}_3$  equal to 1.5 % +  $\text{TiO}_2$  (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  $\text{TiO}_2$  basalts.

The fact that the oxidation state is a function of oxygen fugacity might provide a convenient method to resolve this  $\text{Fe}_2\text{O}_3/\text{FeO}$  ratio problem. In the nature the oxygen fugacity is a function of temperature,

$$\log f_{\text{O}_2} = -\frac{27\,300}{T(^{\circ}\text{K})} + 10.30$$

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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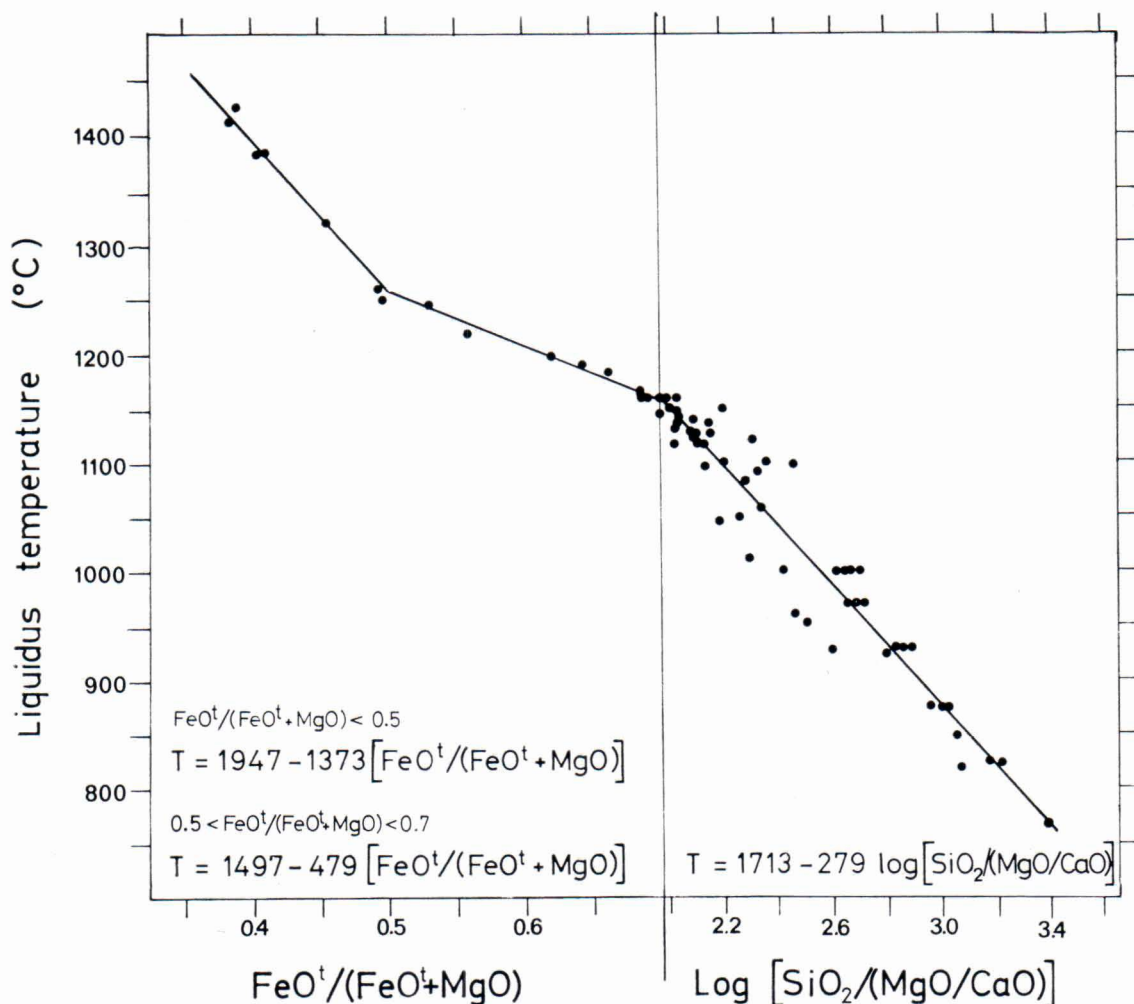


Fig. 1. Experimental liquidus temperatures versus chemical composition of the rock. Experiments: Yoder and Tilley (1962), Carmichael (1967), Egglar (1971), Helz (1976), Mäkipää (1978) and Steinthorsson (unpub.)

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 experiments plotted in Fig. 1.

- (1)  $T (^{\circ}C) = 1947 - 1373 [FeO^t/(FeO^t + MgO)]$   
for  $FeO^t/(FeO^t + MgO) \leq 0.50$
- (2)  $T (^{\circ}C) = 1497 - 479 [FeO^t/(FeO^t + MgO)]$   
for  $0.50 < FeO^t/(FeO^t + MgO) \leq 0.70$

- (3)  $T (^{\circ}C) = 1713 - 279 \log [SiO_2/(MgO/CaO)]$

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 temperature both. Roeder and Emslie (1970) approached the problem by representing an equation at known (1200 °C) temperature:

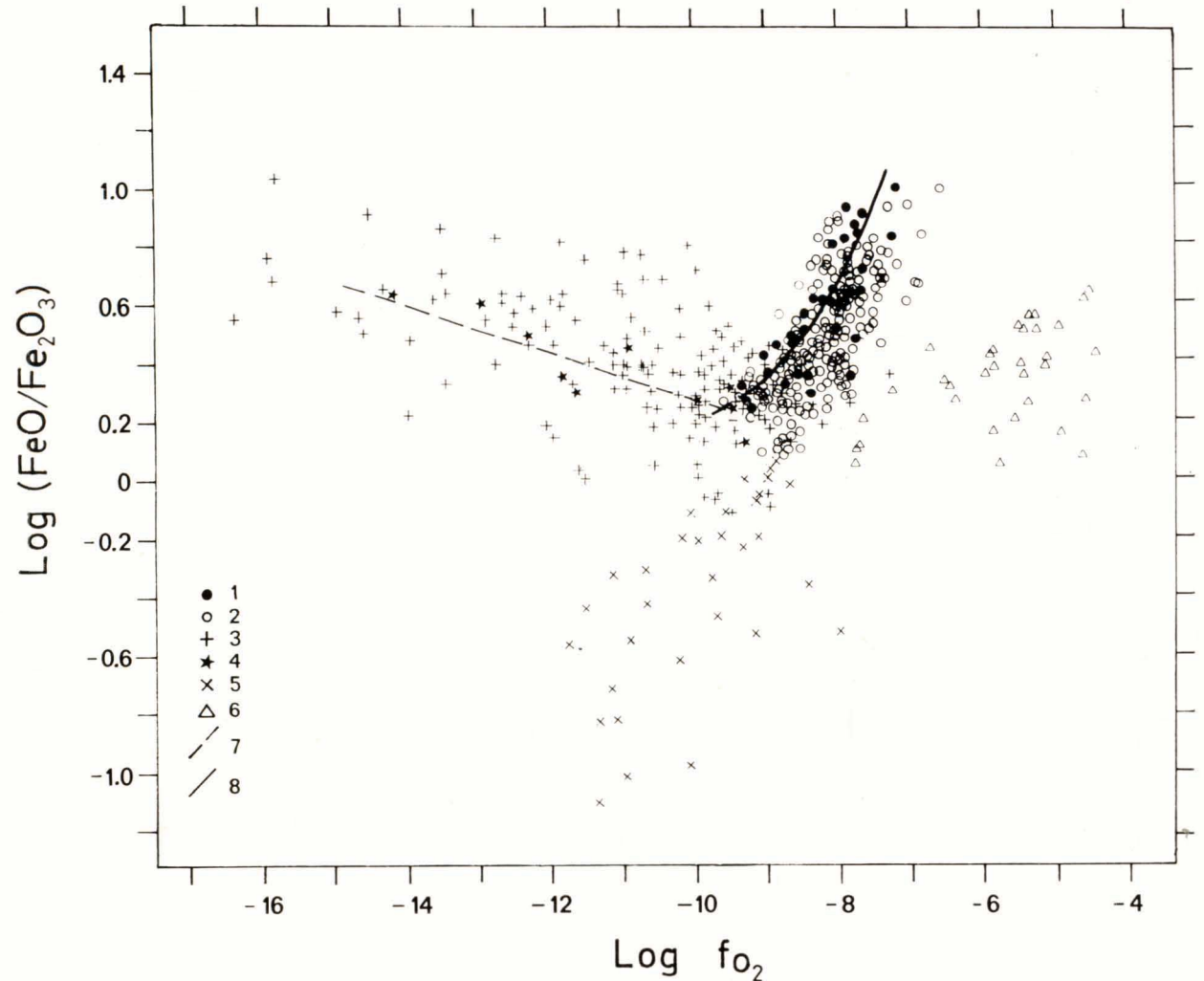


Fig. 2. Oxidation state of iron as a function of oxygen fugacity.

1. Experiments: Kennedy (1948), Yoder and Tilley (1962), Fudali (1965), Green and Ringwood (1967), Roeder and Emslie (1970) and Thompson and Flower (1971)
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

References: Bateman (1961), Buddington (1957), Carmichael (1960, 1967), Cawthorn (1978), Eggler (1972), Esson et al. (1975), Ewart and Stipp (1968), Grapes (1975), Hawkesworth and O'Nions (1977), Huhma (1976), LeMatre (1976), MacGeehan (1978), Mysen and Boettcher (1975), Polyakov et al. (1976), Savolahti (1956), Sigvaldason (1974), Vormo (1977) and Whitney (1975).

$$\log \frac{X_{\text{FeO}}}{X_{\text{FeO}_{1.5}}} = -.20 \log f_{\text{O}_2} - 1.04$$

In attempt to take account both temperature and  $f_{\text{O}_2}$  the author has plotted the rela-

tionship between the oxidation state of iron and the  $f_{\text{O}_2}$  as a function of the calculated temperature using the equations 1—3 (Fig. 2).

All the experimental data by several au-



thors 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:

$$\log (\text{FeO}/\text{Fe}_2\text{O}_3) = 56419 (-\log f_{\text{O}_2})^{-5.44}$$

for basaltic rocks.

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- 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  $f_{\text{O}_2}$  or by other words higher oxidation state. This is caused just by the secondary oxidation.
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